

# Model simulations of stratospheric ozone loss caused by enhanced mesospheric NO<sub>x</sub> during Arctic Winter 2003/2004

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**Abstract.** Satellite observations show that the enormous solar proton events (SPEs) in October–November 2003 had significant effects on the composition of the stratosphere and mesosphere in the polar regions. After the October–November 2003 SPEs and in early 2004, significant enhancements of NO<sub>x</sub>(=NO+NO<sub>2</sub>) in the upper stratosphere and lower mesosphere in the Northern Hemisphere were observed by several satellite instruments. Here we present global full chemistry calculations performed with the CLaMS model to study the impact of mesospheric NO<sub>x</sub> intrusions on Arctic polar ozone loss processes in the stratosphere. Several model simulations are performed with different upper boundary conditions for NO<sub>x</sub> at 2000 K potential temperature ( $\approx 50$  km altitude). In our study we focus on the impact of the non-local production of NO<sub>x</sub>, which means the downward transport of enhanced NO<sub>x</sub> from the mesosphere to the stratosphere. The local production of NO<sub>x</sub> in the stratosphere is neglected. Our findings show that intrusions of mesospheric air into the stratosphere, transporting high burdens of NO<sub>x</sub>, affect the composition of the Arctic polar region down to about 400 K ( $\approx 17$ – $18$  km). We compare our simulated NO<sub>x</sub> and O<sub>3</sub> mixing ratios with satellite observations by ACE-FTS and MIPAS processed at IMK/IAA and derive an upper limit for the ozone loss caused by enhanced mesospheric NO<sub>x</sub>. Our findings show that in the Arctic polar vortex (equivalent lat. $>70^\circ$  N) the accumulated column ozone loss between 350–2000 K potential temperature ( $\approx 14$ – $50$  km altitude) caused by the SPEs in October–November 2003 in the stratosphere is up to 3.3 DU with an upper limit of 5.5 DU until end of November. Further, we

found that about 10 DU, but in any case lower than 18 DU, accumulated ozone loss additionally occurred until end of March 2004 caused by the transport of mesospheric NO<sub>x</sub>-rich air in early 2004. The solar-proton-produced NO<sub>x</sub> above 55 km due to the SPEs of October–November 2003 had a negligibly small impact on ozone loss processes through the end of November in the lower stratosphere (350–700 K  $\approx 14$ – $27$  km). The mesospheric NO<sub>x</sub> intrusions in early 2004 yielded a lower stratospheric ozone loss of about 3.5 DU, and clearly lower than 6.5 DU through the end of March. Overall, the non-local production of NO<sub>x</sub> is an additional variability in the existing variations of the ozone loss observed in the Arctic.

## 1 Introduction

During periods of solar disturbances solar events can affect the concentration of constituents in the middle atmosphere. Protons, electrons, and alpha particles released from the sun are channelled along the Earth's magnetic field and cause ionization, excitation, dissociation, and dissociative ionization of the background constituents when they reach the Earth's atmosphere. Solar disturbances can also lead to solar proton events (SPEs), which are characterized by the emission of protons with higher energies. Some of these highly energetic protons can penetrate to the stratosphere, but generally only in the polar regions. In general, the major effects of solar energetic particle precipitation (EPP) and SPEs have been found to significantly increase the production of odd nitrogen NO<sub>y</sub> (N, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, HO<sub>2</sub>NO<sub>2</sub>, ClONO<sub>2</sub>, and BrONO<sub>2</sub>) and odd hydrogen HO<sub>x</sub> (H, OH, HO<sub>2</sub>) (e.g. Crutzen et al., 1975; Jackman et al.,



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1980; Solomon et al., 1981; López-Puertas et al., 2005a; Verronen et al., 2006). Both NO<sub>y</sub> and HO<sub>x</sub> play a key role in the ozone balance of the middle atmosphere because they destroy odd oxygen by catalytic cycles. During polar night conditions, NO<sub>y</sub> is long-lived and can be transported downwards. Therefore, extra NO<sub>y</sub> produced in the upper atmosphere could be important for the ozone budget of the lower and middle stratosphere. In contrast, enhanced HO<sub>x</sub> produced by SPEs in the mesosphere or upper stratosphere is short-lived and therefore only yields a short-time ozone decrease.

The fourth largest period of SPEs measured in the past 40 years took place in October–November 2003 (known as the “Halloween solar storm”), which resulted in ionization effects in the atmosphere down to 30 km altitude near the geomagnetic poles (e. g. Jackman et al., 2005b). An especially vigorous period of high fluxes of energetic protons occurred from 28–31 October 2003 and a second maximum was found between 2–4 November 2003 (Jackman et al., 2005b). Satellite observations by several instruments have shown that these SPEs have significant effects on the composition of the Arctic stratosphere and mesosphere. After the SPEs, ozone depletion signatures associated with significant enhancements of NO<sub>x</sub> (=NO + NO<sub>2</sub>) (e. g. Seppälä et al., 2004; López-Puertas et al., 2005a; Rohen et al., 2005), of several NO<sub>y</sub> components like HNO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub> (e. g. López-Puertas et al., 2005b; Orsolini et al., 2005), and of HO<sub>x</sub> and ozone depletion signatures associated with HO<sub>x</sub> (e. g. Degenstein et al., 2005; von Clarmann et al., 2005; Verronen et al., 2006) were observed in the upper stratosphere and lower mesosphere.

Further, upper stratospheric and mesospheric enhancements of NO<sub>x</sub> were observed at high northern latitudes in early 2004 (e. g. López-Puertas et al., 2005a, 2006; Randall et al., 2005) due to downward transport of upper atmospheric NO<sub>x</sub> produced throughout the winter by auroral and precipitating electrons (Funke et al., 2007). Results by Randall et al. (2006) confirm that the impact of EPP on the atmosphere is modulated by meteorological conditions; their results suggest that a stronger vortex leads to increasing NO<sub>x</sub> values in the stratosphere caused by the descent of NO<sub>x</sub>-rich air masses from the mesosphere and thermosphere within a well-isolated vortex.

In fact, the dynamic situation of the Arctic winter 2003/2004 was very anomalous. A major warming beginning in late December 2003 led to nearly 2 months of vortex disruption (Manney et al., 2005). The upper stratospheric vortex broke up in late December, but began to recover by early January. In February and March it was the strongest since regular observations began in 1979. The lower stratospheric vortex broke up in late January, split into two fragments on 1 February and the fragments coalesced again by 17 February. Thus the period when the vortex was strong in the upper stratosphere but very small and weak in the lower to middle stratosphere was quite uncommon (Manney et al.,

2005). The temperatures in the lower stratosphere were unusually high and temperatures in the middle and upper stratosphere were unusually low during and after February 2004. These dynamic disturbances supported the downward transport of NO<sub>x</sub> leading to the NO<sub>x</sub> enhancements in the upper stratosphere in early 2004.

In addition to this downward transport of NO<sub>x</sub> in the lower stratosphere, dynamic disturbances of the vortex also yielded enhanced meridional transport of NO<sub>x</sub>-rich and O<sub>3</sub>-rich air masses from the subtropics into the polar regions in the lower stratosphere. This effect was discussed by Konopka et al. (2007a) for the winter 2002/2003. They found that the enhanced meridional transport of NO<sub>x</sub> also caused ozone loss that can outweigh the halogen-induced ozone loss processes occurring in winter and early spring in the Arctic lower and middle stratosphere.

In this paper, model simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b; Konopka et al., 2007b) will be presented. For the Arctic winter 2003/2004 we analyze the long-term impact of enhanced NO<sub>x</sub> in the mesosphere caused by the extremely strong SPEs in October–November 2003 and the effect of the mesospheric intrusion in early 2004 on stratospheric ozone budget. Here we focus on the impact of enhanced NO<sub>x</sub> on ozone loss caused by downward transport from the mesosphere into the stratosphere, whereas enhancements of different NO<sub>y</sub> species below 55 km down to a 30 km altitude observed immediately after the SPEs (e. g. López-Puertas et al., 2005b) due to the local production of NO<sub>x</sub> are not considered.

## 2 The model study

To study the impact of the downward transport of enhanced NO<sub>x</sub> in the Arctic winter 2003/2004 on the stratospheric ozone budget, full chemistry studies were performed with the chemical transport model CLaMS (e. g., Konopka et al., 2003; Groß et al., 2005). The simulations cover the altitude range from 350–2000 K potential temperature ( $\approx$ 14–50 km altitude). The horizontal and vertical transport is driven by ECMWF winds and heating/cooling rates derived from a radiation calculation. The mixing procedure uses the mixing parameter as described in Konopka et al. (2004) with a horizontal resolution of 200 km and a vertical resolution increasing from 3 km at around 350 K potential temperature to approximately 13 km at around 2000 K potential temperature according to the model set-up (Konopka et al., 2007b). The halogen, NO<sub>x</sub>, and HO<sub>x</sub> chemistry is included mainly based on the current JPL evaluation (Sander et al., 2006). Before the first SPE occurred, the model was initialized at 4 October 2003 with mainly MIPAS observations (V3O) from 3–5 October 2003 (CH<sub>4</sub>, CO, N<sub>2</sub>O, O<sub>3</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, H<sub>2</sub>O, and ClONO<sub>2</sub>) processed at the Institut für Meteorologie und Klimaforschung Karlsruhe (IMK) and at the

Instituto de Astrofísica de Andalucía (IAA), Granada, Spain. CFC-11 was provided by L. Hoffmann (Hoffmann et al., 2007). Some species measured by MIPAS are not available over the full model altitude range, therefore these data are interpolated to typical tropospheric and mesospheric values at the lower and upper boundary, respectively. Other species are taken from the HALOE climatology (Groß and Russell, 2005) (HCl and HF) or from results of a simulation with the Mainz 2-D model (Gidel et al., 1983; Groß, 1996). For all species the lower boundary conditions at 350 K are taken through the course of the simulation from these initial values.

