

An enhanced HNO₃ second maximum in the Antarctic midwinter upper stratosphere 2003

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[1] Vertical profiles of stratospheric HNO₃ were retrieved from limb emission spectra recorded by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) aboard the Envisat research satellite during the Antarctic winter 2003. A high second maximum of HNO₃ was found around 34 km altitude with abundances up to 14 ppbv HNO₃ during July. Similar high abundances have not been reported in the literature for previous winters, but for the subsequent Arctic winter 2003/2004, after severe perturbations due to solar proton events. The second HNO₃ maximum in the Antarctic stratosphere started to develop in early June 2003, reached peak values during July 2003, and decreased to about 7 ppbv at the end of August while being continuously transported downward before finally forming a single HNO₃ layer over all latitudes in the lower stratosphere together with the out-of-vortex primary HNO₃ maximum. The HNO₃ decrease in August 2003 was correlated with photochemical buildup of other NO_y species as ClONO₂ and NO_x. From the time scales observed, it can be ruled out that the 2003 long-term HNO₃ enhancements were caused by local gas phase reactions immediately after the solar proton event on 29 May 2003. Instead, HNO₃ was produced by ion cluster chemistry reactions and/or heterogeneous reactions on sulfate aerosols via N₂O₅ from high amounts of NO_x being continuously transported downward from the lower thermosphere during May to August.

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1. Introduction

[2] A layer of increased HNO₃ inside upper stratospheric polar vortices during midwinter was first observed by the Limb Infrared Monitor of the Stratosphere (LIMS) instrument during the Northern winter 1978/79 [Austin *et al.*, 1986]. In the 1990s, the Microwave Limb Sounder (MLS) [Santee *et al.*, 1999, 2004] and the Cryogenic Limb Array Etalon Spectrometer (CLAES) [Kawa *et al.*, 1995], both on the Upper Atmosphere Research Satellite (UARS), also found evidence for formation of a secondary maximum of HNO₃ both in the Arctic and Antarctic winters.

[3] From MLS observations, 11-day averages of HNO₃ volume mixing ratios (vmr) at the 960 K potential temperature level (approximately 32 km altitude) highest abundances of 5 ppbv in Northern hemisphere winters, and values up to 4 ppbv in Southern hemisphere winters were observed [Santee *et al.*, 1999, 2004], while lowest values were about a factor of 0.5 lower. Unfortunately, no values above 960 K have been presented. The high abundances at

960 K seem to occur on the periphery of the primary HNO₃ maximum, since HNO₃ vmr increases monotonically from 960 K toward lower altitudes. CLAES observed a secondary HNO₃ maximum in the Arctic polar vortex during early January 1992 [Kawa *et al.*, 1995]. Vmrs reached values up to 5 ppbv at an isentrope of 1200 K.

[4] Bekki *et al.* [1997] conducted a model study to analyze if the second HNO₃ maximum observed by CLAES in 1992 could be explained by heterogeneous reactions on small sulphate aerosol particles. They concluded that the formation of small sulphate particles via nucleation was likely in the upper stratospheric Arctic vortex in late December 1991/early January 1992, and that the model could reproduce some of the unexpected features in the CLAES data. However, it remained unresolved how much the sulphate aerosol distribution was affected by the Mt Pinatubo volcanic eruption in 1991. De Zafra and Smyshlyaev [2001] used a compilation of polar upper stratospheric HNO₃ abundances measured by ground-based instruments in the Antarctic during the years 1993, 1995, and 1999 [de Zafra *et al.*, 1997; McDonald *et al.*, 2000] and a chemical model to evaluate the role of ion cluster chemistry, heterogeneous chemistry on sulphate aerosols,

and NO_y flux from the mesosphere on the HNO₃ formation. They reached good qualitative agreement between their model results and the observations by reproducing HNO₃ vmrs of up to 8.5 ppbv in midwinter (around day 210) at an altitude range of 30 to 35 km. They found that ion cluster chemistry plays a major role above 40 km, while the HNO₃ formation was augmented by heterogeneous reactions on sulphate aerosols below 40 km. They concluded that HNO₃ production mechanisms became saturated when increasing ion densities or including reactions on sulphate aerosols, while no indication of saturation was found when increasing the NO_y flux from the mesosphere. However, they also pointed out that, within their chemical transport model (CTM), much larger amounts of NO₂ were transported into the upper and middle stratosphere of the winter vortex than in most other models; they concluded that new or adjusted parameterizations for NO_y transport were needed in most models.

[5] Most recently, López-Puertas *et al.* [2005a, 2005b] have reported on enhancements of NO_x, HNO₃, N₂O₅ and ClONO₂ in the upper stratosphere over the Arctic within 2 weeks after several very strong solar proton events (SPE) which occurred between 29 October and 4 November 2003. These authors showed, by using data from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on board the Environmental Satellite (ENVISAT), that generation of enhanced amounts of NO_x and HNO₃ in the upper stratosphere was, because of the short time scale, most probably caused by local production of NO_x and OH in the upper stratosphere. During this period, upper stratosphere HNO₃ was enhanced by 4 to 5 ppbv.

[6] Orsolini *et al.* [2005] and López-Puertas *et al.* [2005b] have reported on enormously increased levels of HNO₃ above 900 K (30 to 35 km) observed by MIPAS during the further evolution of the Arctic winter 2003/2004, until 7–8 January 2004, in the Northern polar vortex. From end of November to early January, a second episode of a HNO₃ maximum in the upper stratosphere after that immediately following the SPEs with values up to 14 ppbv was observed. The second maximum moved downward as the subsidence in the vortex proceeded.

[7] Stimulated by these latest observations, we have investigated HNO₃ MIPAS measurements covering the Antarctic winter pole in 2003. Compared to observations in previous years from the literature and earlier MIPAS observations, the second layer of HNO₃ in the upper stratosphere was found to be unusually high, reaching values as high as those reported for the Arctic winter 2003/2004. In the following, we present data sets of stratospheric HNO₃ and other related species derived from MIPAS spectra, discuss the temporal evolution of the second HNO₃ layer during Antarctic winter 2003, relate HNO₃ fields to the potential instantaneous local production of HNO₃ precursors by the observed solar proton fluxes, and analyze sources, formation, and sinks of HNO₃.

2. MIPAS Data and Retrieval

[8] MIPAS is a limb emission FTIR spectrometer designed for measurement of atmospheric trace species from space [European Space Agency, 2000; Fischer and Oelhaf, 1996]. It is part of the instrumentation of the Environmental Satellite (ENVISAT) which was launched

into its Sun-synchronous polar orbit of 98.55° inclination at about 800 km altitude on 1 March 2002. MIPAS was operational from July 2002 to March 2004 with full specification, in particular 0.05 cm⁻¹ spectral resolution in terms of full width at half maximum (apodized with the “strong” Norton and Beer [1976] function). MIPAS is able to observe during day and night, covering the globe from pole to pole, and thus provides trace gas distributions also during polar night. Within its standard observation mode, MIPAS covers the altitude range from 6 to 68 km with tangent altitudes from 6 to 42 km every 3 km, and further tangent altitudes at 47, 52, 60, and 68 km. MIPAS passes the equator in southerly direction at 10.00 am local time 14.3 times a day. During each orbit up to 72 limb scans are recorded. The Level-1b processing of the data, including processing from raw data to calibrated phase-corrected and geolocated radiance spectra, was performed by the European Space Agency (ESA) [Nett *et al.*, 1999].

