An upper stratospheric layer of enhanced HNO_3 following exceptional solar storms

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[1] An analysis of stratospheric nitric acid (HNO_3) observed by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) reveals a distinct, high-altitude maximum, that appeared in late November 2003 in the polar upper stratosphere. Confined to the polar vortex, the enhanced HNO_3 layer intensified while descending to the middle stratosphere, and disappeared between mid-January and mid-February. The high-altitude maximum is considerably enhanced compared to the weak, secondary maxima previously reported in the literature. Analysis of MIPAS stratospheric nitrogen dioxide (NO_2) and correlations with the geomagnetic Ap index suggest that particle precipitation from the intense solar storms of October–November 2003 was responsible for this extraordinary high-altitude HNO_3 layer. The detailed morphology and time-evolution of such a distinct, high-altitude HNO_3 layer have not been observed before, nor the link to geomagnetic activity through contemporaneous upper stratospheric NO_2 measurements. **Citation:** Orsolini, Y. J., G. L. Manney, M. L. Santee, and C. E. Randall (2005), An upper stratospheric layer of enhanced HNO_3 following exceptional solar storms, *Geophys. Res. Lett.*, *32*, L12S01, doi:10.1029/2004GL021588.

1. Introduction

[2] Nitric acid (HNO_3) is an important minor constituent in the middle atmosphere, and a key species of the odd nitrogen (NO_y) family; active odd nitrogen (NO_x = NO + NO_2) is responsible for the major ozone loss catalytic cycle in the middle stratosphere. In the lower stratosphere, HNO_3 plays a multi-facetted role in chlorine-induced ozone loss processes in the winter and spring. The distribution of HNO_3 in the middle atmosphere has been studied by means of ground-based, satellite and airborne observations in the last 3 decades. The 3-year climatology (1993, 1995, 1999) of millimetre-wave measurements at the South Pole by *de Zafra and Smyshlaev* [2001] (hereinafter referred to as ZS2001) shows a pronounced annual cycle with a maximum in winter and a minimum in summer, and an HNO_3-rich layer that peaks near 25 km. Satellite observations from the Limb Infrared Monitor of the Stratosphere (LIMS) [*Austin et al.*, 1986] during the winter 1978–79, from the Microwave Limb Sounder (MLS) [*Santee et al.*, 1999, 2004] during much of the 1990s, and from the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument in 1992 [*Kawa et al.*, 1995] have allowed mapping of inter-hemispheric variations in the upper and lower stratosphere. These observations revealed a meridional, equator-to-pole gradient, and a strong seasonal cycle at high latitudes in both hemispheres. While HNO_3 is abundant in the 20–30 km height range in the Arctic, where its mixing ratio exceeds 10 ppbv [*Santee et al.*, 2004], some observations revealed a weak, but distinct secondary HNO_3 maximum into the upper stratosphere, within the winter polar vortex [*Austin et al.*, 1986; *Kawa et al.*, 1995; *McDonald et al.*, 2000].

[3] Several mechanisms have been proposed to explain these high-altitude HNO_3 enhancements in the polar winter. Gas phase reactions involving nitrogen species lead to the formation of N_2O_5, which is then converted into HNO_3 by heterogeneous reactions. The high altitudes preclude such reactions occurring on polar stratospheric clouds. *Kawa et al.* [1995] rather investigated heterogeneous reactions on hydrated ion clusters to speed up the conversion of N_2O_5 into HNO_3. They concluded that the ion concentration needed to generate the second peak in HNO_3 was too large. *Bekki et al.* [1997] invoked heterogeneous chemistry on aerosol sulfate particles to explain the HNO_3 enhancements, but the sulfate aerosol layer caps near 30–35 km. ZS2001 successfully modelled high-altitude mid-winter enhancements by combining these two mechanisms, with ion cluster chemistry playing a dominant role in the mid and upper stratosphere. Their study required a large, but not unrealistic, downward flux of NO_x from the polar winter mesosphere.