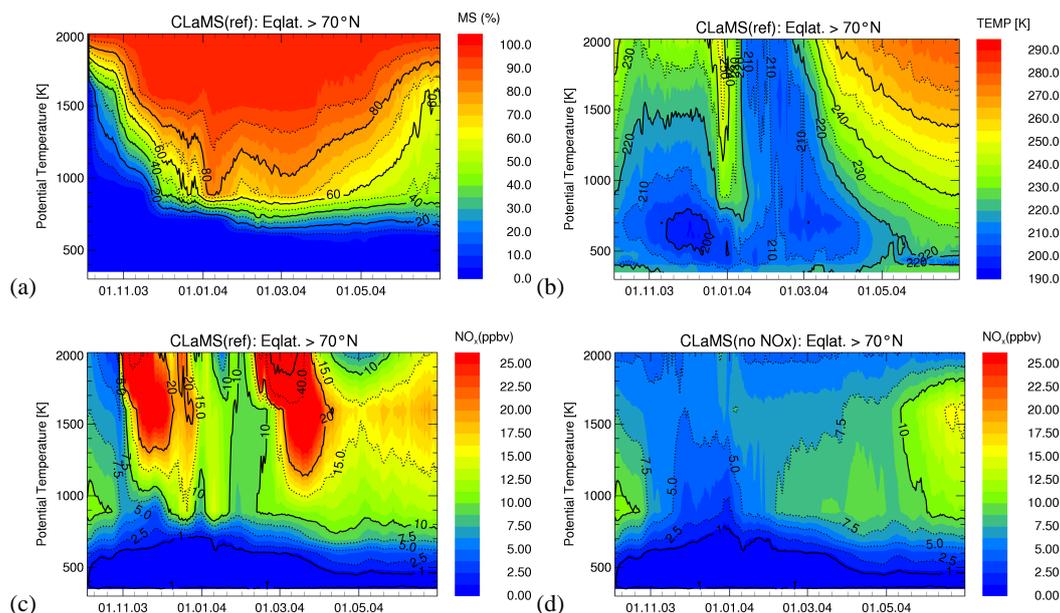
In the model, the flux of enhanced NO<sub>x</sub> from the mesosphere is implemented in the form of the upper boundary conditions at 2000 K potential temperature ( $\approx 50$  km altitude), which are updated every 24 h. The NO<sub>y</sub> constituents NO<sub>x</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub> and the tracers CH<sub>4</sub>, CO, H<sub>2</sub>O, N<sub>2</sub>O, and O<sub>3</sub> are taken from results of a long-term simulation performed with the KASIMA model (Karlsruhe Simulation Model of the middle Atmosphere) (Kouker et al., 1999). In this KASIMA simulation (T. Reddmann, personal communication, 2007), enhanced NO<sub>x</sub> concentrations in the mesosphere during disturbed periods were derived above 55 km from MIPAS observations (provided by the European Space Agency, ESA).

In addition to this CLaMS reference model run (referred to as “ref” run), a model simulation without an additional NO<sub>y</sub> entry (i. e. no NO<sub>x</sub>, N<sub>2</sub>O<sub>5</sub>, and HNO<sub>3</sub>) was performed at the upper boundary. Because most NO<sub>y</sub> at the upper boundary is NO<sub>x</sub>, in the following we refer to this simulation without an additional NO<sub>x</sub> source at the upper boundary as “no NO<sub>x</sub>” run. In addition, to estimate the possible maximum impact of NO<sub>x</sub> on stratospheric ozone loss, we derive a maximum NO<sub>x</sub> entry at the upper boundary condition from several satellite measurements of NO and NO<sub>2</sub> by the MIPAS instrument on board the ENVISAT satellite (provided by IMK/IAA) (Fischer et al., 2007), by the HALOE instrument on board the UARS satellite (Russell et al., 1993), and by the ACE-FTS instrument on board the SCISAT satellite (Bernath et al., 2005). To this end, we modify the upper boundary conditions derived from KASIMA. For each day at the upper boundary the NO<sub>x</sub> mixing ratios for equivalent latitudes greater than or equal to 60° N are replaced by the maximum NO<sub>x</sub> value observed by any satellite instruments within 60° and 90° N at 2000 K potential temperature on that day, or by the maximum NO or NO<sub>2</sub> value if no NO<sub>x</sub> measurement is available for this 24 h period. For days where no satellite observations are available we take the maximum NO<sub>x</sub> derived by KASIMA on that day. This model simulation is referred to as “max NO<sub>x</sub>” run.

### 3 Model results

To facilitate an analysis of the downward transport in CLaMS, a mesospheric tracer (MS) is implemented in the model which is initialized with 100% at the upper boundary and with zero below. During the model simulation this tracer is kept constant at the upper and lower boundary with 100% and 0%, respectively. This tracer quantifies the percentage of air originating from the upper boundary at 2000 K potential temperature. Figure 1a shows that the influence of the upper boundary and mesosphere, respectively, extends downward to about 600–700 K potential temperature from February until June 2004, i. e. slightly above the region where halogens typically effectively destroy ozone in the Arctic polar winter. Strong downward transport from the mesosphere down to 900 K (MS=80%) occurs at the beginning of January caused by the recovery of the upper vortex in early January. Further, strong transport down to 1000 K (MS=80%) is found at the beginning of March when the vortex was very strong (cf. Sect. 1, Manney et al., 2005). Figure 1b shows that the upper and middle stratospheric temperatures become atypically low during and after February as also reported by Manney et al. (2005). The lower stratospheric temperatures remain extremely high after the major warming. The final warming and the vortex breakup did not occur until end of April 2004, which is very late compared to other winters (WMO, 2007). Figure 1c shows clear signatures of enhanced NO<sub>x</sub>, which start in October 2003 caused by the large SPEs in October–November 2003 and propagate downwards from 2000 K to about 800 K potential temperature. Further, Fig. 1c shows that model signatures of increased NO<sub>x</sub> in February and March due to downward transport of upper atmospheric NO<sub>x</sub> produced throughout the winter by auroral and precipitating electrons (Funke et al., 2007) propagate down to approximately 800 K–900 K until March 2004. Figure 1d shows NO<sub>x</sub> without mesospheric NO<sub>x</sub> sources as simulated in the “no NO<sub>x</sub>” run. Here a typical seasonal variation of NO<sub>x</sub> can be seen that is not disturbed by an additional downward transport.

In our studies we found enhanced NO<sub>x</sub> of about 20 ppbv transported downwards to approximately 1200 K potential temperature ( $\approx 38$  km) until the end of March 2004 for equivalent latitudes greater than 70° N (see Fig. 1d). Randall et al. (2006) analyzed NO<sub>x</sub> enhancements in early 2004 measured by ACE-FTS. They found NO<sub>x</sub> enhancements in the range of 20 ppbv transported downwards until the end of March 2004 in altitude regions around 40 km poleward of 50° N (Randall et al., 2006) (Fig. 1). Further, a study by Randall et al. (2005) based on numerous satellite measurements (mainly HALOE, SAGE II, POAM II & III) show that a systematic descent of NO<sub>x</sub>-rich air occurred in the vortex that led to NO<sub>x</sub>-enhancements in the upper stratospheric vortex from March to May 2004. The anomalies declined as the vortex broke up, but were still evident even in July 2004. The model simulations presented here show similar results



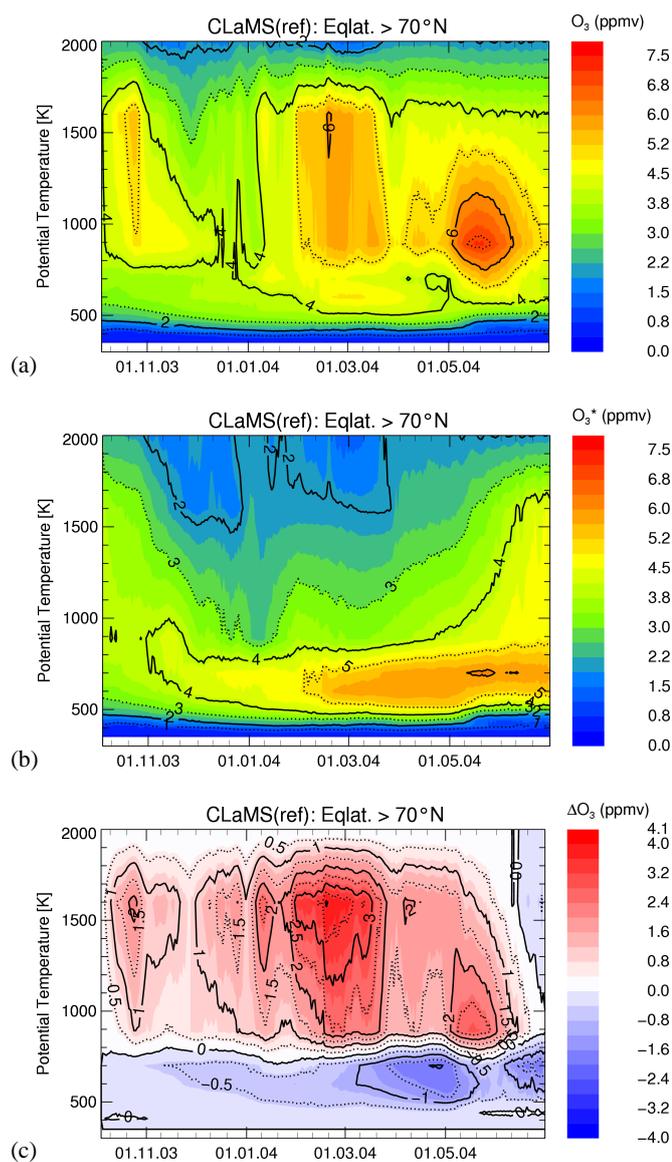
**Fig. 1.** Mean distributions, poleward of 70° N equivalent latitude, of (a) the mesospheric tracer MS, (b) the temperature, (c) NO<sub>x</sub> (=NO+NO<sub>2</sub>) for the reference model run (“ref”) and (d) for a simulation without an additional NO<sub>x</sub> source at the upper boundary (“no NO<sub>x</sub>”). To compare panel (c) and (d) the color range are the same, but in panel (c) the maximum NO<sub>x</sub> mixing ratios are much higher than the color range (see isolines). The potential temperature range from 350 to 2000 K corresponds to ≈14 to 50 km altitude.

as shown in Fig. 1c. Thus experimental results confirm the descent rate of NO<sub>x</sub>-rich air masses in the model simulations presented here.

The accumulated chemical ozone change ( $\Delta O_3$ ) shown in Fig. 2c is derived from the difference between the simulated (see Fig. 2a) and passively transported (see Fig. 2b) ozone. It allows the quantification of the chemical contribution to ozone change during the winter. From late January on, meridional transport of ozone-rich air from low-latitudes into the polar regions yields high ozone mixing ratios of up to 5–6 ppmv between 500–800 K (see Fig. 2b) caused by the vortex disruption in late January and the very weak lower stratospheric vortex during February and March (cf. Sect. 1). Below about 800 K, accumulated ozone loss dominates the ozone evolution during the winter and early spring (see Fig. 2c). Here, about 0.5 ppmv of accumulated ozone loss is simulated from December 2003 until February 2004 and about 1.0–2.0 ppmv in March and April 2004. Above about 800 K, accumulated ozone production dominates the ozone evolution during the winter and early spring (see Fig. 2c). The accumulated ozone production is strongest in late February and early March and yields values of up to 4 ppmv between 1300–1700 K. Here the accumulated ozone production increases because the sunlight returns after the polar night. Our findings show that above 800 K the impact of highly enhanced NO<sub>x</sub> values in the stratosphere due to downward transport from the mesosphere on ozone is small since these NO<sub>x</sub> values do not yield accumulated ozone loss as in altitudes below 800 K. Thus, above 800 K, the ozone

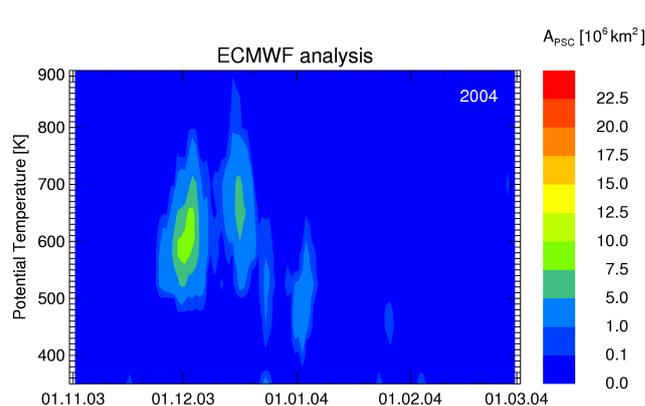
production in the descending mesospheric air is only counteracted to a certain extent by ozone loss caused by the very high NO<sub>x</sub> intrusion from the mesosphere. In the Arctic polar vortex in winter 2002/2003, only small enhancements of NO<sub>x</sub> were found in the stratosphere, but enhanced ozone was found in an intrusion of mesospheric air descending into the lower stratosphere (Müller et al., 2007). The fact that air masses originating from the mesosphere are characterized by enhanced O<sub>3</sub> values is consistent with our simulations showing ozone production in the descending mesospheric air for the Arctic winter 2003/2004.