[9] Data presented here are vertical profiles of abundances of HNO₃, N₂O₅, and ClONO₂, which were retrieved with the dedicated scientific IMK-IAA data processor [von Clarmann *et al.*, 2003a, 2003b] from MIPAS spectra (versions 4.55 to 4.59) recorded during April to October 2003 (temporal sampling of one full day per ten days). Retrieval strategies, error budget, and altitude resolution for the species under investigation are reported in Mengistu Tsidu *et al.* [2005] for HNO₃, Mengistu Tsidu *et al.* [2004a] for N₂O₅, and Höpfner *et al.* [2004] for ClONO₂. In order to better account for the particular HNO₃ profiles reported in this paper, dedicated error analysis and data characterization was performed for a typical 2003 Antarctic midwinter profile (11 July 2003, 86.4°S latitude, 115.5°E longitude). The precision in terms of the quadratic sum of all random error components between 25 and 45 km is between 2 and 6%, while the estimated accuracy, derived by quadratically adding the systematic error due to spectroscopic uncertainty to the random error budget, is between 5 and 15%. Below 32 km, measurement noise is the dominating error source, while above, residual elevation pointing uncertainty is the leading error component. The altitude resolution, defined as the full width at half maximum of a column of the averaging kernel matrix, is around 3 km at the second HNO₃ vmr maximum, decreasing to 6 and 8 km at lower (25 km) and higher (45 km) altitudes, respectively.

[10] To complement this data set, the operational ESA data (reprocessed data, version 4.61/4.62) for HNO₃ vmr profiles for the Southern polar winter 2003 were used, since, contrary to the episode-based scientific MIPAS-IMK-IAA data, these data were available for longer continuous periods. The MIPAS operational data, which do not include ClONO₂ and N₂O₅, is retrieved by ESA using the operational retrieval algorithm as described by Ridolfi *et al.* [2000] and Carli *et al.* [2004]. ESA version 4.61 HNO₃ data have successfully been validated, with negative deviations from correlative field campaign data of less than 0.5 ppbv between 30 and 4 hPa, and positive deviations of less than 1 ppbv at lower altitudes [Oelhaf *et al.*, 2004]. ESA and IMK-IAA data are largely consistent except for a shift in altitude, a high bias (IMK-IAA being higher than ESA) of 0.1 ppbv between 30 and 2 hPa, and a low bias of less than 0.6 ppbv at lower altitudes [Mengistu Tsidu *et al.*, 2004b]. The shift in altitude is caused since,

contrary to IMK-IAA data, ESA data are not tangent-altitude corrected [von Clarmann *et al.*, 2003b]. Since ESA-retrieved pressures are not affected, we have resampled ESA data on a pressure grid.

3. Comparison of MIPAS HNO₃ Data to Other Sources

[11] In this section we assess the quality of IMK-IAA MIPAS data by comparing them to other observational data. These are field campaign data obtained from balloon-borne Fourier transform spectrometers operating in the infrared, and climatological data sets from the MLS instrument covering the years 1992 to 1998; MLS data have been included, although they do not coincide in time with the MIPAS measurements, because a potential MIPAS bias would be difficult to be detected on basis of the few field campaign observations available.

3.1. Field Campaign Data

[12] *Mengistu Tsidu* [2005] has validated IMK-IAA generated HNO₃ vmr profiles retrieved from MIPAS spectra, using HNO₃ vmr profiles measured by the balloon-borne FTIR limb sounders MIPAS-B [Oelhaf *et al.*, 2004] and Mark-IV [Toon, 1991]. Agreement with a MIPAS-B observation with close to perfect spatial coincidence on 24 September at 46°N is good with deviations below 0.5 ppbv throughout the entire altitude range up to about 38 km, and below 0.2 ppbv above 30 km. A MIPAS-B observation at 40°N during the same balloon flight exhibits more pronounced discrepancies, in particular at the altitude region of the HNO₃ maximum, where MIPAS vmrs were higher by 1.2 ppb. This difference is attributed to less perfect coincidence. Nevertheless, above 30 km no substantial difference between MIPAS and MIPAS-B HNO₃ profiles was found. These MIPAS-B observations have also been used for validation of the ESA version 4.61 operational HNO₃ data product [Oelhaf *et al.*, 2004].

[13] Comparison with Mark-IV observations in higher Northern latitudes during winter and spring exhibit higher deviations, in particular when the potential vorticity for the correlative observations deviated from that at the geolocations of MIPAS/ENVISAT observations. However, the highest deviations in HNO₃ vmr were found below 17 km, with Mark-IV being 1.5 ppbv lower than IMK-IAA retrieved MIPAS HNO₃ vmr. In the primary HNO₃ vmr maximum around 23 km and above, deviations were around 0.5 ppbv. Unfortunately, no Mark-IV data are available for altitudes above 30 km. All conclusions drawn in this paper are robust against deviations of the magnitudes observed.

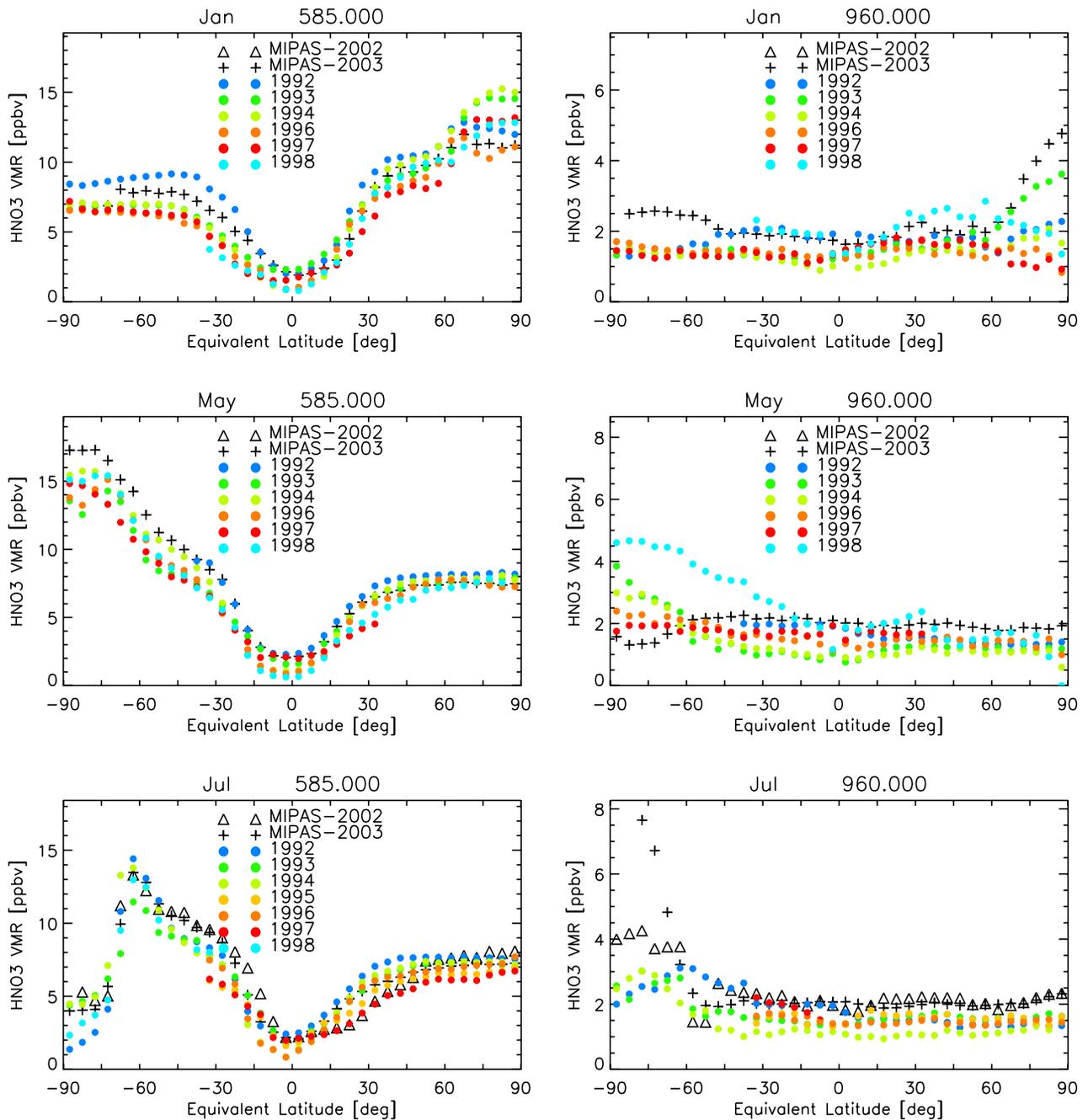
3.2. MLS Climatology

[14] *Santee et al.* [2004] have provided a climatology of HNO₃ abundances as function of equivalent latitude (EquLat), month, and potential temperature from MLS data. Figure 1 compares January, May and July monthly means of IMK-IAA MIPAS HNO₃ vmr along equivalent latitudes on the 585 and 960 K potential temperature levels with those from MLS for all observational years. At the 585 K level (Figure 1, left), the general agreement in the summer hemisphere is very good. In the winter hemisphere, slightly higher HNO₃ abundances in midlatitudes are observed by

