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# Time Series of HNO<sub>3</sub> Column Amounts Measured by Ground-Based FTIR Spectroscopy at Kiruna (Sweden) in Winter 1995/96 and 1996/97

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# INTRODUCTION

Atmospheric absorption spectra using the sun as the source of radiation were recorded by groundbased FTIR (Fourier Transform InfraRed) spectrometers at Kiruna (Sweden, 68°N, 20°E) during winter and early spring since winter 1990. While a Bruker 120 M was used from winter 1993/94 until winter 1995/96 at Esrange, a Bruker 120 HR is in operation at the Institute of Space Physics (IRF) since March 1996. The latter one is operated continuously and is part of the ILAS validation experiment (Improved Limb Atmospheric Spectrometer onboard of the Japanese Advanced Earth Observing Satellite). Zenith column amounts (ZCA) of several trace gases like Q<sub>3</sub>, H<sub>2</sub>O, HDO, N<sub>2</sub>O, CH<sub>4</sub>, HF, HCl, CIONO<sub>2</sub>, NO, NO<sub>2</sub>, and HNO<sub>3</sub> have been retrieved from these spectra. HNO<sub>3</sub> will be discussed along with other nitrogen compounds like CIONO<sub>2</sub>, and NO<sub>2</sub>.

# EXPERIMENTAL

In winter 1996 infrared absorption spectra were recorded from Feb. 6 until March 30 at Esrange near Kiruna (67.9°N, 21.1°E, 470 m a.s.l.). In winter 1997 observations were made at the IRF, Kiruna (67.8°N, 20.4°E, 420 m a.s.l.). Data covering the period from Jan. 23 until March 30, 1997 are included in this paper. While at Esrange a Bruker 120 M was used as FTIR instrument, a Bruker 120 HR is operated at the IRF. The optical path difference (OPD) is 250 cm for the 120 M and 360 cm for the HR yielding a spectral resolution of 0.003 cm<sup>-1</sup> and 0.002 cm<sup>-1</sup>, respectively. In both instruments 2 detectors (MCT and InSb) and several optical filters are used, covering the spectral range of 700 - 5000 cm<sup>-1</sup>. Solar absorption spectra were recorded, while coadding up to 15 min.

## DATA ANALYSIS AND ERRORS

For the analysis of the spectra synthetic spectra were calculated with SCAIS (Simulation Code for Atmospheric Infrared Spectra) using daily ozone sonde and ECMWF data for  $O_3$ , p, T, and H<sub>2</sub>O. Spectroscopic data were taken from HITRAN 96 data base. The synthetic spectra were fitted to the measured ones by the non-linear least-squares-fitting algorithm RAT (Retrieval of Atmospheric Trace Gases) [1]. The errors of the ZCA were estimated taking into account several sources of error like spectral noise, uncertainties of the observation angle, of the temperature, errors of the shape of the initial volume mixing ratio profile, and errors due to interfering gases.

	HNO <sub>3</sub>	ClONO <sub>2</sub>	$NO_2$	HF
Precision $(1\sigma)$ [%]	4	8	10	3
Accuracy $(1\sigma)$ [%]	11	14	11	6

**Table 1**: Typical errors in % of the zenith column amounts.



**Fig. 1**: ZCA of HNO<sub>3</sub>, ClONO<sub>2</sub> and NO<sub>2</sub> in Kiruna during winter 1996. The shaded areas mark observations inside the polar vortex or at its edge (PV >  $36 \times 10^{-6} \text{Km}^2 \text{kg}^{-1} \text{s}^{-1}$  (pvu) on 475 K level).



**Fig. 2**: ZCA of HNO<sub>3</sub>, ClONO<sub>2</sub> and NO<sub>2</sub> in Kiruna during winter 1997. The shaded areas mark observations inside the polar vortex or at its edge (PV > 36 pvu on 475 K level).



**Fig. 3:** Ratios of ZCA of  $HNO_3$  to the ZCA of HF during winters 1996 and 1997. Only days of observation with PV > 36 pvu on the 475 K level are shown.



**Fig. 4:** The ZCA of HNO<sub>3</sub> plotted versus temperature on the 475 K level. Only days of observation with PV > 36 pvu on the 475 K level are shown; the date of observation is marked at each data point.



**Fig. 5:** The ZCA of HNO<sub>3</sub> plotted versus the ZCA of ClONO<sub>2</sub>. Only days of observation with PV > 36 pvu on the 475 K level are shown; the date of observation is marked at each data point.