Besides NO<sub>x</sub>-induced ozone loss, halogen-induced and HO<sub>x</sub>-induced ozone losses also have an important impact on polar ozone loss processes. However, halogen-induced ozone loss played a minor role during the winter 2003/2004, because the lower stratospheric temperatures were unusually high due to the vortex disruption in the lower stratosphere at the end of January. An analysis of ECMWF temperature data shows that PSCs could only occur during December 2003 and January 2004 between approximately 400–800 K potential temperatures (see Fig. 3). Limited to this time period the model simulates a small chlorine activation of up to 700 pptv ClO<sub>x</sub> (see Fig. 4a). Note that chlorine activation is only confined to the lower part of the region where most ozone depletion occurred in this time period (see Fig. 4b). This is consistent with results obtained by Vogel et al. (2003) and Konopka et al. (2007a), who found that NO<sub>x</sub>-induced ozone loss occurs slightly above the region where halogens destroy ozone in the Arctic polar winter. Consequently, the



**Fig. 2.** Mean distributions, poleward of 70° N equivalent latitude, of (a) ozone, (b) passively transported ozone (O<sub>3</sub><sup>\*</sup>), and (c) the accumulated chemical ozone change ( $\Delta O_3 = O_3 - O_3^*$ ) from the reference simulation performed with CLaMS.

ozone loss between 500–800 K is not only driven by ClO<sub>x</sub> chemistry. Above 800 K, the ClO<sub>x</sub> altitude profiles have a maximum at around 1600 K potential temperature ( $\approx 43$  km) during sunlight conditions. During polar night conditions the ClO mixing ratios are low in these altitudes (see Fig. 4a). In general, the destruction of ozone is mainly driven by NO<sub>x</sub> in the middle stratosphere with the absence of PSCs, whereas HO<sub>x</sub>-induced ozone loss plays an important role in the lowermost stratosphere and in the upper stratosphere and mesosphere, respectively.

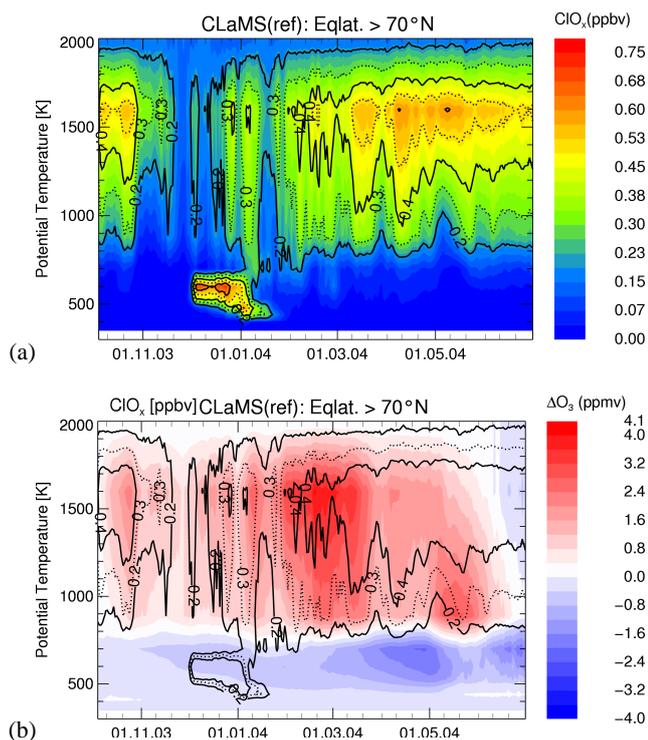


**Fig. 3.** Time series of the areas of potential PSC occurrence ( $A_{PSC}$ ) derived from ECMWF temperatures and  $T_{NAT}$  estimate. The color code indicates that the  $A_{PSC}$  are very small compared to a cold Arctic winter where  $A_{PSC}$  up to  $22 \times 10^6$  km<sup>2</sup> can occur (Tilmes et al., 2004).

## 4 Intercomparison of model results with satellite observations

### 4.1 NO<sub>x</sub> mixing ratios

To compare our simulated NO<sub>x</sub> mixing ratios with satellite observations conducted by MIPAS (processed at IMK/IAA; version: V3O\_NO\_9 and V3O\_NO<sub>2</sub>\_9) and ACE-FTS (V2.2) the model results were interpolated to the locations of the observations. Figure 5 shows the mean deviations of the simulated NO<sub>x</sub> mixing ratios from the satellite observations. The mean deviations are calculated for bins with an altitude range of 200 K potential temperature and for equivalent latitudes poleward of 70° N. Figure 5 shows that the reference run (top row) yields lower NO<sub>x</sub> mixing ratios than observed by satellites for the upper levels. This effect is still small at about −15% in November (−5 ppbv at 1800 K–2000 K) and increased to −101% (−17 ppbv at 1600 K–1800 K) and −151% (−19 ppbv at 1800 K–2000 K), respectively, in December. In January, no satellite data are available poleward of 70° N equivalent latitude for these altitudes. In February a deviation of up to −129% (−77 ppbv at 1800 K–2000 K) is found from ACE-FTS measurements. In March the deviation is even as much as −398% (−121 ppbv at 1600 K–1800 K) and −379% (−136 ppbv at 1800 K–2000 K) measured by MIPAS and up to −146% (−76 ppbv at 1600 K–1800 K) and −202% (−129 ppbv at 1800 K–2000 K) measured by ACE-FTS. The underestimation of upper stratospheric NO<sub>x</sub> in the reference run during periods of enhanced transport of NO<sub>x</sub>-rich air masses from the mesosphere into the stratosphere indicates that the NO<sub>x</sub> mixing ratios prescribed at the upper boundary are too low. As shown above, this effect is very small during the SPEs in October–November, but larger a few weeks after the SPEs in December and enormous during the strong mesospheric intrusion in February and March

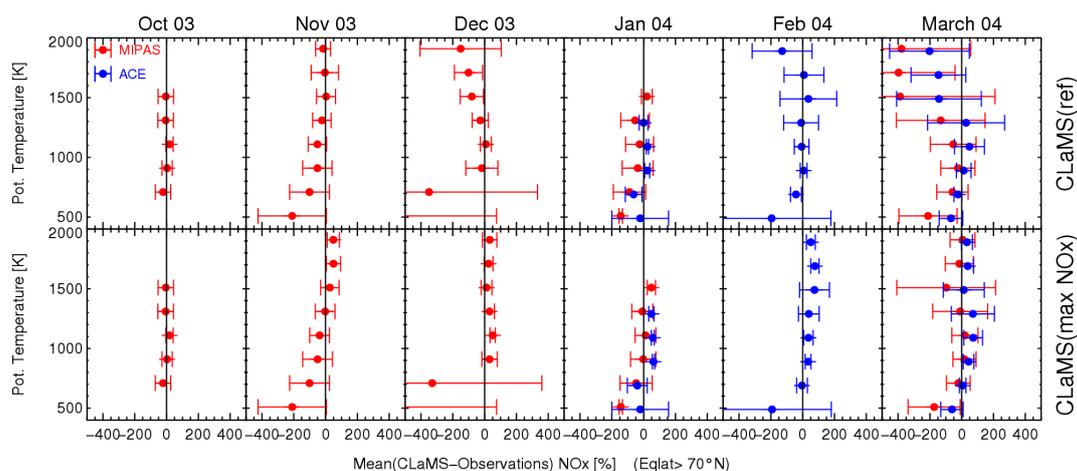


**Fig. 4.** (a) Time series of the mean distribution of activated chlorine ( $\text{ClO}_x = \text{ClO} + 2 \times \text{Cl}_2\text{O}_2$ ) poleward of  $70^\circ$  equivalent latitude for the reference model run. Panel (b) shows the chemical ozone change in the same way as Fig. 2c, but with contour lines of the mean distribution of  $\text{ClO}_x$ . It is clearly shown that the region of chlorine activation caused by PSC occurrence is mainly in the lower part of the region where most ozone loss occurred at that time.

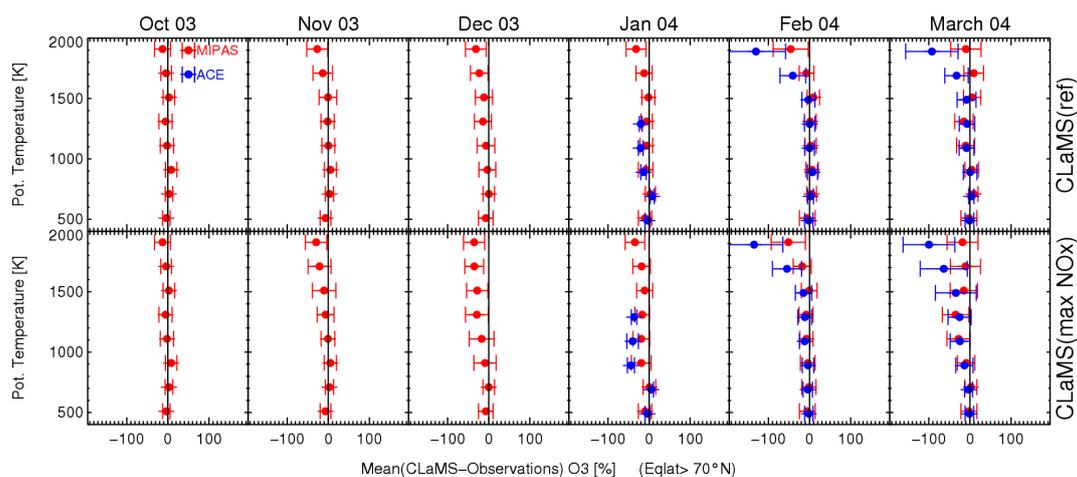
2004. Thus, these deviations are found during periods of strong downward transport of NO<sub>x</sub> from the mesosphere into the stratosphere. This means that in the KASIMA long-term simulations the NO<sub>x</sub> mixing ratios are underestimated at around 2000 K potential temperature ( $\approx 50$  km altitude). These large differences in NO<sub>x</sub> between the KASIMA simulations and the MIPAS IMK/IAA observations are mainly due to the fact that in KASIMA NO<sub>2</sub> nighttime measurements provided by ESA are used as a proxy for NO<sub>x</sub>. In the lower mesosphere, NO and NO<sub>2</sub> are not in a steady state. Thus, at the local time of MIPAS nighttime measurements (10 pm) NO is only partially converted to NO<sub>2</sub> via  $\text{NO} + \text{O}_3$ . Further, transport of NO from illuminated regions into the polar night region can act faster than photochemical NO losses, which leads to a significant NO contribution even during polar night. In consequence, the average NO contribution to NO<sub>x</sub> at 55 km depends on the availability of ozone and on the extension of the polar night area. Therefore NO<sub>2</sub> nighttime measurements are clearly a lower boundary for NO<sub>x</sub>. Further, two retrieval codes are used. For the KASIMA long-term simulations the ESA operational processor (Raspollini et al., 2006) is used because more NO<sub>2</sub> data are available, which is essential to perform the simulations. The obser-

vations shown in this work are NO<sub>x</sub> data provided by the IMK/IAA retrieval code (Funke et al., 2005), which allows, in contrast to the ESA operational processor, accurate inference of NO<sub>2</sub> volume mixing ratios giving consideration to all important non-LTE processes. The findings of a validation study of MIPAS-ENVISAT NO<sub>2</sub> operational data by Wetzel et al. (2007) show that large differences appear between both retrieval results. Especially at higher latitudes above about 50 to 55 km in February and March 2004 the NO<sub>2</sub> values provided by ESA are lower than by IMK/IAA. This is exactly the region where NO<sub>2</sub> mixing ratios for the KASIMA simulations are derived from MIPAS observations. Below this altitude region mean differences between both processors are up to 40% under perturbed polar night conditions in February and March 2004.