MIPAS than MLS through the various years, in particular in the months May and July (Figure 1, left middle and left bottom). In the Northern polar vortex (January data, Figure 1, top left) MIPAS HNO₃ measurements are consistent with MLS observations, which show an interannual variability of about 4 ppbv. In the Antarctic vortex (EquLat >60°S) MIPAS HNO₃ vmrs in May 2003 are higher by about 3 ppbv than the MLS multiannual mean, while in July they match very well the MLS climatology, representing severe HNO₃ loss, probably due to denitrification. At the 960 K level (Figure 1, right), which is the highest altitude MLS data are provided for, MIPAS HNO₃ stands out by Arctic polar values of 2003 being 2 ppbv higher than the highest values observed by MLS (Figure 1, top right). However, the interannual variability in MLS data again is high with a range of 3.5 ppbv. At the summer pole, MIPAS values are 1 to 1.5 ppbv higher than the MLS multiannual data, while for midlatitudes and tropics, the agreement between MIPAS and MLS is good. In May, MIPAS HNO₃ vmr are nearly constant over all equivalent latitudes with a value around 2 ppbv (Figure 1, middle right). MLS shows somewhat more latitudinal variability with enhanced values in the Southern polar vortex, being subject to high interannual variability. In particular, 1998 appears to be an exceptional year with drastically enhanced abundances up to 4.5 ppbv there. Besides the Southern vortex, the mean values of MLS over all latitudes are about 0.5 ppbv lower than MIPAS vmrs. *Santee et al.* [2004] report an accuracy for their individual profiles of 3 ppbv above 760 K, and, in particular, a low bias of 1–3 ppbv above 760 K, which is in agreement with the MIPAS-MLS comparison shown here. On 960 K in July (Figure 1, bottom right) the MIPAS data reflect the extraordinary high HNO₃ second maximum in the Southern polar vortex in 2003, and some enhancement for 2002. Similar enhancement as for MIPAS HNO₃ vmrs in July 2002 and January 2003 is obvious in the MLS data in January 1993 and in July 1998. For other latitudes besides the Southern polar vortex, MIPAS HNO₃ vmr again is about 0.5 ppbv higher than the MLS multiannual mean.

[15] In summary, MIPAS temporal and latitudinal HNO₃ distributions agree well with the MLS HNO₃ climatology, except for special episodes where different HNO₃ abundances are explained by particular atmospheric processes, which gives confidence in the general reliability of MIPAS vmr data. Unfortunately, the highest MLS data available are at 960 K (approximately 29–32 km). For this reason, we have performed test calculations to investigate if, in case that the second HNO₃ maximum was only an artifact in the retrieval, it would remain undiscovered in the altitude range below 32 km. This is not the case. If the retrieval was forced to produce a pronounced second HNO₃ maximum as an artifact, strong oscillations in the vmr profiles below 32 km would occur with deviations of more than 5 ppbv around 32 km, and 2–3 ppbv in the primary HNO₃ maximum. Since deviations of this magnitude have not been detected in the validation analysis, we conclude that the enhanced second HNO₃ maximum is not an artifact within the MIPAS data.

[16] Since altitudes above 960 K are only sparsely covered by these comparisons because of restricted availability of independent validated experimental data, some uncertainty on the actual accuracy of high-altitude MIPAS HNO₃ data is left. However, no indication of any bias has been



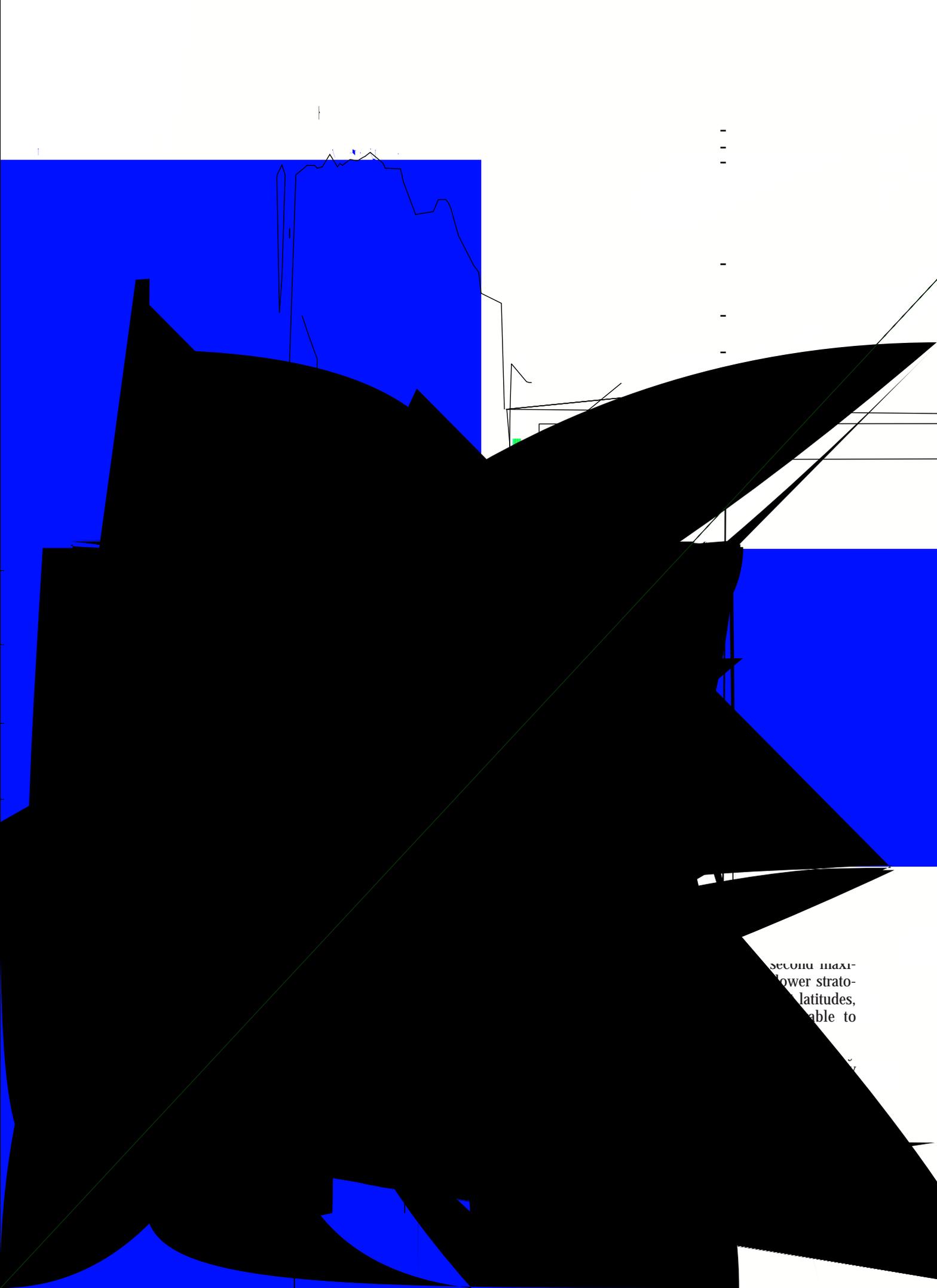
found, and our conclusions do not depend on the absolute accuracy of the data.