[4] Energetic particle precipitation (EPP) is known to create NO_x in the mesosphere and thermosphere, and hence to strongly influence its flux into the upper stratosphere. First predicted by *Solomon et al.* [1982], observational evidence for stratospheric NO_x enhancements during and after periods of high geomagnetic activity has been extensively documented [e.g., *Callis and Lambeth*, 1998; *Randall*

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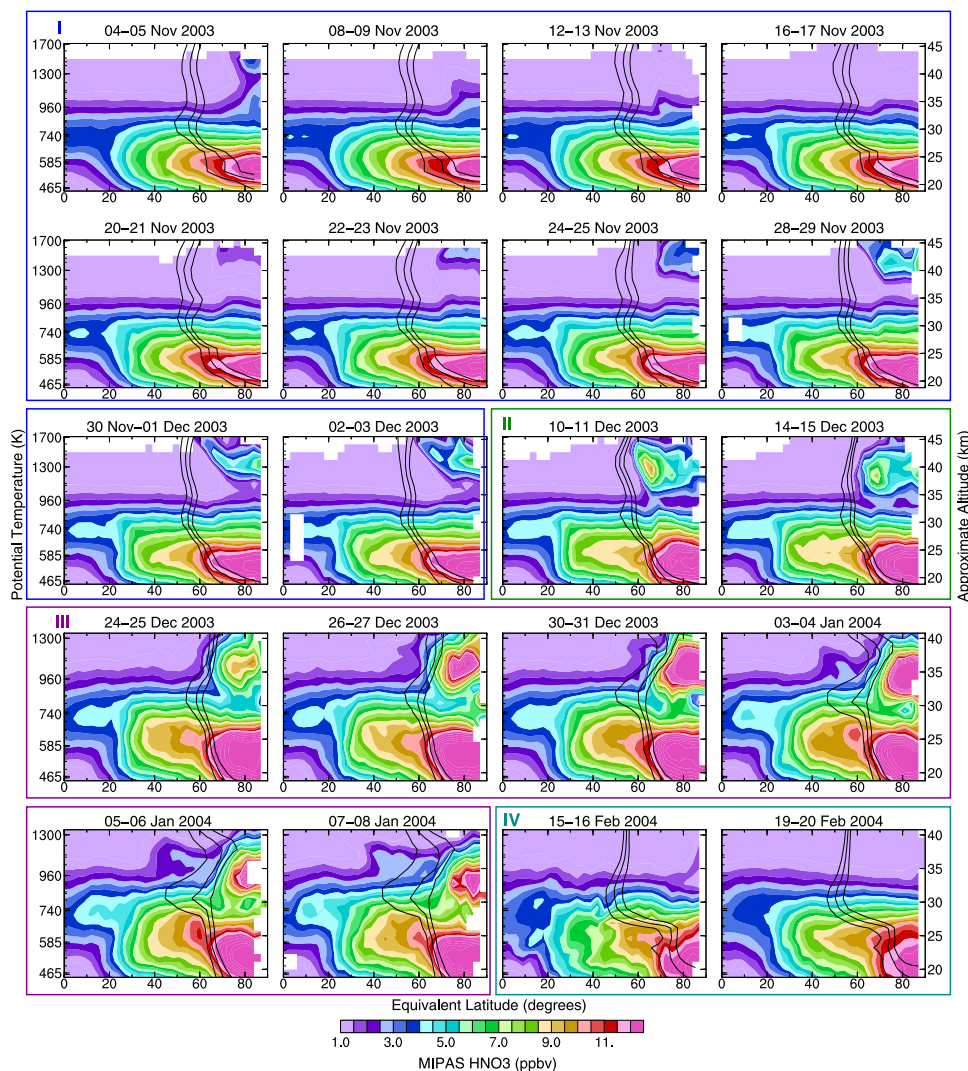
Figure 1. Potential temperature/equivalent latitude cross-sections of HNO3 (ppbv) for a series of selected 2-day periods, between November 4, 2003 and February 20, 2004. Cross-sections pertain to 4 continuous data-acquisition periods (see text), as indicated by coloured frames. Cross-sections extend up to 1710 K during periods I–II, and to 1300K during periods III–IV. Overlaid contours show sPV values of 1.4, 1.6, and 1.8×10^{-4} 1/s.

et al., 2001; *Siskind et al.*, 2000, and references therein). Most recently, *Natarajan et al.* [2004] have described stratospheric NO_x enhancements during April 2004, tentatively attributing them to the large solar storm events of October–November 2003.

[5] The aim of this paper is to show an extraordinary, distinctive double-peaked layer in stratospheric HNO₃ in the Northern Hemisphere winter 2003/04, and to relate it to the solar storms of 2003. Our analysis is based on measurements by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument.

2. Characteristics of MIPAS Observations

[6] MIPAS is an infrared limb sounder aboard the Environment Satellite (ENVISAT) [*Fischer et al.*, 2000]. Near-Real-Time (NRT) observations are provided by European Space Agency (ESA). The instrument was switched off in late March 2004, after intermittent disruptions in preceding months. Improved retrieval algorithms were implemented in NRT mode on November 4, 2003, the starting date of our analysis.