To study the impact of the underestimation of NO<sub>x</sub> mixing ratios at the upper boundary, we perform sensitivity tests with modified upper boundary conditions. At the upper boundary all NO<sub>x</sub> mixing ratios for equivalent latitudes greater than or equal to  $60^\circ$  N are replaced by the maximum NO<sub>x</sub> value derived by the IMK/IAA-MIPAS retrieval code (V30\_NO\_9 and V30\_NO2\_9), observed by HALOE (V19) or by ACE-FTS (V2.2) as described in Sect. 2. In general for this “max NO<sub>x</sub>” run the simulated NO<sub>x</sub> mixing ratios at the upper levels are somewhat higher than the satellite observations (see Fig. 5, bottom row). In February the deviation is up to 51% (154 ppbv at 1600 K–1800 K) and 77% (163 ppbv at 1800 K–2000 K) and in March only up to –15% (7 ppbv at 1600 K–1800 K) and 5% (33 ppbv at 1800 K–2000 K) measured by MIPAS and up to 38% (107 ppbv at 1600 K–1800 K) and 33% (116 ppbv at 1800 K–2000 K) measured by ACE-FTS. This is because at the upper boundary the NO<sub>x</sub> mixing ratios for equivalent latitudes greater than or equal  $60^\circ$  N are mainly replaced by the maximum NO<sub>x</sub> value observed by satellites on that day (see Sect. 2). Thus for the “max NO<sub>x</sub>” run the CLaMS NO<sub>x</sub> values are clearly on average higher than the satellite data as expected. Further, significant differences occur between the mean deviation calculated with IMK/IAA-MIPAS and ACE-FTS observations. Since NO<sub>x</sub> decays from the vortex center towards the vortex boundary in the reference run while it remains constant in the “max NO<sub>x</sub>” run, differences in the spatial NO<sub>x</sub> distribution between the reference and the “max NO<sub>x</sub>” run are most pronounced in the outer part of the vortex, i.e. the region where ACE-FTS observations were taken. This is because the solar occultation technique is used by ACE-FTS observations and therefore no profiles during polar night conditions can be derived in contrast to the MIPAS measurements. A recently reported validation between MIPAS and ACE-FTS measurements yields a good agreement of the NO<sub>x</sub> values in the frame of these exceptional atmospheric conditions in the Arctic winter 2003/2004 (Kerzenmacher et al., 2007). Nevertheless, the “max NO<sub>x</sub>” run represents an upper limit for the additional NO<sub>x</sub> entry at the upper boundary compared to both MIPAS and ACE-FTS observations.



**Fig. 5.** The mean deviations of the simulated NO<sub>x</sub> mixing ratios from MIPAS observations processed at IMK/IAA (red) and from ACE-FTS observations (blue, from January 2004). The mean deviations are calculated for bins with an altitude range of 200 K potential temperature and for equivalent latitudes poleward of 70° N. In the columns, the mean deviations from October 2003 until March 2004 are shown. In the top row the results for the reference run and in the bottom row the “max NO<sub>x</sub>” run are shown. The standard deviation of the mean deviations is indicated by error bars. We note that for February 2004 no NO<sub>x</sub> data from MIPAS processed at IMK/IAA are available. The plot symbols are shifted by a small range in the y-direction to distinguish more easily between MIPAS and ACE-FTS observations.



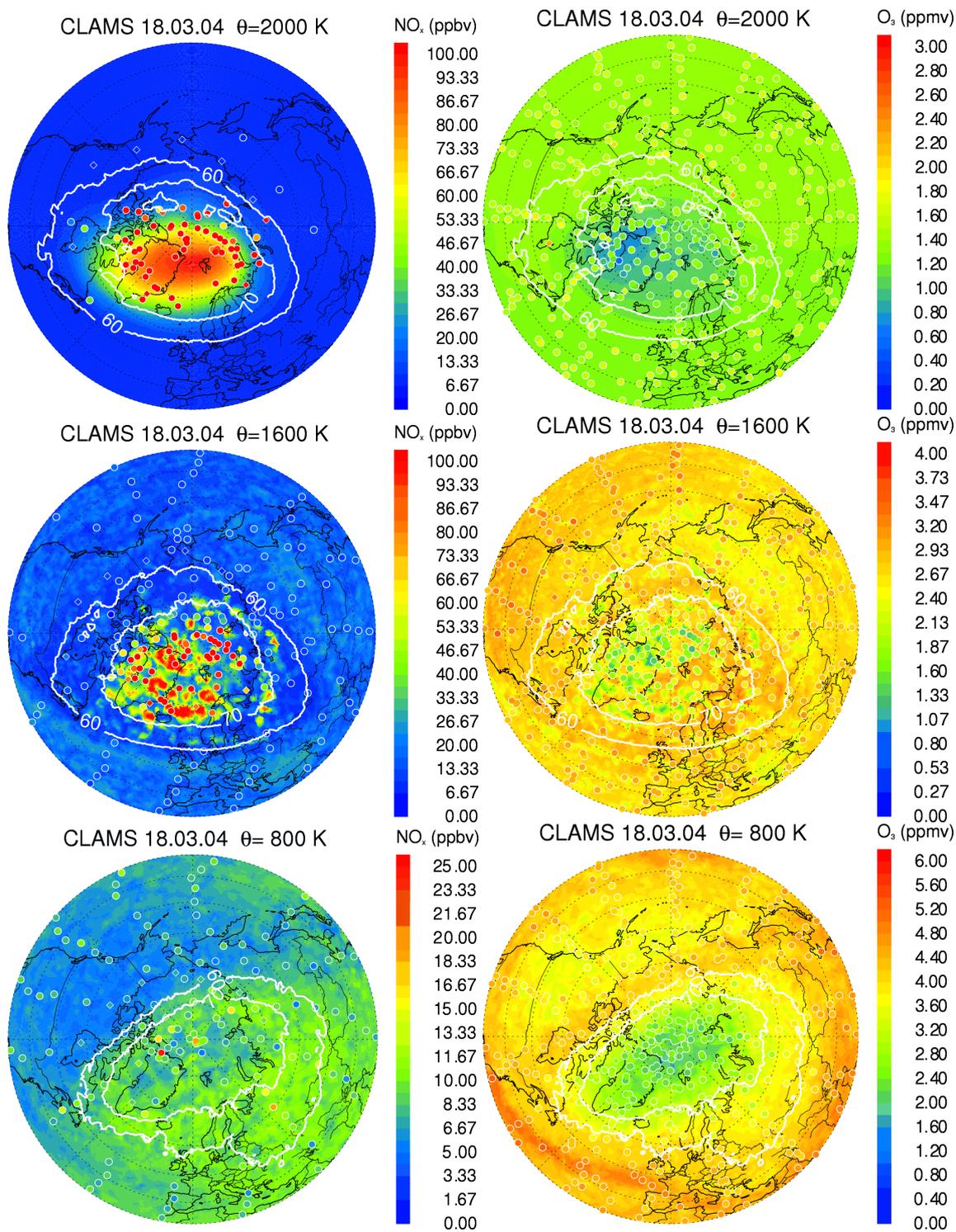
**Fig. 6.** As Fig. 5, but for ozone.

For the MIPAS measurements in the lower and middle stratosphere (below about 45 km), an overall accuracy of about 10–20% is indicated for NO<sub>2</sub> provided by IMK/IAA-MIPAS, but in cases of extremely high NO<sub>2</sub> in the mesosphere, uncertainties in NO<sub>x</sub> between 10–30% are derived (Funke et al., 2005).

In CLaMS the spatial distributions of NO<sub>x</sub> and ozone are very homogeneous at 2000 K caused by the upper boundary conditions taken from KASIMA results (see Fig. 7, top panel). In contrast, NO<sub>x</sub> and also ozone are distributed very inhomogeneously at levels below (see Fig. 7, middle and bottom panels). Even if these spatial distributions are highly inhomogeneous, these inhomogeneities are enhanced during the downward transport mainly within the po-

lar vortex as found by Ray et al. (2002). The corresponding patchy CLaMS distribution of NO<sub>x</sub> and ozone at levels below 2000 K (see Fig. 7, middle and bottom panels) is mainly due to a strong differential descent, i.e. adjacent air parcels experience different diabatic descent due to strong and spatially inhomogeneous descent rates at these altitudes. The CLaMS mixing algorithm preserves these inhomogeneities, which is consistent with satellite observations as shown in Fig. 7.

Further, Fig. 7 illustrates, as discussed before, that ACE-FTS and IMK/IAA-MIPAS NO<sub>x</sub> at 2000 K are much higher than the CLaMS reference run. On 18 March 2004, the maximum NO<sub>x</sub> mixing ratio measured by MIPAS and ACE-FTS is 328 ppbv and 216 ppbv, respectively, at 2000 K. That is a factor of 2–3 higher than the NO<sub>x</sub> values simulated by



**Fig. 7.** Horizontal view of NO<sub>x</sub> and O<sub>3</sub> at 2000 K, 1600 K, and 800 K potential temperature for the reference model run. The isolines for the equivalent latitude at 60° N and 70° N are marked by white lines. The model results and satellite observations (IMK/IAA-MIPAS: circles and ACE-FTS: diamonds) are shown for noon time. We note that all NO<sub>x</sub> mixing ratios beyond the scale are also plotted in red.

the CLaMS reference run for that day. Nevertheless, Fig. 7 shows that simulated and observed ozone mixing ratios are in very good agreement for that day (see additional scatter plots in the supplement <http://www.atmos-chem-phys.net/8/5279/2008/acp-8-5279-2008-supplement.pdf>). We will discuss this in the next section in more detail. Finally, Fig. 7 shows that an equivalent latitude of 60° N describes very well the areas of enhanced NO<sub>x</sub> mixing ratios because the enhancements depend on the downward transport of NO<sub>x</sub>, which in turn depends on the vortex strength.