4. HNO₃ Distribution and Evolution During Antarctic Winter 2003

4.1. Long-Term Time Series

[17] The second HNO₃ maximum started to develop on 6 June 2003 (reaching the 1-ppbv level then) and was

centered around 1 hPa (~48 km altitude) (Figure 2). On 20 June 2003 it reached values up to 5 ppbv at about 1.5 hPa (~45 km altitude) for the first time. The second HNO₃ maximum peaked during July with zonally averaged HNO₃ vmrs up to 9 ppbv. Until end of July, a strong downward shift of the peak's altitude from about 2 hPa (~41 km altitude) to about 4.5 hPa (~36 km) is observed. From end of July on, the second HNO₃ maximum started to decrease in magnitude and reached mean values of only



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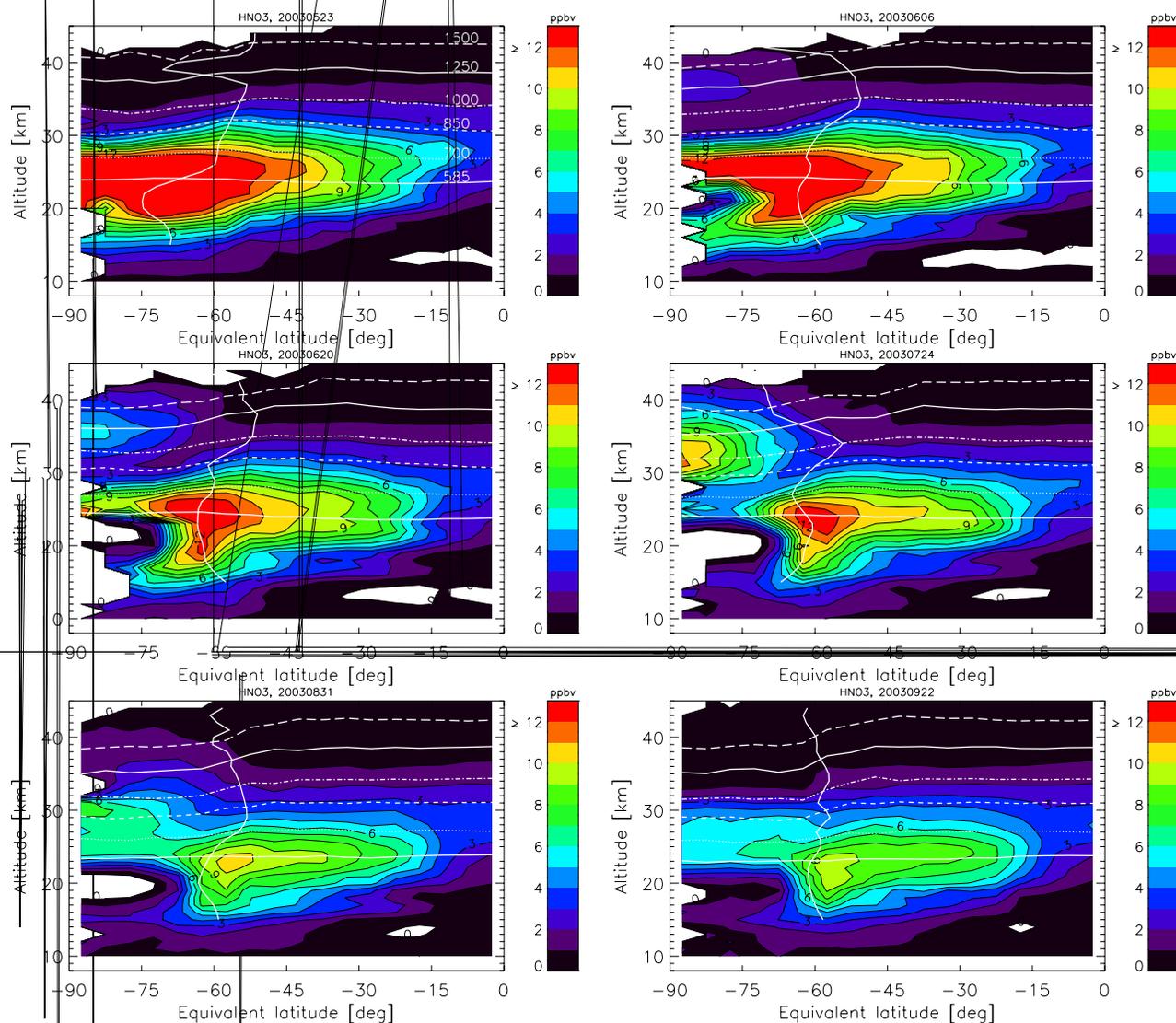


Figure 3. Altitude-equivalent latitude daily mean cross sections of HNO₃ for the days 23 May, 6 June, 20 June, 24 July, 31 August, and 22 September 2003. The solid white lines near -60° equivalent latitude mark the boundary of the Antarctic polar vortex according to the *Nash et al.* [1996] criterion. Dashed or solid white horizontal lines indicate levels of constant potential temperature (bottom solid, 585 K; dotted, 700 K; short-dashed, 850 K; dash-dotted, 1000 K; top solid, 1250 K; and long-dashed, 1500 K). Note that HNO₃ vmr values above 12 ppbv are not distinguished by the color coding; peak values observed in the lower stratospheric maximum reach up to 21 ppbv. White areas indicate missing data, either due to clouds in the field of view, or due to insignificance of measurements (diagonal element of averaging kernel matrix too small).

2003/2004 were attributed to the severe solar proton events in October/November 2003 which are known to produce high amounts of NO_x from the thermosphere down to the upper stratosphere [Randall *et al.*, 2005; Orsolini *et al.*, 2005; López-Puertas *et al.*, 2005a]. The second HNO₃ maximum in Antarctic winter 2003, however, extended to wider latitudinal regions and lasted much longer. In terms of 65° to 90° zonal means, Arctic values were lower by 2 ppbv and extended to a much shorter period of about 5 weeks.

[21] In summary, while MIPAS observations in the winters 2002 and 2002/2003 were consistent with former observations of upper stratospheric HNO₃ maxima available so far, the Antarctic winter 2003 was an outstanding one. High HNO₃ vmrs in the upper stratosphere were also

observed, although not as large and as long as for the Antarctic winter 2003, in the subsequent Arctic winter 2003/2004 and are related to high solar activity in early winter.

4.2. Altitude-Equivalent Latitude Cross Sections

[22] Figure 3 shows the distribution of HNO₃ (IMK-IAA data) in the stratosphere as a series of altitude-equivalent latitude cross sections, for selected days during the period 23 May to 22 September 2003. The equivalent latitudes were calculated from the potential vorticity of assimilated winds provided by the United Kingdom Meteorological Office (MetO) according to the procedure described by *Nash et al.* [1996]. The vortex edge as derived according