[7] We used retrieved profiles of HNO₃, methane (CH_4) and NO_2 in the approximate height range 18 to 50 km, with a vertical resolution of about 3 km, and an along-track horizontal resolution of about 500 km. NRT data contain missing orbits, and thus were aggregated in 2-day periods. The time coverage is somewhat irregular, and consists of four separate periods when a continuous stream of observations was acquired: period I (Nov 4–Dec 3), II (Dec 10–Dec 15), III (Dec 24–Jan 8), and IV (Feb 13–Mar 26). Validation studies for 2002 indicated that the accuracy of the HNO₃ and NO_2 retrievals was around 10% [*ESA*, 2005].

[8] Along-track mixing ratios were interpolated onto potential temperature (theta) levels using the retrieved temperatures. Geographical coordinates were also converted into equivalent latitudes (EqLat) using the Met Office potential vorticity (PV). *Manney et al.* [1999] described the use of scaled PV (sPV) in EqLat vs. theta cross-sections of the type constructed in this study, and *Orsolini et al.*
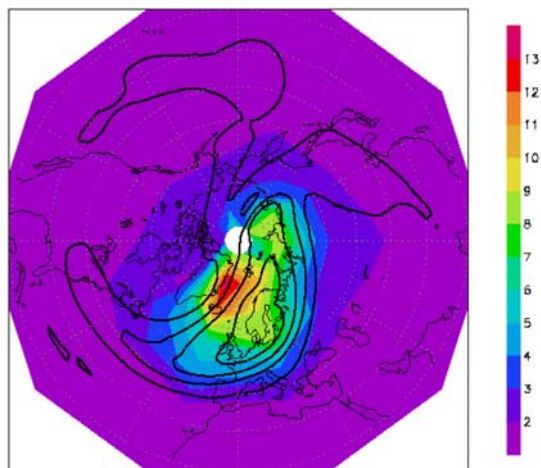
Figure 2. An isentropic map of HNO_3 and sPV at 1000K on 25 December 2003. HNO_3 mixing ratios range from 1. to 14. ppbv. Contours of sPV range from 0.6 to 1.8 10^{-4} 1/s by interval of 0.4 10^{-4}.

[2005] used this technique for mapping MIPAS observations in the Austral spring 2002.

3. The Anomalous HNO₃ Layer in Winter 2003/04

[9] Figure 1 shows the distribution of HNO_3 from early November through mid-February, in the form of a series of EqLat/theta cross-sections, for selected days during the four periods. The vertical span varies in order to follow the evolution of the secondary HNO_3 maximum. Overlaid are contours of sPV (1.4, 1.6 and 1.8 10^{-4} 1/s), typical vortex edge values in undisturbed conditions.

[10] The primary wintertime stratospheric HNO_3 layer is largely confined below 900K, and HNO_3 increases with EqLat. However, a well-defined, long-lasting maximum appears in the upper stratosphere in late November. Starting with small amplitude, the persistent feature intensifies until early January, while descending into the middle stratosphere, over a period of 6−7 weeks. It reaches highest mixing ratios in late December and early January near 1000 K, descending still further to about 900 K (30−35 km) by January 8. The rate of descent at high latitudes is of the order of 0.3 km per day, qualitatively consistent with wintertime downward transport and previous South Pole observations [*McDonald et al.*, 2000]. In early January, areas of high HNO_3 mixing ratios in the enhanced upper layer start to shrink, and the high-latitude maximum has disappeared by the time processed NRT observations resume in mid-February. In their analysis of the CLAES observations of 1992, *Kawa et al.* [1995] showed a secondary maximum, albeit considerably weaker than the one investigated here, in January but not in mid-February. In early January, the HNO_3 mixing ratios at 1000 K are as high as in the main layer below (the two peaks have the same magnitude, so the high-altitude peak can hardly be described as a secondary maximum in this case). Since the interrupted data sequence does not show the final decay stage of the enhanced layer below 30 km, we cannot conclude whether the two enhanced layers mix later in

January or early February in the lower stratosphere. It must be emphasized that the high-altitude enhanced HNO_3 layer appears consistently in individual profiles that are inside the polar vortex, as revealed by our PV mapping cross-sections. Figure 2 shows an isentropic map of HNO_3 and sPV contours at 1000 K on December 25, demonstrating that the elevated HNO_3 regions are largely confined to the polar vortex. The consistency of the HNO_3 enhancements in position (inside the polar vortex), in time and altitude (the slow descent throughout the winter), rules out the possibility that the feature is a retrieval artifact. The time scale for the build-up of the HNO_3 enhancements (e.g. 10 ppbv increase over 40 days) is consistent with the observations of ZS2001.