To summarize, we compared the results of two model simulations with the observations: the reference run yielded rather lower NO<sub>x</sub> mixing ratios than observed and the “max NO<sub>x</sub>” run yielded in general clearly higher NO<sub>x</sub> mixing ratios and a larger area of enhanced NO<sub>x</sub> mixing ratios compared to satellite observations. Thus these two simulations represent a lower and a clear upper limit of the real distribution and absolute values of NO<sub>x</sub> within the Arctic polar vortex (see additional discussion of discrepancies between MIPAS and simulated NO<sub>x</sub> below 750 K in supplement <http://www.atmos-chem-phys.net/8/5279/2008/acp-8-5279-2008-supplement.pdf>).

#### 4.2 O<sub>3</sub> mixing ratios

To compare our simulated O<sub>3</sub> mixing ratios with satellite observations conducted by IMK/IAA MIPAS (Version: V3O.O<sub>3</sub>.7 to V3O.O<sub>3</sub>.9) and ACE-FTS (V2.2 update) (Dupuy et al., 2007) we calculate the mean deviations of the simulated ozone mixing ratios from the satellite observations as in Sect. 4.1 for NO<sub>x</sub> mixing ratios. A comparison between MIPAS ozone data retrieved by the IMK/IAA processor with several ground-based, balloon-borne, and satellite instruments for stratospheric ozone yields mean differences of generally ±10% (Steck et al., 2007). A currently reported validation of ozone from ACE-FTS (V2.0 update) with MIPAS ESA ozone found that the O<sub>3</sub> data are within ±10% between 10–42 km altitude, but increase above this range, with ACE-FTS reporting larger volume mixing ratios than MIPAS by up to 40% at around 53 km altitude (Cortesi et al., 2007). Figure 6 shows that for October 2003 the simulations and the observations of O<sub>3</sub> agree over all altitudes, as expected because the simulations are initialized with MIPAS observations. From November until March 2004 the simulations and the observations are in very good agreement for the reference run, except at the upper levels. Here in general the mean deviation at the upper level until February increases up to −45% (−0.9 ppmv, IMK/IAA-MIPAS) and −97% (−1.9 ppmv, ACE-FTS), respectively. However, in March 2004 the mean deviation at the upper level is only −10% (−0.08 ppmv, IMK/IAA-MIPAS) and −72% (−1.4 ppmv, ACE-FTS), respectively. The “max NO<sub>x</sub>” run yields in general smaller O<sub>3</sub> mixing ratios than in the reference run, because the NO<sub>x</sub>-induced ozone loss is higher in the “max NO<sub>x</sub>” run. Thus in February and March 2004,

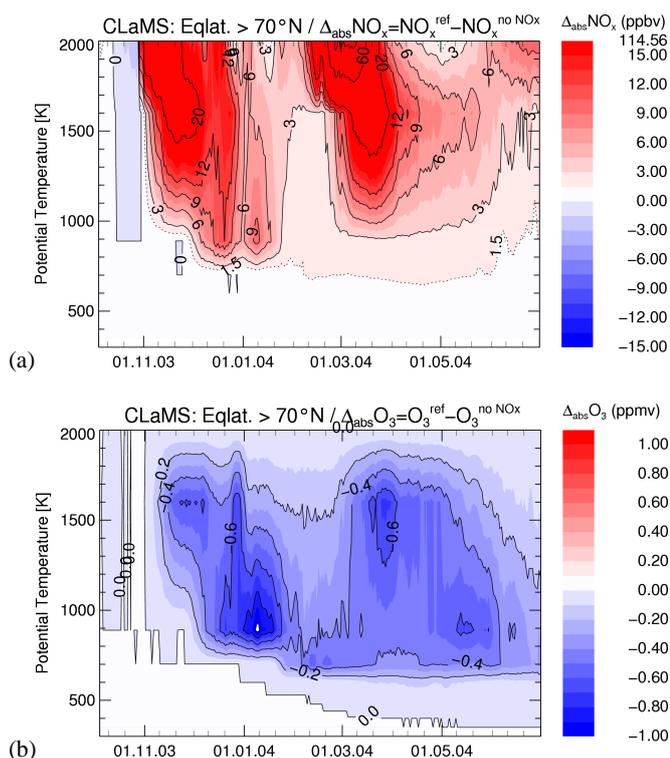
where the largest discrepancies between simulated and observed NO<sub>x</sub> occur (cf. Sect. 4.1) the simulated O<sub>3</sub> agrees best with the reference run. For these months simulated O<sub>3</sub> values in the “max NO<sub>x</sub>” are clearly lower than the satellite observations. Thus the “max NO<sub>x</sub>” run is a clear lower limit for O<sub>3</sub> compared to satellite observations. Furthermore, Fig. 6 shows that enhanced NO<sub>x</sub> at the upper boundary has an impact on the O<sub>3</sub> mixing ratios over the whole altitude profile (cf. below, Sect. 5). Finally, it is shown in Fig. 6 that the ozone mixing ratios at the upper boundary (i. e. in the KASIMA model) are somewhat too low compared to satellite observations.

In general, differences between observations conducted by IMK/IAA-MIPAS or ACE-FTS and the CLaMS simulations increase with altitude, but the form of both altitude profiles is very similar. This is consistent with the fact that above approximately 40 km altitude ACE-FTS reports larger volume mixing ratios than ESA-MIPAS by up to 40% (Cortesi et al., 2007). The length of the error bars in Fig. 6 indicates the variability in the difference between simulated and observed O<sub>3</sub> values.

In summary, the comparison between simulated and observed ozone mixing ratios confirms that the “max NO<sub>x</sub>” run is an upper limit case which overestimates the strength of the NO<sub>x</sub> intrusions at the upper boundary and underestimates the ozone mixing ratios, i. e. the O<sub>3</sub> destruction in this model run is too high compared to IMK/IAA-MIPAS and ACE-FTS measurements. Thus, the reference run yields the best agreement with O<sub>3</sub> satellite observations.

## 5 Ozone loss

To answer the question of what is the quantitative influence of the mesospheric NO<sub>x</sub> sources on stratospheric ozone loss, CLaMS simulations with and without a mesospheric NO<sub>x</sub> source at the upper model boundary are compared. For the reference model run the respective differences of NO<sub>x</sub> ( $\Delta_{\text{abs}}\text{NO}_x$ ) and O<sub>3</sub> ( $\Delta_{\text{abs}}\text{O}_3$ ) shown in Fig. 8a and b quantify the increase of NO<sub>x</sub> and the ozone loss triggered by the intrusion of mesospheric air. The strong enhancements of NO<sub>x</sub> in November/December 2003 and in February/March 2004 are clearly visible in Fig. 8a. The highest mean values (70°–90° N equivalent latitude) of additional NO<sub>x</sub> are up to approximately 115 ppbv and occur at the upper boundary in March 2004. The spatial distribution between  $\Delta_{\text{abs}}\text{NO}_x$  and  $\Delta_{\text{abs}}\text{O}_3$  correlates fairly well. The strongest impact of enhanced NO<sub>x</sub> on O<sub>3</sub> mixing ratios is found in January between 850 K and 1100 K potential temperature. Here, as shown before (cf. Sect. 3), there is a strong downward transport due to the recovery of the upper vortex occur that causes up to 1 ppmv (28%) lower ozone mixing ratios than in the “no NO<sub>x</sub>” run. Further, during the period of the very strong upper vortex in February and March 2004 (cf. Sect. 1) our model results show up to 0.6–0.7 ppmv (17%) lower O<sub>3</sub> mixing ratios

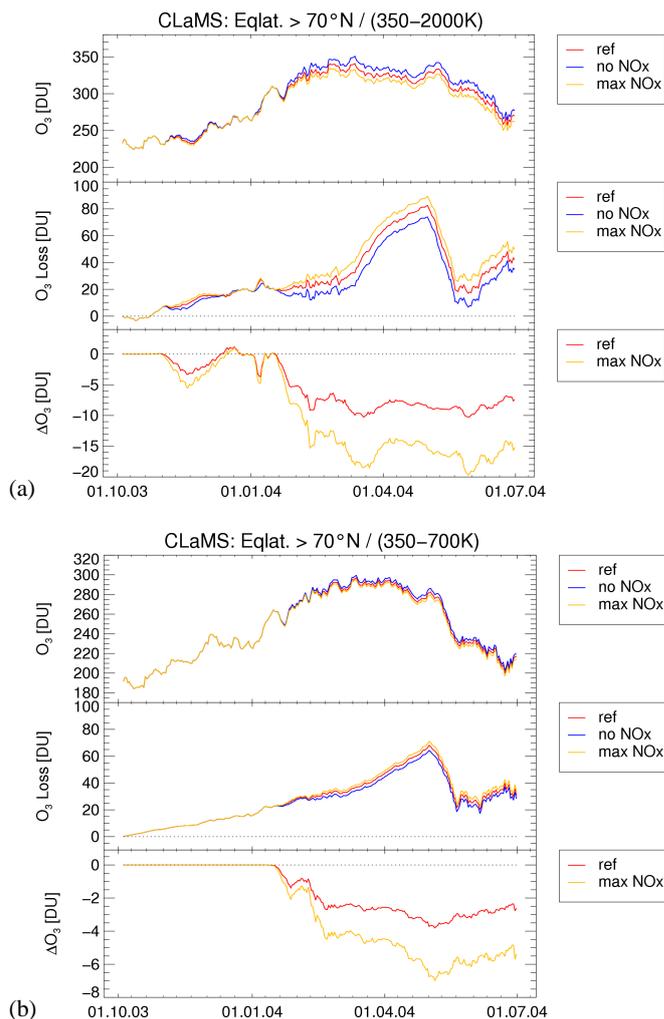


**Fig. 8.** (a) Additional NO<sub>x</sub> ( $\Delta_{\text{abs}}\text{NO}_x$ ) and (b) ozone reduction  $\Delta_{\text{abs}}\text{O}_3$  poleward of 70° N equivalent latitude due to mesospheric NO<sub>x</sub> intrusions over the course of the winter 2003–2004 for the reference model run.

at the end of March 2004 between 1300 K and 1700 K potential temperature. Furthermore, from the beginning of March onwards a small impact of enhanced NO<sub>x</sub> on ozone is found down to 400 K potential temperature (17–18 km altitude).

The enhanced NO<sub>x</sub> mixing ratios also have an impact on HO<sub>x</sub>. The spatial distribution of the minima and maxima between  $\Delta_{\text{abs}}\text{O}_3$  and  $\Delta_{\text{abs}}\text{HO}_x$  correlates fairly well (not shown here). Up to approximately 150 pptv (112%) lower HO<sub>x</sub> mixing ratios than in the “no NO<sub>x</sub>” run are found in January between 850 K and 1100 K potential temperature. That means the HO<sub>x</sub>-induced ozone loss is lower in the reference run than in the “no NO<sub>x</sub>” run.