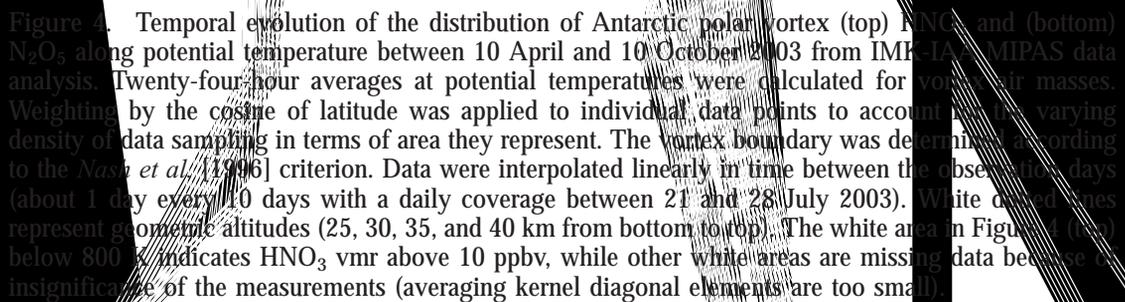
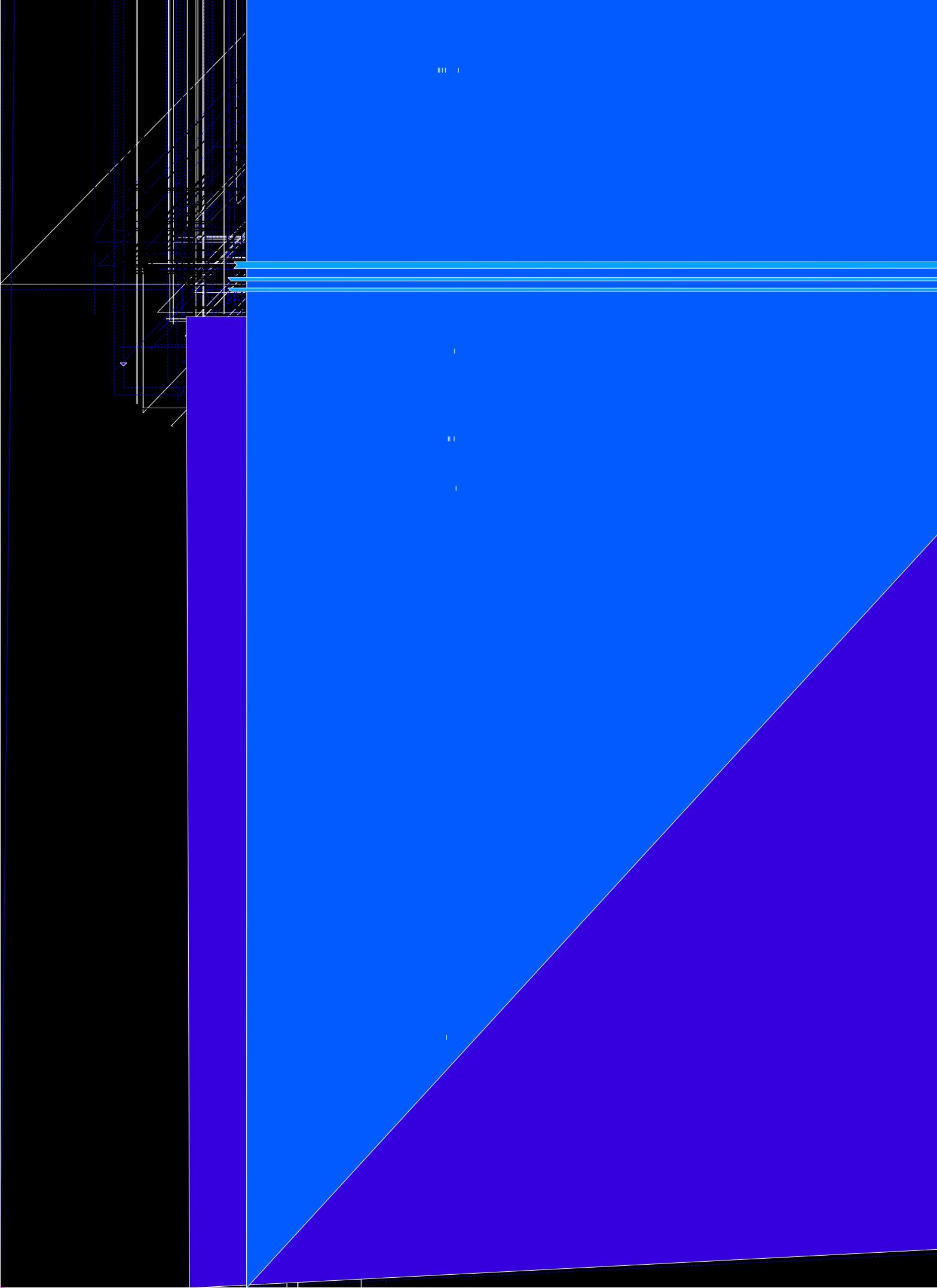


Figure 4. Temporal evolution of the distribution of Antarctic polar vortex (top) HNO₃ and (bottom) N₂O₅ along potential temperature between 10 April and 10 October 2003 from IMK-IAA MIPAS data analysis. Twenty-four-hour averages at potential temperatures were calculated for vortex air masses. Weighting by the cosine of latitude was applied to individual data points to account for the varying density of data sampling in terms of area they represent. The vortex boundary was determined according to the Nash *et al.* [1996] criterion. Data were interpolated linearly in time between the observation days (about 1 day every 10 days with a daily coverage between 21 and 28 July 2003). White dashed lines represent geometric altitudes (25, 30, 35, and 40 km from bottom to top). The white area in Figure 4 (top) below 800 K indicates HNO₃ vmr above 10 ppbv, while other white areas are missing data because of insignificance of the measurements (averaging kernel diagonal elements are too small).



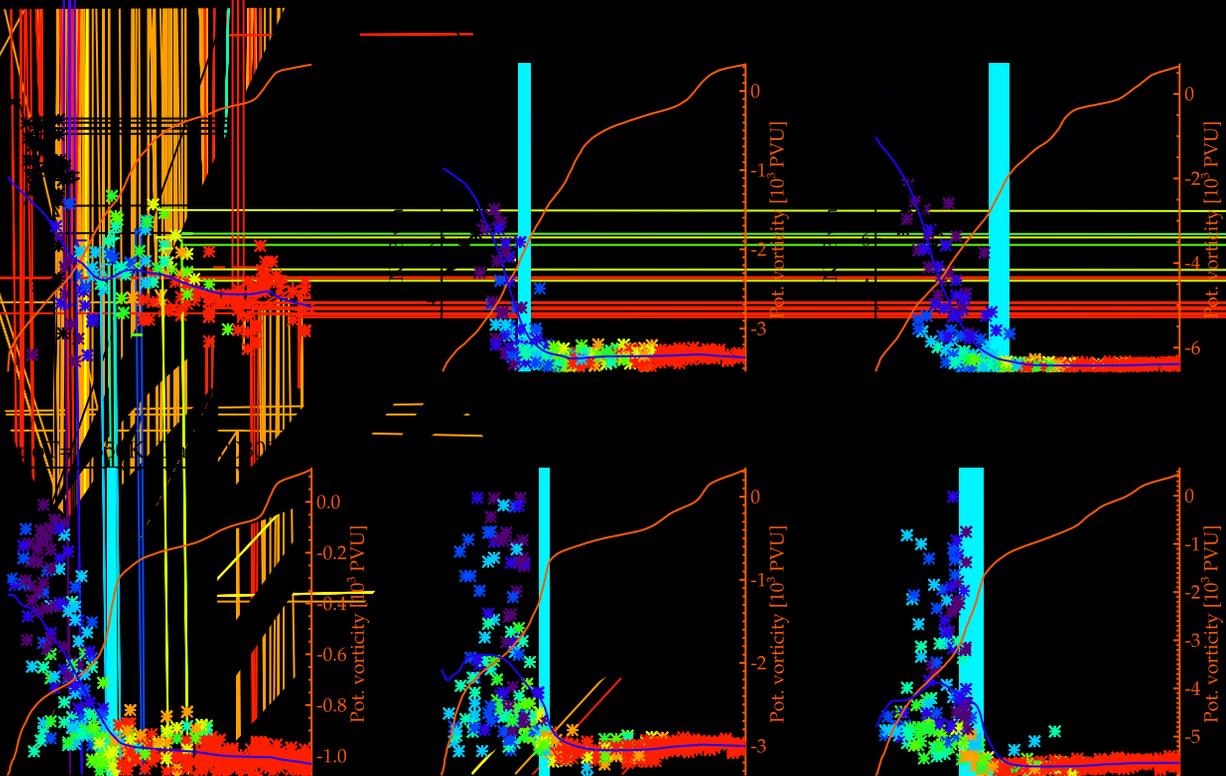


Figure 6. HNO₃ vmr versus equivalent latitude at potential temperature levels of (left) 850 K, (middle) 1000 K, and (right) 1200 K for the days (first row) 23 May, (second row) 6 June, (third row) 11 July, and (fourth row) 31 August. The color coding of the markers indicates the solar zenith angle at local noon, where black indicates poleward night and red indicates values $<50^\circ$. The blue line gives the HNO₃ mean value averaged over 20° latitudes at the given potential temperature level, while the orange line denotes the potential vorticity. The light blue bar gives the position and width of the vortex boundary according to the Manabe *et al.* [1996] criterion. Note the different scales for HNO₃ vmr and potential vorticity.