4. Elevated Levels of Stratospheric NO₂

[11] The HNO_3 production mechanism upon hydrated ion clusters invoked by *Kawa et al.* [1995] and ZS2001 requires large fluxes of NO_x into the stratosphere. Autumn 2003 witnessed exceptional solar storms, and EPP is a known source of NO_x enhancements. The daily Ap index (Figure 3) is a common indicator of EPP [e.g., *Randall et al.*, 1998]. It peaked around October 29−31 after a strong solar proton event and again on November 20. Figure 3 shows night time (solar zenith angle larger than 90°) MIPAS NO_2 mixing ratios averaged poleward of 60°N on 4 isentropes in the upper stratosphere. *Callis and Lambeth* [1998] reported ISAMS (Improved Stratospheric And Mesospheric Sounder) observations of mesospheric NO_2 mixing ratios before and after precipitation events in 1991 and 1992, which jumped from a background of 1−5 ppbv to about 30−40 ppbv in the zonal mean, and local maxima in excess of 140 ppbv near 0.1 mb. Shortly after the Ap index maxima, MIPAS polar-averaged NO_2 increased significantly at both 1705 and 1880 K, nearly doubling to 100 ppbv on Nov. 6 at 1880 K. Large stratospheric enhancements of NO_2 were observed by various satellite instruments in November−December 2003 [*Randall et al.*, 2005; *Seppälä et al.*, 2004], and in non-LTE MIPAS retrievals immediately following the first solar
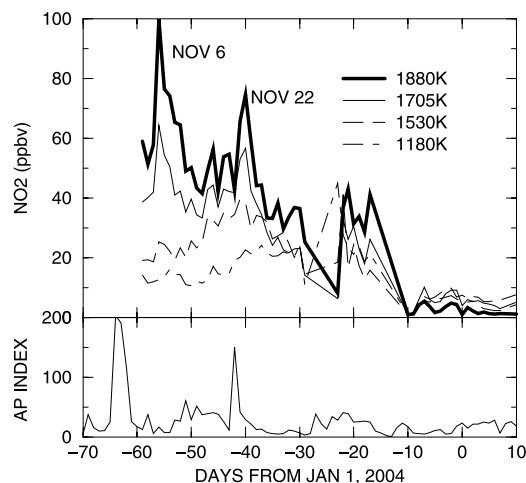

Figure 3. Time series of night time NO2 (ppbv) averaged north of 60°N, from early November to early January, on 4 isentropes (1880, 1705, 1530, and 1180 K). Also shown is the daily Ap index.

proton event (M. López-Puertas et al., Observation of NO_x enhancement and ozone depletion in the northern and Southern Hemispheres after the October–November 2003 solar proton events, submitted to *Journal of Geophysical Research*, 2004, hereinafter referred to as López-Puertas et al., submitted manuscript, 2004). Previous studies [e.g., *Randall et al.*, 2001; *Siskind et al.*, 2000] have also attributed excess NO_x to either local production of stratospheric NO_x by EPP, or to production of mesospheric NO_x by EPP, followed by descent to the stratosphere. Examination of MIPAS CH_4 (not shown) confirms that NO_2 enhancements at high EqLats in November are associated with CH_4 mixing ratio less than 0.3 ppmv, indicating air that had already descended from the mesosphere. The coincidence of the second NO_2 enhancement with a maximum in the daily Ap index, and its near-simultaneous appearances on several isentropes (Figure 3) suggest direct production of NO_x in the stratosphere. Hence we show evidence that the enhanced upper stratospheric HNO₃ layer is the indirect result of EPP, in that it appears at a time when enhanced geomagnetic activity led to stratospheric levels of NO_2 that are well in excess of background values.

5. Discussion

[12] A long-lasting, high-altitude HNO₃ layer was observed by MIPAS in autumn and early winter 2003, confined to the polar vortex. The HNO₃-enhanced layer was first seen around 20 November 2003 in the upper stratosphere, and descended to near 30 km by early January. While unique in magnitude, these enhancements are consistent with previously reported high-altitude HNO₃ layers. Further inspection of Figure 1 indicates a weak, but deep HNO₃ enhancement during the first two days of observations, November 4–5 (see also López-Puertas et al., submitted manuscript, 2004). The current dataset does not allow us to investigate when this weak enhancement originated. HNO₃ is photolysed in daylight, and dynamical confinement to high latitudes in dark conditions is needed for enhancements to persist. Model studies are under way to unravel the history of air masses sampled by MIPAS from early November 2003 to mid January 2004. Such model studies are needed to quantitatively test our understanding of the repartitioning of NO_y species during the formation and descent of the HNO₃-enhanced layer.

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