The impact of mesospheric NO<sub>x</sub> sources on the column ozone is shown in Fig. 9a (top panel) integrated over the entire simulated altitude range ( $\approx 14$ –50 km). The column ozone is shown in red for the reference model simulation (“ref”), in blue for the simulation without mesospheric sources (“no NO<sub>x</sub>”), and in yellow for the run with a maximum NO<sub>x</sub> source (“max NO<sub>x</sub>”). The corresponding accumulated column ozone loss in the stratosphere calculated from the simulated O<sub>3</sub> values minus the passively transported ozone (as shown in Fig. 2) is shown in Fig. 9a (middle panel). Until the end of April a column ozone loss of up to approximately 80 DU is simulated for the reference run and up to approximately 90 DU for the “max NO<sub>x</sub>” run. Thereafter the column ozone loss strongly decreases because the



**Fig. 9.** (a) Top panel: Column ozone (in Dobson units) with (red), without (blue), and with maximum (yellow) mesospheric NO<sub>x</sub> sources integrated over the entire simulated altitude range from 350 K to 2000 K ( $\approx 14$ –50 km) for equivalent latitudes poleward of 70° N. Middle panel: Ozone loss in DU for these model runs. Bottom panel:  $\Delta\text{O}_3$  caused by the additional NO<sub>x</sub> source at the upper boundary. Shown is the ozone column of the “no NO<sub>x</sub>” run minus the ozone column of the “ref” (red) and the “max NO<sub>x</sub>” run (yellow). (b) same as (a), but for an altitude range from 350 K to 700 K ( $\approx 14$ –27 km) potential temperature.

final warming occurred at the end of April 2004 resulting in transport of mid-latitude air masses to the pole that have encountered less chemical ozone depletion. In Fig. 9a (bottom panel) the ozone losses attributable to enhanced mesospheric NO<sub>x</sub> intrusion are shown. This value is calculated from the difference between the “no NO<sub>x</sub>” run and the reference run (red) and the “max NO<sub>x</sub>” run (yellow), respectively. At the end of March the ozone loss attributable to mesospheric NO<sub>x</sub> intrusion in early 2004 is up to 10 DU (equivalent to  $\approx 3\%$  of the ozone column) for the reference run and up to 18 DU (equivalent to  $\approx 6\%$  of the ozone column) for the “max

NO<sub>x</sub>run (see Fig. 9a, bottom panel). That means that nearly twice the ozone loss occurs in the “max NO<sub>x</sub>” run than for the reference run. Further, Fig. 9a (bottom panel) shows  $\Delta O_3$  of approximately 19 DU at the end of May. This is after the final warming occurred at the end of April. This feature shows that enhanced mesospheric NO<sub>x</sub> values still have an impact on ozone chemistry even during the change from polar winter to summer conditions. Thus we conclude that the column ozone loss in the stratosphere at the end of March assigned to mesospheric NO<sub>x</sub> sources is about 10 DU, but lower than 18 DU. The column ozone loss in the stratosphere caused by the solar protons producing NO<sub>x</sub> at altitudes above 55 km in October–November 2003 is up to 3.3 DU with an upper limit of 5.5 DU in mid-November. These absolute values are small compared to the ozone loss in spring 2004 caused by the mesospheric NO<sub>x</sub> intrusions, but their fraction of the total accumulated ozone loss that occurred until mid-November is up to 36% and 48%, respectively.

The presented column ozone loss in the stratosphere is derived for equivalent latitudes greater than 70° N. The impact of mesospheric enhanced NO<sub>x</sub> is strongest for high equivalent latitudes because the downward transport depends on the vortex strength. Therefore choosing a wider latitude range to analyze the average column ozone loss yields lower column ozone loss.

Further, we also calculated the ozone loss over the winter and the ozone loss caused by mesospheric NO<sub>x</sub> sources for the lower stratosphere over an altitude range from 350 K to 700 K ( $\approx 14$ –27 km, see Fig. 9b). Here a total ozone loss until end of April of up to 68 DU for the “ref” run and up to 71 DU for the “max NO<sub>x</sub>” run is found. A maximum column ozone loss at the end of April assigned to mesospheric NO<sub>x</sub> sources is up to 3.5 DU for the reference run and 6.5 DU for the “max NO<sub>x</sub>” run, respectively. Unfortunately, no analyses of the polar stratospheric ozone loss for the Arctic winter 2003/2004 exist so far because the halogen-induced ozone loss plays a minor role and yields very low ozone loss over the winter as mentioned before. But a three-dimensional model study of the Arctic ozone loss in that winter results in an O<sub>3</sub> change of approximately 50 DU between 345–670 K (poleward of 65° equivalent latitude) until the end of March and beginning of April (Feng et al., 2005). Our simulations yield 45–50 DU (“ref” run) and 47–52 DU (“max NO<sub>x</sub>” run) until the end of March and beginning of April. However, the simulation by Feng et al. (2005) started at the beginning of December 2003 and our simulations started at the beginning of October 2003, and secondly our analysis is for equivalent latitudes poleward of 70° in contrast to 65° in the Feng et al. (2005) study. Nevertheless, we can conclude that our simulations are the same range as the results by Feng et al. (2005). Thus our finding shows that the impact due to enhanced mesospheric NO<sub>x</sub> values on ozone loss processes in the lower stratosphere (350–700 K) is about 5% but lower than 9% for the Arctic winter 2003/2004.

For cold Arctic winters an accumulated ozone loss in the lower stratosphere was derived in the range of about 100 DU (e. g. Rex et al., 2004; Tilmes et al., 2006). Thus in cold Arctic winters with strong halogen-induced ozone loss the impact on the column ozone of enhanced mesospheric NO<sub>x</sub> values as analyzed in this work would be very small. Moreover, Fig. 9b (bottom panel) shows that enhanced mesospheric NO<sub>x</sub> values have an impact on ozone loss below 700 K from mid-February during the period of the very strong upper stratospheric vortex. Thus in the lower stratosphere (350–700 K) the non-local production of NO<sub>x</sub> caused by SPEs of October–November 2003 have a negligibly small impact on ozone loss.

In our simulations, the enhancements of different NO<sub>y</sub> species below 55 km down to 30 km altitude observed immediately after the SPEs (e. g. López-Puertas et al., 2005b) caused by particle precipitation reaching the stratosphere are not considered. The impact of local NO<sub>x</sub> production on polar ozone loss is considered in a study by Jackman et al. (2005b), where the influence of the solar proton events in October–November 2003 is simulated with a 2-D CTM. They calculated a total column ozone loss of 0.4 % (1.5 DU) in mid-November 2003 increasing to about 1.1 % (4.1 DU) between mid-February and the end of March 2004 for latitudes < 70° N, which is caused by the October–November 2003 SPEs (C. Jackman, personal communication, 2008). We derive a column ozone loss of about 3.3 DU, but lower than 5.5 DU in mid-November caused by the solar protons producing NO<sub>x</sub> at altitudes above 55 km in October–November 2003. The reason for this discrepancy is not clear at the present, but the representation of diabatic descent in the vortex and vortex confinement are rather different in a 2-D CTM and in the 3-D Model CLaMS. The difference might be an indication that in mid-November 2003 also the transport of enhanced NO<sub>x</sub> not caused directly by the SPEs in October–November 2003 from the mesosphere into the stratosphere had an impact on the total ozone loss in the stratosphere during this period. On an absolute scale, the differences are small and our results support the conclusion by Jackman et al. (2005b) that the impact of solar proton events on the northern hemisphere total polar ozone decreases is small.

## 6 Summary and conclusions

The impact of the downward transport of enhanced upper atmospheric NO<sub>x</sub> caused by solar proton events in October–November 2003 and by mesospheric NO<sub>x</sub> intrusions in early 2004 produced throughout the winter by auroral and precipitating electrons on the stratospheric ozone budget was studied by performing model simulations with the chemical transport model CLaMS. Upper boundary conditions were taken from the results of a long-term simulation conducted with KASIMA, where increased NO<sub>x</sub> concentration in the mesosphere was derived from MIPAS measurements

(reference run). For the Arctic polar region (equivalent lat. >70° N) we found that enhanced NO<sub>x</sub> caused by solar protons only for altitudes above 55 km in October–November 2003 was transported downward into the middle stratosphere to about 800 K potential temperature (≈30 km) until the end of December 2003. The mesospheric NO<sub>x</sub> intrusion due to downward transport of upper atmospheric NO<sub>x</sub> produced by auroral and precipitating electrons (Funke et al., 2007) affected NO<sub>x</sub> mixing ratios down to about 700 K potential temperature (≈27 km) until March 2004. A comparison of the reference run with a simulation without an additional NO<sub>x</sub> source at the upper boundary shows that O<sub>3</sub> mixing ratios are affected by transporting high burdens of NO<sub>x</sub> down to about 400 K (≈17–18 km) during the winter. Locally, an additional ozone loss of the order of 1 ppmv is simulated for January between 850–1200 K potential temperature during the period of the strong polar vortex in the middle stratosphere.

We emphasize that the enhancements of different NO<sub>y</sub> species below 55 km downward to 30 km altitude due to the local production of NO<sub>x</sub> observed immediately after the SPEs (e. g. López-Puertas et al., 2005b) caused by particle precipitation down in to the stratosphere are not considered in our simulations nor is the local production of HO<sub>x</sub>. Thus, in our simulations only the transport of enhanced NO<sub>x</sub> from the mesosphere (upper boundary condition) to the stratosphere is considered and the local production of NO<sub>x</sub> and HO<sub>x</sub> below 55 km altitude is neglected.

An intercomparison of simulated NO<sub>x</sub> and O<sub>3</sub> mixing ratios with satellite observations by ACE-FTS and MIPAS shows that the NO<sub>x</sub> mixing ratios at the upper boundary derived from KASIMA simulations are in general too low. Therefore a model simulation was performed with higher NO<sub>x</sub> mixing ratios at the upper boundary derived from satellite measurements. For this model run (“max NO<sub>x</sub>”) the simulated NO<sub>x</sub> mixing ratios and the total area of enhanced NO<sub>x</sub> mixing ratios are in general higher compared to satellite observations and provide an upper limit for the impact of mesospheric NO<sub>x</sub> on stratospheric ozone chemistry. The comparison between simulated and observed ozone mixing ratios confirms the “max NO<sub>x</sub>” run is an upper limit which overestimates the NO<sub>x</sub> entry at the upper boundary and underestimates O<sub>3</sub> due to stronger O<sub>3</sub> destruction. Moreover in the “ref” run the simulated O<sub>3</sub> is in very good agreement with satellite measurements.

Our findings show that halogen-induced ozone loss plays a minor role in the Arctic winter 2003/2004 because the lower stratospheric temperatures were unusually high. Therefore the ozone loss processes in the Arctic winter stratosphere 2003/2004 were mainly driven by NO<sub>x</sub> chemistry. Further, in addition to the transport of NO<sub>x</sub>-rich mesospheric air masses in the stratosphere due to SPEs in October–November 2003 and the downward transport of upper atmospheric NO<sub>x</sub> produced by auroral and precipitating electrons in early 2004, the ozone loss processes were also strongly affected by meridional transport of subtropical air masses. Likewise,

in this case air masses rich in both ozone and NO<sub>x</sub> were transported into the lower polar stratosphere during the major warming that occurred in December 2003 and January 2004.