N₂O₅ is involved [de Zafra and Smyshlyayev, 2001]. Further reactions as listed by Austin *et al.* [1986] are reported to be even less probable.

[30] In a companion paper, Funke *et al.* [2005] show that high amounts of NO were produced in the lower thermosphere around 95 km during long periods of the year 2003. They relate the NO production to high geomagnetic activity, which was enhanced nearly all the year 2003 and in January 2004. They discuss in their paper the processes which rule the downward transport of NO_x into the stratosphere, and find phases of favorable conditions in terms of dynamical situation and illumination during the Antarctic winter 2003. Continuous severe injection of upper atmospheric NO_x abundances into the Antarctic upper stratosphere (50 km altitude) begins around mid-May with mean NO_x vmrs of 20 ppbv and has its maximum around 1 July 2003 (NO_x vmr around 40 ppbv at 50 km altitude), while lasting until mid-August. In particular, high NO_x abundances in the upper stratosphere/mesosphere were not correlated with proton or energetic electron precipitation. This excludes local production by energetic particles similar to the Arctic winter 2003/2004. The 20 ppbv isoline reached altitudes below 45 km around 23 May. The downward transport of high NO_x into the upper stratosphere was most efficient in the dark part of the polar vortex where the mesospheric barrier due to photolysis of NO could be overcome. Transport processes are well reflected by observation of CO of typically mesospheric volume mixing ratios in the stratosphere. From end of July on, a tongue of enhanced NO_x is visible in the time series presented by Funke *et al.* [2005], starting at about 1300 K (38 km) and moving downward to 700 K (28 km) until 1 October. From end of July on, the highest part of the remnant of the stratospheric vortex (after the stratospheric/mesospheric part had weakened) at potential temperature levels above 1250 K was partly exposed to sunlight again, leading to re-formation of NO_x by photolysis. The high NO_x abundances originating from the mesosphere/lower thermosphere and transported downward into the upper stratosphere could be the source of HNO₃ formation, both via (R1) and (R2). N₂O₅ takes several days, at most, to be converted from NO₂.

[31] In order to produce HNO₃ from (R1), OH is needed. However, OH is not available during polar night in the upper stratosphere except during SPEs. Enhancements of HNO₃ under these conditions have been recently observed during the SPEs in October/November 2003 [López-Puertas *et al.*, 2005b] and attributed mainly to gas phase chemistry (R1) after local production of NO₂ and OH. During the Antarctic 2003 winter, a small solar proton event happened on 29 May 2003 with ≥ 100 MeV proton (which are believed to penetrate into the stratosphere) flux increased by a factor of approximately 100 relative to the background level, as observed by Geostationary Operational Environmental Satellites (GOES) (see <http://sec.noaa.gov/Data/goes.html>). However, this proton flux is still 100 times smaller than that during the solar proton events of October/November 2003, when HNO₃ was enhanced by 4 ppbv at 35 km [López-Puertas *et al.*, 2005b]. As expected, no significant HNO₃ enhancement was observed immediately after the solar proton event on 29 May 2003 (see Figure 2). This rules out that local stratospheric formation of OH and NO₂ immediately after the SPE on 29 May 2003, via (R1),

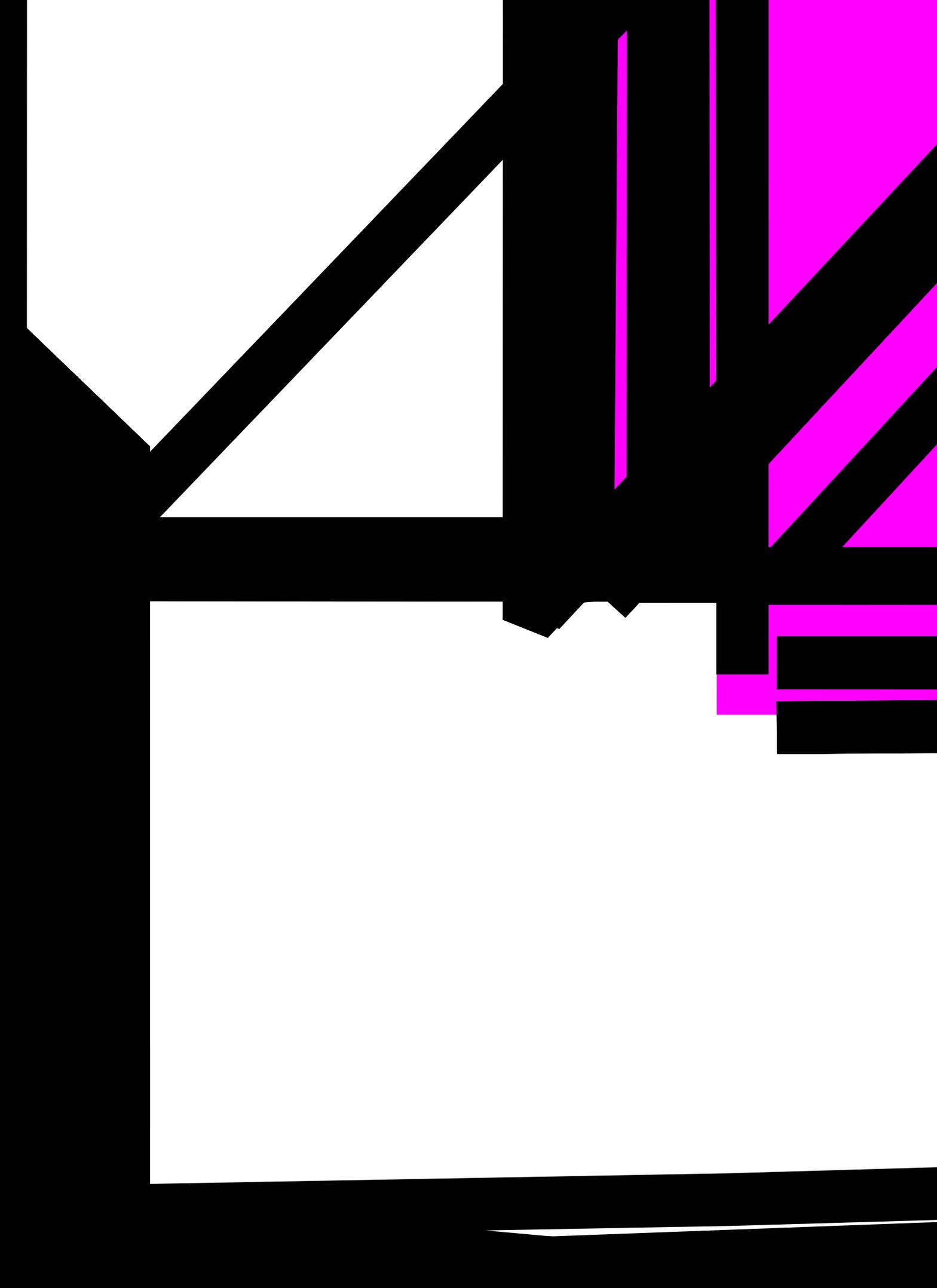
was the source of the upper stratospheric HNO₃ in the Antarctic winter 2003.