#### **RESULTS AND DISCUSSION**

In Figs. 1 and 2 the time series of ZCA of HNO<sub>3</sub>, ClONO<sub>2</sub> and NO<sub>2</sub> during winters 1996 and 1997 are shown. The ZCA of HNO<sub>3</sub> and ClONO<sub>2</sub> are rather small from day 45 until 53, 1996, indicating

sequestration in PSC (Polar Stratospheric Clouds) (HNO<sub>3</sub>) and chlorine activation (ClONO<sub>2</sub>). Inside the vortex (marked by shaded areas) ClONO<sub>2</sub> varies strongly, but is mostly large (except for that period) indicating ClONO<sub>2</sub> production. During winter 1997 the ZCA of NO<sub>2</sub> is rather low from day 53 until 58, while ClONO<sub>2</sub> is strongly increasing, indicating production of ClONO<sub>2</sub> from ClO and NO<sub>2</sub>.

In order to reduce dynamic effects the ratios of the ZCA of  $HNO_3$  to that of HF are shown in Fig.3. Days of observation with potential vorticity less than 36 pvu on the 475K level are omitted in Figs. 3-5. In winter 1997  $HNO_3/HF$  is decreasing towards the end of the winter, probably due to photolysis. In winter 1996  $HNO_3/HF$  is rather small also for the days 45 to 53, 1996, suggesting sequestration into PSCs.

Fig. 4 shows the ZCA of  $HNO_3$  versus the temperature on the 475 K level. For winter 1996 the columns of  $HNO_3$  correlate rather well with the stratospheric temperature, except from March 25 until March 30. These data with small columns of  $HNO_3$  correspond to large columns of  $CIONO_2$  (Fig. 1) indicating that  $NO_2$  was released by photolysis of  $HNO_3$  reacting with CIO to  $CIONO_2$ . From February 6 until March 6, 1996 the columns of  $HNO_3$  are controlled by the stratospheric temperature, indicating that heterogeneous processes play a major role. In winter 1997 the stratospheric temperatures above Kiruna were higher as compared to winter 1996, and a temperature dependence of  $HNO_3$  is less obvious.

In Fig. 5 the ZCA of HNO<sub>3</sub> are plotted versus the ZCA of ClONO<sub>2</sub>. For both winters the plots show 2 types of data with different behavior. Up to a column amount of ClONO<sub>2</sub> of about  $4x10^{15}$  molec./cm<sup>2</sup>, HNO<sub>3</sub> correlates well with ClONO<sub>2</sub>. For larger columns of ClONO<sub>2</sub>, HNO<sub>3</sub> is lower as compared to the first case and depends less on ClONO<sub>2</sub> (end of March). These 2 types of behavior may correspond to the 2 different sources of NO<sub>2</sub> necessary to produce ClONO<sub>2</sub>, i. e. in-situ production out of HNO<sub>3</sub> or mixing at the vortex boundary. The first type (increase of HNO<sub>3</sub> with increasing ClONO<sub>2</sub>) indicates transport of NO<sub>2</sub> into the vortex at its edge. The other type with reduced columns of HNO<sub>3</sub> represents in-situ production of NO<sub>2</sub> from HNO<sub>3</sub>. The data from March 4 and 5, 1996 as well as those from February 26 to March 15, 1997 cannot be associated with one of these types, they might represent a combination of both processes. A model study performed by Chipperfield et al. [2] concludes that in-situ production of NO<sub>2</sub> is more important than mixing. This is in agreement with our data for columns of ClONO<sub>2</sub> greater than  $4x10^{15}$  molec./cm<sup>2</sup>, but not for smaller column amounts of ClONO<sub>2</sub>.

## CONCLUSION

The ZCA of HNO<sub>3</sub> behave differently in winter 1996 and 1997. While in 1997 HNO<sub>3</sub> is mainly controlled by photolysis, a temperature dependence can be found in 1996, indicating that HNO<sub>3</sub> is controlled by heterogeneous processes. In 1996, the ZCA of HNO<sub>3</sub> and ClONO<sub>2</sub> correlate well up to a column of  $4x10^{15}$  molec./cm<sup>2</sup> of ClONO<sub>2</sub>. During periods with greater ZCA of ClONO<sub>2</sub> a decrease of HNO<sub>3</sub> is observed indicating photolysis of HNO<sub>3</sub>.

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