We found that up to 80 DU total ozone loss occurred in the stratosphere until the end of April 2004 between 350–2000 K potential temperature (≈14–50 km). The additional ozone loss caused by transport of mesospheric NO<sub>x</sub>-rich air into the stratosphere is about 10 DU (3%) but lower than the 18 DU (6%) found at the end of March 2004. Due to the solar protons producing NO<sub>x</sub> above 55 km during the Halloween solar storm event, an additional accumulated ozone loss of approximately 3.3 DU (36%) but below 5.5 DU (48%) was simulated through mid-November 2003. Thus the absolute impact on total accumulated ozone loss of the mesospheric NO<sub>x</sub> intrusion in early 2004 is stronger than that of the SPEs in October–November 2003, but the relative impact is smaller. In the lower stratosphere (350–700 K ≈14–27 km), the non-local production of NO<sub>x</sub> caused by SPEs of October–November 2003 has a negligibly small impact on ozone loss until the end of November and the mesospheric NO<sub>x</sub> intrusions in early 2004 yield a small ozone loss of about 3.5 DU (5%), but lower than 6.5 DU (9%) until end of March. Thus, owing to the meteorological conditions, NO<sub>x</sub> enhancements caused by the mesospheric NO<sub>x</sub> intrusion in early 2004 have a stronger impact on ozone loss processes in the low stratosphere than the solar proton-produced NO<sub>x</sub> at altitudes above 55 km caused by the October–November 2003 SPEs. Because the strength of the upper stratospheric vortex after the major warming in early 2004 is stronger than for the vortex in late 2003, the downward transport of enhanced NO<sub>x</sub> from the mesosphere down into the lower stratosphere in early 2004 is more effective.

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## References

- Bernath, P., McElroy, C., Abrams, M., et al.: Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, 32, L15S01, doi:10.1029/2005GL022386, 2005.
- Cortesi, U., Lambert, C., De Clercq, G., et al.: Geophysical validation of MIPAS-ENVISAT operational ozone data, *Atmos. Chem. Phys.*, 7, 4807–4867, 2007, <http://www.atmos-chem-phys.net/7/4807/2007/>.
- Crutzen, P. J., Isaksen, I. A. S., and Reid, G. C.: Solar proton events: Stratospheric sources of nitric oxide, *Science*, 189, 457–459, 1975.
- Degenstein, D. A., Lloyd, N. D., Bourassa, A. E., Gattinger, R. L., and Llewellyn, E. J.: Observations of Mesospheric Ozone Depletion during the October 28, 2003 Solar Proton Event by OSIRIS, *Geophys. Res. Lett.*, 32, L03S11, doi:10.1029/2004GL021521, 2005.
- Dupuy, E., Walker, K. A., Kar, J., Boone, C. D., McElroy, C. T., Bernath, P. F., Drummond, J. R., Skelton, R., McLeod, S. D., Hughes, R. C., Nowlan, C. R., Dufour, D. G., Zou, J., Nichitiu, F., Strong, K., Baron, P., Bevilacqua, R. M., Blumenstock, T., Bodeker, G. E., Borsdorff, T., Bourassa, A. E., Bovensmann, H., Boyd, I. S., Bracher, A., Brogniez, C., Burrows, J. P., Catoire, V., Ceccherini, S., Chabrillat, S., Christensen, T., Coffey, M. T., Cortesi, U., Davies, J., De Clercq, C., Degenstein, D. A., De Mazière, M., Demoulin, P., Dodion, J., Firanski, B., Fischer, H., Forbes, G., Froidevaux, L., Fussen, D., Gerard, P., Godin-Beekman, S., Goutail, F., Granville, J., Griffith, D., Haley, C. S., Hannigan, J. W., Höpfner, M., Jin, J. J., Jones, A., Jones, N. B., Jucks, K., Kagawa, A., Kasai, Y., Kerzenmacher, T. E., Kleinböhl, A., Klekociuk, A. R., Kramer, I., Küllmann, H., Kutippurath, J., Kyrölä, E., Lambert, J.-C., Livesey, N. J., Llewellyn, E. J., Lloyd, N. D., Mahieu, E., Manney, G. L., Marshall, B. T., McConnell, J. C., McCormick, M. P., McDermid, I. S., McHugh, M., McLinden, C. A., Mellqvist, J., Mizutani, K., Murayama, Y., Murtagh, D. P., Oelhaf, H., Parrish, A., Petelina, S. V., Piccolo, C., Pommereau, J.-P., Randall, C. E., Robert, C., Roth, C., Schneider, M., Senten, C., Steck, T., Strandberg, A., Strawbridge, K. B., Sussmann, R., Swart, D. P. J., Tarasick, D. W., Taylor, J. R., Tétard, C., Thomason, L. W., Thompson, A. M., Tully, M. B., Urban, J., Vanhellefont, F., von Clarmann, T., von der Gathen, P., von Savigny, C., Waters, J. W., Witte, J. C., Wolff, M., and Zawodny, J. M.: Validation of ozone measurements from the Atmospheric Chemistry Experiment (ACE), *Atmos. Chem. Phys. Discuss.*, 8, 2513–2656, 2008, <http://www.atmos-chem-phys-discuss.net/8/2513/2008/>.
- Feng, W., Chipperfield, M. P., Davies, S., Sen, B., Toon, G., Blavier, J. F., Webster, C. R., Volk, C. M., Ulanovsky, A., Ravegnani, F., von der Gathen, P., Jost, H., Richard, E. C., and Claude, H.: Three-dimensional model study of the Arctic ozone loss in 2002/2003 and comparison with 1999/2000 and 2003/2004, *Atmos. Chem. Phys.*, 5, 139–152, 2005, <http://www.atmos-chem-phys.net/5/139/2005/>.
- Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehhalt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopman, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G., and Zander, R.: MIPAS: an instrument for atmospheric and climate research, *Atmos. Chem. Phys.*, 8, 2151–2188, 2008, <http://www.atmos-chem-phys.net/8/2151/2008/>.
- Funke, B., von Clarmann, M. L.-P. T., Stiller, G. P., Fischer, H., Glatthor, N., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Tsidu, G. M., Milz, M., Steck, T., and Wang, D. Y.: Retrieval of stratospheric NO<sub>x</sub> from 5.3 and 6.2 μm nonlocal thermodynamic equilibrium emissions measured by Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on Envisat, *J. Geophys. Res.*, 110, D09302, doi:10.1029/2004JD005225, 2005.
- Funke, B., López-Puertas, M., Fischer, H., Stiller, G., von Clarmann, T., Wetzel, G., Carli, B., and Belotti, C.: Comment on “Origin of the January–April 2004 increase in stratospheric NO<sub>2</sub> observed in northern polar latitudes” by Jean-Baptist Renard et al., *Geophys. Res. Lett.*, 34, L07813, doi:10.1029/2006GL027518, 2007.
- Gidel, L. T., Crutzen, P. J., and Fishman, J.: A two-dimensional photochemical model of the atmosphere; 1: Chlorocarbon emissions and their effect on stratospheric ozone, *J. Geophys. Res.*, 88, 6622–6640, 1983.
- Groß, J.-U.: Modelling of Stratospheric Chemistry based on HALOE/UARS Satellite Data, PhD thesis, University of Mainz, 1996.
- Groß, J.-U. and Russell III, J. M.: Technical note: A stratospheric climatology for O<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NO<sub>x</sub>, HCl and HF derived from HALOE measurements, *Atmos. Chem. Phys.*, 5, 2797–2807, 2005, <http://www.atmos-chem-phys.net/5/2797/2005/>.
- Groß, J.-U., Günther, G., Müller, R., Konopka, P., Bausch, S., Schlager, H., Voigt, C., Volk, C. M., and Toon, G. C.: Simulation of denitrification and ozone loss for the Arctic winter 2002/2003, *Atmos. Chem. Phys.*, 5, 1437–1448, 2005, <http://www.atmos-chem-phys.net/5/1437/2005/>.
- Hoffmann, L., Kaufmann, M., Spang, R., Müller, R., Remedios, J. J., Moore, D. P., Volk, C. M., von Clarmann, T., and Riese, M.: Envisat MIPAS measurements of CFC-11: retrieval, validation, and climatology, *Atmos. Chem. Phys.*, 8, 3671–3688, 2008, <http://www.atmos-chem-phys.net/8/3671/2008/>.
- Jackman, C. H., Frederick, J. E., and Stolarski, R. S.: Production of odd nitrogen in the stratosphere and mesosphere – an intercomparison of source strengths, *J. Geophys. Res.*, 85, 7495–7505, 1980.
- Jackman, C. H., DeLand, M. T., Labow, G. J., Fleming, E. L., Weisenstein, D. K., Ko, M. K. W., Sinnhuber, M., Anderson, J., and Russell, J. M.: The influence of the several very large solar proton events in years 2000–2003 on the neutral middle atmosphere, *Adv. Space Res.*, 35, 445–450, 2005a.
- Jackman, C. H., DeLand, M. T., Labow, G. J., Fleming, E. L., Weisenstein, D. K., Ko, M. K. W., Sinnhuber, M., and Russell, J. M.: Neutral atmospheric influences of the solar proton events in October–November 2003, *J. Geophys. Res.*, 110, A09S27, doi:10.1029/2004JA010888, 2005b.
- Kerzenmacher, T., Wolff, M. A., Strong, K., Dupuy, E., Walker, K. A., Amekudzi, L. K., Batchelor, R. L., Bernath, P. F., Berthet, G., Blumenstock, T., Boone, C. D., Bramstedt, K., Brogniez, C., Brohede, S., Burrows, J. P., Catoire, V., Dodion, J., Drummond, J. R., Dufour, D. G., Funke, B., Fussen, D., Goutail, F., Griffith, D. W. T., Haley, C. S., Hendrick, F., Höpfner, M., Huret, N., Jones, N., Kar, J., Kramer, I., Llewellyn, E. J., López-Puertas, M., Manney, G., McElroy, C. T., McLinden, C. A., Melo, S.,