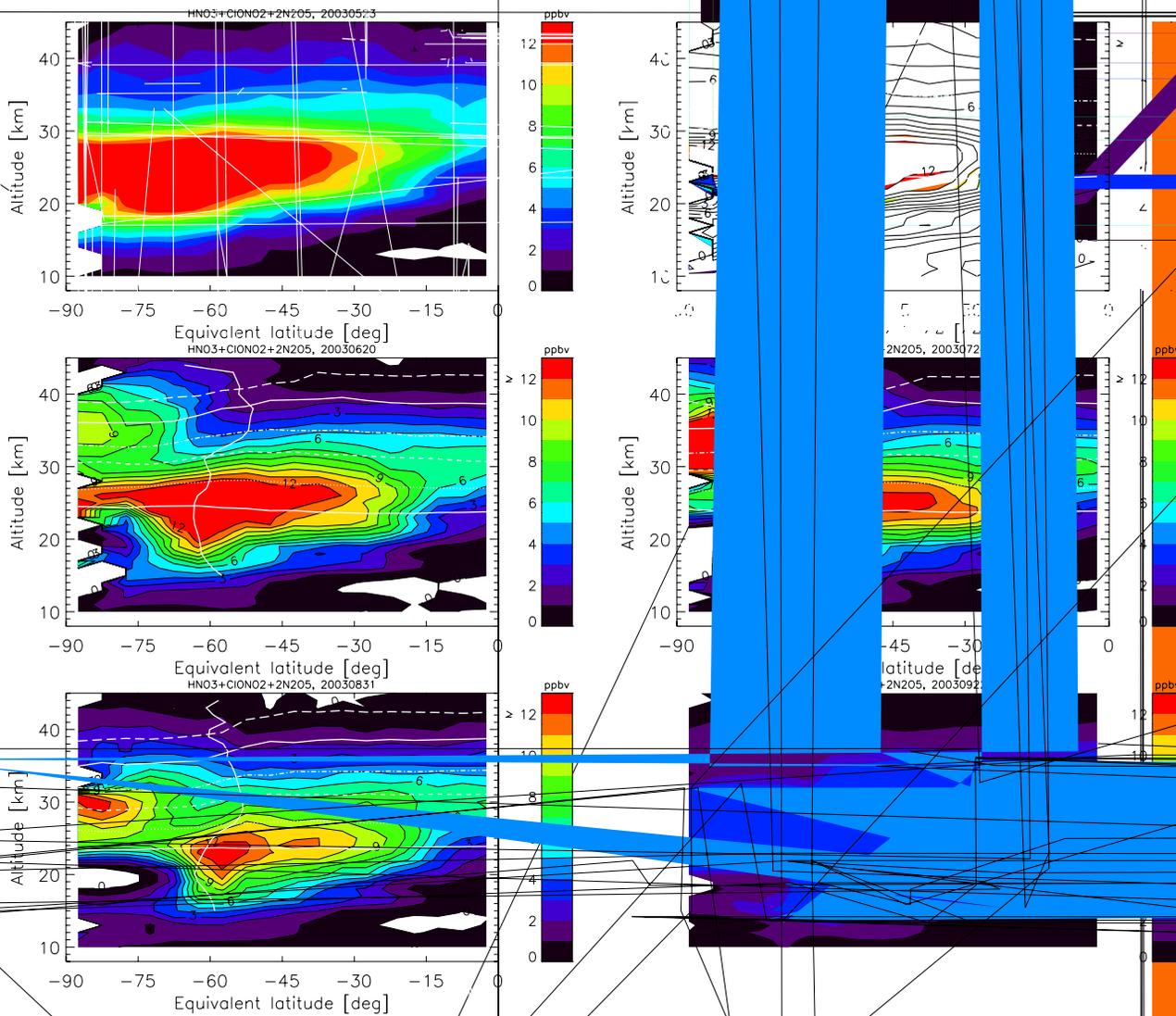
[32] The solar proton event may have led to additional production of NO_x in the mesosphere/lower thermosphere (MLT), being transported downward during the following weeks, and then converted into HNO₃ by the processes described below. However, high NO_x occurred in the upper stratosphere/mesosphere already before the solar proton event on 29 May 2003. Besides this, OH has a very short lifetime and thus will not survive downward transport during several days. Further, the solar proton event could have increased the ion cluster density which would also make formation of HNO₃ via N₂O₅ more probable, provided that enough N₂O₅ is available.

[33] In summary, for reasons discussed above, a direct and exclusive relation to the SPE on 29 May is very improbable. However, it cannot entirely be ruled out that the SPE somewhat amplified the HNO₃ formation by additional production of NO_x in the MLT being transported downward during the following weeks, and by producing additional ion clusters for (R2).

[34] Both ion cluster chemistry (R2) and heterogeneous reactions on sulphate aerosols require availability of N₂O₅ as a precursor of HNO₃ as well as high ion densities in case of (R2). De Zafra and Smyshlyayev [2001] reported on model studies with ion densities representative for galactic cosmic ray background. For these ion densities and NO_y abundances up to 50 ppbv entering the upper stratosphere from above, they modeled production of HNO₃ abundances up to 8 ppbv at 32 km. The HNO₃ maximum always occurred around day 210 in 36 km (29 July) and day 220 in 32 km (8 August). Either by increasing the ion density or the downward NO_y flux by a factor of 4 each, they modeled HNO₃ abundances larger than 10 ppbv at 32 km, which is in accordance to our observations. These model results imply high amounts of N₂O₅ which were produced from NO_x injected into the stratosphere. For this reason, we have analyzed the N₂O₅ distributions (see Figure 7) for Antarctic winter 2003 and time series (see Figure 4, bottom) in the upper stratosphere.

[35] Figure 4 shows that from 17 May 2003 on the usual N₂O₅ layer below 1000 K started to expand into the region up to 1500 and even 2000 K. This increase is observed two weeks before the onset of the HNO₃ maximum in early June, 12 days before the SPE on 29 May 2003, and roughly at the same time when NO_x produced in the MLT started to enter the upper stratosphere. The 2-week time delay gives an indication of the rate constants for the relevant processes. Besides this, the area of polar night became larger. Abundances of about 2.5 ppbv N₂O₅ in 32 to 40 km altitude (mean values averaged over 5° equivalent latitude) were reached during June and July 2003 (see Figure 7) with a maximum on 11 July (not shown). During August, N₂O₅ decreased rapidly, falling below levels of 1 ppbv after 1 September. The N₂O₅ vmr peak values were reached 3 to 4 weeks before the peak values of the HNO₃ second maximum, indicating that photochemical equilibrium was achieved at that time. This means that excess abundances of N₂O₅ (as well as NO_x) were always available during the buildup of the second HNO₃ layer in the upper stratosphere, indicating that availability of these substances were not the limiting factor for the HNO₃ formation.





which presents the development of total reservoir NO_y ($\text{HNO}_3 + 2\text{N}_2\text{O}_5 + \text{ClONO}_2$) during Antarctic winter 2003. Total reservoir NO_y above 30 km altitude increases until 24 July and decreases from then on. This leads to the question what the sinks of upper stratospheric HNO_3 are.

6. Sinks of Upper Stratospheric HNO_3

[38] Figure 8 shows that total upper stratospheric reservoir NO_y was decreasing from the last third of July on, while in Figure 4 we found that the 2 ppbv HNO_3 vmr isoline descended by about 20 km within 2.5 months, namely from 1750 K on 15 July to 1000 K on 10 October. This could either be due to subsidence of the NO_y maximum, which finally reached the altitude of the ex-vortex lower stratosphere maximum, or due to chemical loss. Earlier we have noted that a descent rate of about 20 km within 2.5 months is rather high. For example, descent rates of about 3.25 km/months had been observed before [Abrams *et al.*, 1996]. Similar descent rates can be deter-

mined from CH_4 time series, measured also by MIPAS (not shown). From 1 July to 31 August we derive a descent of 7 km (35 km to 28 km) which is in consistency with the observations of Abrams *et al.* [1996]. For this reason the steeper descent in the 2 ppbv isoline of HNO_3 must be attributed to chemical loss processes besides pure subsidence of air.

[39] From end of July on, the highest altitudes of the remnant of the stratospheric vortex (potential temperature levels above 1250 K) were partly exposed to sunlight again, leading to photolysis of HNO_3 and N_2O_5 , and formation of NO_x . The NO_x abundances along isentropes increased by approximately 5 ppbv compared to the period before. In the 1000 K potential temperature level, the decrease in total reservoir NO_y was about 12.5 ppbv from 11 July to 30 September, while HNO_3 decreased by 8 ppbv during the same period. The part of this decrease which was compensated by NO_x increase might have been due to the descent of vortex air. We have noted earlier that in the 1000 K level, highest values of HNO_3

when large parts of the polar vortex already were exposed to sunlight again (compare Figure 6, fourth row, left). This indicates that in this altitude region HNO₃ decrease by photolysis and increase by subsidence were competing processes. On the 700 K potential temperature level, total reservoir NO_y as well as HNO₃ mixing ratios increased by 1 ppbv, which also was caused by descent of NO_y loaded airmasses. Increase in ClONO₂ was compensated to some extent by decrease of N₂O₅. Figure 9 demonstrates that, below 30 km altitude, ClONO₂ was built up and appears to have been the major sink of N₂O₅ which had been photolyzed to NO_x in a previous step.

7. Summary and Conclusion

[40] A very high second maximum of HNO₃ vmr was observed by MIPAS at altitudes of 32 to 40 km during the Antarctic winter 2003. The observed zonal mean vmrs of up to 14 ppbv in July 2003 exceeded those in previous winters as observed by various instruments as well as MIPAS by at least 6 ppbv. The second stratospheric HNO₃ maximum started to form in early June, reached maximum vmrs in July and decreased while continuously being transported downward during August and September. In polar spring it reached the altitude of the ex-vortex primary maximum, forming a single HNO₃ layer in the lower stratosphere. The most probable explanation for these HNO₃ enhancements is production of NO_x in the lower thermosphere and upper mesosphere, which was caused by continuously high geomagnetic activity. This NO_x-rich air subsided to the stratosphere, where N₂O₅ was formed, and then was converted to HNO₃ via ion cluster chemistry and/or heterogeneous processes at sulphate aerosols. Since HNO₃ formation depends on formation of N₂O₅ as an interim step, the second HNO₃ maximum in the upper stratosphere was restricted to the polar night part of the Antarctic vortex. The formation of HNO₃ via ion cluster chemistry/heterogeneous production on sulphate aerosols took about 2 weeks between the first occurrence of enhanced N₂O₅ and the onset of the HNO₃ maximum, while photochemical equilibrium was achieved within 3 to 4 weeks. This is in very good agreement with simulations by *de Zafra and Smyshlyayev* [2001]. High NO_x and N₂O₅ abundances above 35 km occurred well before a solar proton event on 29 May 2003 which strictly excludes this SPE as the only source of enhanced NO_y in the upper stratosphere, as well as local production of HNO₃ by gas phase reactions from OH and NO_x generated locally by high-energetic particles. The major sink of the enhanced HNO₃ in the upper stratosphere was photolysis in the partly illuminated polar vortex from mid of August on.

[41] Similar high upper stratospheric abundances of HNO₃ were observed during Arctic winter 2003/2004 [*López-Puertas et al.*, 2005b; *Orsolini et al.*, 2005] when several very strong SPEs occurred between 29 October and 4 November 2003. Local production of NO_x and OH by high-energetic particles penetrating into the stratosphere and subsequent gas phase chemistry production of HNO₃ led to considerably enhanced amounts of HNO₃ in the upper stratosphere immediately after the October/November SPEs [*López-Puertas et al.*, 2005a, 2005b]. *Orsolini et al.* [2005] and *López-Puertas et al.* [2005a, 2005b] reported on very

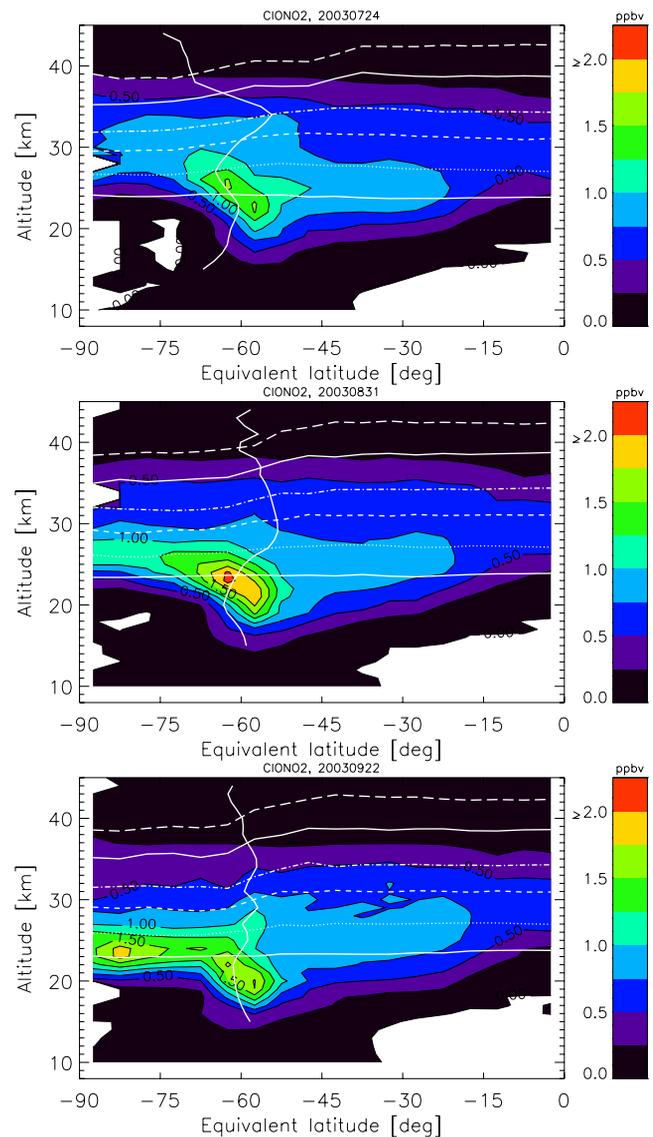


Figure 9. Daily altitude-equivalent latitude cross section of ClONO₂ for the days 24 July, 31 August, and 22 September 2003. For more details, see Figure 3.

high NO_x and HNO₃ abundances in the upper stratosphere in the first half of the winter, while *Randall et al.* [2005], *Natarajan et al.* [2004], *Seppälä et al.* [2004] and *Rinsland et al.* [2005] reported on severely enhanced NO_x abundances in late winter and spring. In this paper we have shown that HNO₃ abundances of similar peak values, and even larger spatial and temporal extension can occur in the upper stratosphere without bombardment of the atmosphere by high-energetic particles from solar flares. Instead, NO_x production in the lower thermosphere by auroral activity alone, together with favourable dynamical conditions which enhance downward transport, most efficiently through the mesosphere in the dark part of the vortex, can lead to similar or even higher levels of upper stratospheric HNO₃ being formed from its precursor NO_x. We conclude therefore that SPEs are not a necessary precondition for pronounced long-term HNO₃ enhancements in the upper stratosphere, since similar HNO₃ enhancements

have been found in Antarctic winter 2003 without any indication of a dependence on energetic particle events.

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