- Mikuteit, S., Murtagh, D., Nichitiu, F., Notholt, J., Nowlan, C., Piccolo, C., Pommereau, J.-P., Randall, C., Raspollini, P., Ridolfi, M., Richter, A., Schneider, M., Schrems, O., Silicani, M., Stiller, G. P., Taylor, J., Tétard, C., Toohey, M., Vanhellefont, F., Warneke, T., Zawodny, J. M., and Zou, J.: Validation of NO<sub>2</sub> and NO from the Atmospheric Chemistry Experiment (ACE), *Atmos. Chem. Phys. Discuss.*, 8, 3027–3142, 2008, <http://www.atmos-chem-phys-discuss.net/8/3027/2008/>.
- Konopka, P., Grooß, J.-U., Bausch, S., Müller, R., McKenna, D. S., Morgenstern, O., and Orsolini, Y.: Dynamics and chemistry of vortex remnants in late Arctic spring 1997 and 2000: Simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS), *Atmos. Chem. Phys.*, 3, 839–849, 2003, <http://www.atmos-chem-phys.net/3/839/2003/>.
- Konopka, P., Steinhilber, H.-M., Grooß, J.-U., Günther, G., Müller, R., Elkins, J. W., Jost, H.-J., Richard, E., Schmidt, U., Toon, G., and McKenna, D. S.: Mixing and Ozone Loss in the 1999–2000 Arctic Vortex: Simulations with the 3-dimensional Chemical Lagrangian Model of the Stratosphere (CLaMS), *J. Geophys. Res.*, 109, D02315, doi:10.1029/2003JD003792, 2004.
- Konopka, P., Engel, A., Funke, B., Müller, R., Grooß, J.-U., Günther, G., Wetter, T., Stiller, G., von Clarmann, T., Glatthor, N., Oelhaf, H., Wetzel, G., López-Puertas, M., Pirre, M., Huret, N., and Riese, M.: Ozone loss driven by nitrogen oxides and triggered by stratospheric warmings may outweigh the effect of halogens, *J. Geophys. Res.*, 112, D05105, doi:10.1029/2006JD007064, 2007a.
- Konopka, P., Günther, G., Müller, R., dos Santos, F. H. S., Schiller, C., Ravegnani, F., Ulanovsky, A., Schlager, H., Volk, C. M., Viciani, S., Pan, L. L., McKenna, D.-S., and Riese, M.: Contribution of mixing to upward transport across the tropical tropopause layer (TTL), *Atmos. Chem. Phys.*, 7, 3285–3308, 2007, <http://www.atmos-chem-phys.net/7/3285/2007/>.
- Kouker, W., Langbein, I., Reddmann, T., and Ruhnke, R.: The Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA), Version 2, Wissenschaftliche Berichte FZKA 6278, Forschungszentrum Karlsruhe, 1999.
- López-Puertas, M., Funke, B., Gil-López, S., von Clarmann, T., Stiller, G. P., Höpfner, M., Kellmann, S., Fischer, H., and Jackman, C. H.: Observation of NO<sub>x</sub> enhancement and ozone depletion in the Northern and Southern hemispheres after the October–November 2003 Solar Proton Events, *J. Geophys. Res.*, 110, A09S43, doi:10.1029/2005JA011050, 2005a.
- López-Puertas, M., Funke, B., Gil-López, S., von Clarmann, T., Stiller, G. P., Höpfner, M., Kellmann, S., Mengistu Tsidu, G., Fischer, H., and Jackman, C. H.: HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub> Enhancements after the October–November 2003 Solar Proton Events, *J. Geophys. Res.*, 110, A9, doi:10.1029/2005JA011051, 2005b.
- López-Puertas, M., Funke, B., Clarmann, T., Fischer, H., and Stiller, G.: The Variability of Stratospheric and Mesospheric NO<sub>y</sub> in the Arctic and Antarctic 2002–2004 Polar Winters, *Space Sci. Rev.*, 125, 403–416, doi:10.1007/s11214-006-9073-2, 2006.
- Manney, G. L., Krüger, K., Sabutis, J. L., Amina Sena, S., and Pawson, S.: The remarkable 2003–2004 winter and other recent warm winters in the Arctic stratosphere in the late 1990s, *J. Geophys. Res.*, 110, D04107, doi:10.1029/2004JD005367, 2005.
- McKenna, D. S., Grooß, J.-U., Günther, G., Konopka, P., Müller, R., Carver, G., and Sasano, Y.: A new Chemical Lagrangian Model of the Stratosphere (CLaMS): 2. Formulation of chemistry scheme and initialization, *J. Geophys. Res.*, 107(D15), 4256, doi:10.1029/2000JD000113, 2002a.
- McKenna, D. S., Konopka, P., Grooß, J.-U., Günther, G., Müller, R., Spang, R., Offermann, D., and Orsolini, Y.: A new Chemical Lagrangian Model of the Stratosphere (CLaMS): 1. Formulation of advection and mixing, *J. Geophys. Res.*, 107(D16), 4309, doi:10.1029/2000JD000114, 2002b.
- Müller, R., Tilmes, S., Grooß, J.-U., Engel, A., Oelhaf, H., Wetzel, G., Huret, N., Pirre, M., Catoire, V., Toon, G., and Nakajima, H.: Impact of mesospheric intrusions on ozone–tracer relations in the stratospheric polar vortex, *J. Geophys. Res.*, 112, D23307, doi:10.1029/2006JD008315, 2007.
- Orsolini, Y. J., Manney, G., Santee, M., and Randall, C.: An upper stratospheric layer of enhanced HNO<sub>3</sub> following exceptional solar storms, *Geophys. Res. Lett.*, 32(12), L12S01, doi:10.1029/2004GL021588, 2005.
- Randall, C. E., Harvey, V. L., Manney, G. L., Orsolini, Y., Codrescu, M., Sioris, C., Brohede, S., Haley, C. S., Gordley, L. L., Zawodny, J. M., and Russell, J. M.: Stratospheric effects of energetic particle precipitation in 2003–2004, *Geophys. Res. Lett.*, 32, 5, L05802, doi:10.1029/2004GL022003, 2005.
- Randall, C. E., Harvey, V. L., Singleton, C. S., Bernath, P. F., Boone, C. D., and Kozyra, J. U.: Enhanced NO<sub>x</sub> in 2006 linked to strong upper stratospheric Arctic vortex, *Geophys. Res. Lett.*, 33, L18811, doi:10.1029/2006GL027160, 2006.
- Raspollini, P., Belotti, C., Burgess, A., Carli, B., Carlotti, M., Ceccherini, S., Dinelli, B. M., Dudhia, A., Flaud, J.-M., Funke, B., Höpfner, M., López-Puertas, M., Payne, V., Piccolo, C., Remedios, J. J., Ridolfi, M., and Spang, R.: MIPAS level 2 operational analysis, *Atmos. Chem. Phys.*, 6, 5605–5630, 2006, <http://www.atmos-chem-phys.net/6/5605/2006/>.
- Ray, E. A., Moore, F. L., Elkin, J. W., Hurst, D. F., Romashkin, P. A., Dutton, G. S. and Fahey, D. W.: Descent and mixing in the 1999–2000 northern polar vortex inferred from in situ tracer measurements, *J. Geophys. Res.*, 107, 8285, doi:10.1029/2001JD000961, 2002.
- Rex, M., Salawitch, R. J., von der Gathen, P., Harris, N. R. P., Chipperfield, M. P., and Naujokat, B.: Arctic ozone loss and climate change, *Geophys. Res. Lett.*, 31, L04116, doi:10.1029/2003GL018844, 2004.
- Rohen, G., von Savigny, C., Sinnhuber, M., Llewellyn, E. J., Kaiser, J. W., Jackman, C. H., Kallenrode, M.-B., Schröter, J., Eichmann, K.-U., Bovensmann, H., and Burrows, J. P.: Ozone depletion during the solar proton events of October/November 2003 as seen by SCIAMACHY, *J. Geophys. Res.*, 110, A09S39, doi:10.1029/2004JA010984, 2005.
- Russell, J. M., Gordley, L. L., Park, J. H., Drayson, S. R., Tuck, A. F., Harries, J. E., Cicerone, R. J., Crutzen, P. J., and Frederick, J. E.: The Halogen Occultation Experiment, *J. Geophys. Res.*, 98, 10 777–10 797, 1993.
- Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Wine, P. H., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Evaluation number 15, Chemical kinetics and photochemical data for use in atmospheric studies, NASA Panel for Data Evaluation, JPL Publication 06-2, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 2006.
- Seppälä, A., Verronen, P., Kyrölä, E., Hassinen, S., Backman,

- L., Hauchecorne, A., Bertaux, J., and Fussen, D.: Solar proton events of October–November 2003: Ozone depletion in the Northern Hemisphere polar winter as seen by GOMOS/Envisat, *Geophys. Res. Lett.*, 31, L19107, doi:10.1029/2004GL021042, 2004.
- Solomon, S., Rusch, D. W., J. C. Gerard, G. C. R., and Crutzen, P. J.: The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere: II. Odd hydrogen, *Planet. Space Sci.*, 29(8), 885–892, 1981.
- Steck, T., von Clarmann, T., Fischer, H., Funke, B., Glatthor, N., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Milz, M., Stiller, G. P., Wang, D. Y., Allaart, M., Blumenstock, Th., von der Gathen, P., Hansen, G., Hase, F., Hochschild, G., Kopp, G., Kyrö, E., Oelhaf, H., Raffalski, U., Redondas Marroero, A., Remsberg, E., Russell III, J., Stebel, K., Steinbrecht, W., Wetzol, G., Yela, M., and Zhang, G.: Bias determination and precision validation of ozone profiles from MIPAS-Envisat retrieved with the IMK-IAA processor, *Atmos. Chem. Phys.*, 7, 3639–3662, 2007, <http://www.atmos-chem-phys.net/7/3639/2007/>.
- Tilmes, S., Müller, R., Groöß, J.-U., and Russell III, J. M.: Ozone loss and chlorine activation in the Arctic winters 1991–2003 derived with the tracer-tracer correlations, *Atmos. Chem. Phys.*, 4, 2181–2213, 2004, <http://www.atmos-chem-phys.net/4/2181/2004/>.
- Tilmes, S., Müller, R., Engel, A., Rex, M., and Russell III, J.: Chemical ozone loss in the Arctic and Antarctic stratosphere between 1992 and 2005, *Geophys. Res. Lett.*, 33, L20812, doi:10.1029/2006GL026925, 2006.
- Verronen, P. T., Seppälä, A., Kyrölä, E., Tamminen, J., Pickett, H. M., and Turunen, E.: Production of odd hydrogen in the mesosphere during the January 2005 solar proton event, *Geophys. Res. Lett.*, 33(24), L24811, doi:10.1029/2006GL028115, 2006.
- Vogel, B., Müller, R., Deshler, T., Groöß, J.-U., Karhu, J., McKenna, D. S., Müller, M., Toohey, D., Toon, G. C., and Stroth, F.: Vertical profiles of activated ClO and ozone loss in the Arctic vortex in January and March 2000: In situ observations and model simulations, *J. Geophys. Res.*, 108(D22), 8334, doi:10.1029/2002JD002564, 2003.
- von Clarmann, T., Glatthor, N., Höpfner, M., Kellmann, S., Ruhnke, R., Stiller, G. P., Fischer, H., Funke, B., Gil-López, S., and López-Puertas, M.: Experimental Evidence of Perturbed Odd Hydrogen and Chlorine Chemistry After the October 2003 Solar Proton Events, *J. Geophys. Res.*, 110(A9), A09S45, doi:10.1029/2005JA011053, 2005.
- Wetzel, G., Bracher, A., Funke, B., Goutail, F., Hendrick, F., Lambert, J.-C., Mikuteit, S., Piccolo, C., Pirre, M., Bazureau, A., Bellotti, C., Blumenstock, T., De Mazière, M., Fischer, H., Huret, N., Ionov, D., López-Puertas, M., Maucher, G., Oelhaf, H., Pommereau, J.-P., Ruhnke, R., Sinnhuber, M., Stiller, G., Van Roozendaal, M., and Zhang, G.: Validation of MIPAS-ENVISAT NO<sub>2</sub> operational data, *Atmos. Chem. Phys.*, 7, 3261–3284, 2007, <http://www.atmos-chem-phys.net/7/3261/2007/>.
- WMO: Scientific assessment of ozone depletion: 2006, Global Ozone Research and Monitoring Project Report No. 50, Geneva, Switzerland, 2007.