

Denitrification in the Arctic mid-winter 2004/2005 observed by airborne submillimeter radiometry

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[1] We present measurements of unusually low mixing ratios of HNO₃ in the exceptionally cold Arctic vortex of late-January and early-February 2005. The measurements were obtained by the airborne submillimeter radiometer ASUR during the polar aura validation experiment (PAVE). The distribution of HNO₃ inside the vortex reaches minima below 4 ppbv around 22 km altitude and maxima above 13 ppbv around 16 km altitude, with a considerable spatial variability. We estimate a vortex averaged denitrification of 3.1 ± 0.8 ppbv around 20 km altitude, and slight reinitiation below ~ 15.5 km altitude. The observed HNO₃ deficit is largest (~ 6 ppbv) near the center of the vortex, where the air masses had experienced temperatures below the NAT formation threshold for 80–100% of the previous 20 days according to back trajectories. This suggests that the main denitrification mechanism is based on sedimenting nitric acid trihydrate particles. **Citation:** Kleinböhl, A., H. Bremer, H. Küllmann, J. Kuttippurath, E. V. Browell, T. Canty, R. J. Salawitch, G. C. Toon, and J. Notholt (2005), Denitrification in the Arctic mid-winter 2004/2005 observed by airborne submillimeter radiometry, *Geophys. Res. Lett.*, 32, L19811, doi:10.1029/2005GL023408.

1. Introduction

[2] Denitrification is the irreversible removal of reactive nitrogen from an air mass by the sedimentation of HNO₃-containing particles. The resulting lack of reactive nitrogen causes a delay in chlorine deactivation and hence a more prolonged period of ozone loss [Rex *et al.*, 1997; Waibel *et al.*, 1999; Tabazadeh *et al.*, 2000]. Denitrification occurs frequently in the Antarctic winter [Fahey *et al.*, 1990; Santee *et al.*, 1999], and has also been observed several times in the Arctic [Sugita *et al.*, 1998; Rex *et al.*, 1999; Kondo *et al.*, 2000]. The most severe and extensive Arctic denitrification was observed in the unusually cold winter of 1999/2000 [Popp *et al.*, 2001; Kleinböhl *et al.*, 2002]. The Arctic winter of 2004/2005 was exceptionally cold and showed a larger area of potential PSC formation on the 475 K surface than any other winter in recent years (Figure 1). Also, the area for potential ice formation was

larger than in the previous winters. Here we present measurements of HNO₃ and N₂O that were taken by the airborne submillimeter radiometer on board the NASA DC-8 research aircraft during the polar aura validation experiment (PAVE) between 24 Jan. and 9 Feb. 2005. We quantify the denitrification in the Arctic vortex and study how it correlates with equivalent latitude and airparcel temperature history, which provides information on the plausibility of denitrification mechanisms.

2. Measurements

[3] Remote measurements of gas-phase HNO₃ and N₂O were performed by the Airborne SUBmillimeter Radiometer ASUR [von König *et al.* [2000], and references therein]. The instrument operates in a frequency range between 604.3 and 662.3 GHz and uses a liquid helium cooled detector and an acousto-optical spectrometer for the acquisition of spectra. By analyzing the spectrally resolved pressure broadened emission lines using the optimal estimation method [Rodgers, 1976], vertical profiles of the volume mixing ratio (VMR) of HNO₃, N₂O, and other trace gases are retrieved in an altitude range of about 15–40 km with a typical vertical resolution of 6–10 km in the lower stratosphere. For a more detailed description of the measurement and retrieval the reader is referred to Kleinböhl *et al.* [2002].

[4] ASUR was operated on board the NASA DC-8 research aircraft during PAVE. Deployed from Portsmouth, NH, ASUR performed trace gas measurements inside the Arctic vortex on five research flights, which will

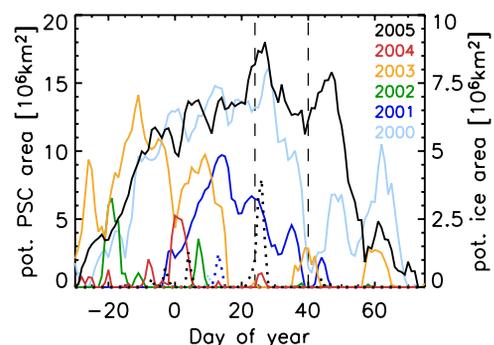


Figure 1. Potential PSC area (area below T_{NAT} , solid) and potential ice area (dotted) on a potential temperature level of 475 K for the Arctic winters since 1999/2000, based on meteorological analyses by ECMWF and assuming an HNO₃ VMR of 10 ppb and an H₂O VMR of 5 ppm. The dashed lines indicate the time period during which the DC-8 was deployed in 2005.

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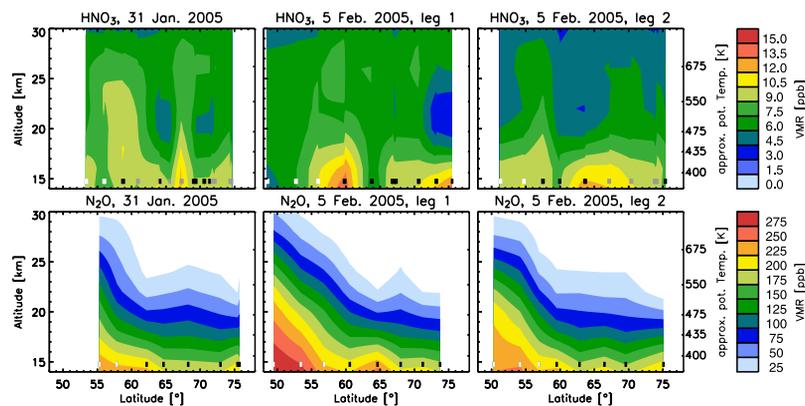


Figure 2. ASUR measurements of HNO_3 and N_2O on flights that penetrated deeply into the vortex. The dashes at the bottom indicate the actual measurement positions (black: inside inner vortex boundary, white: outside inner vortex boundary, gray: HNO_3 inside inner vortex boundary with PSC coverage).

be analyzed in the following sections. Figure 2 shows the measurements of HNO_3 and N_2O on the two flights that penetrated most deeply into the vortex. The inner vortex boundary on the 475 K potential temperature surface, defined by the *Nash et al.* [1996] criterion, was located at equivalent latitudes (EQLs) between 65° and 70° during the campaign, corresponding to actual latitudes around 58°N for the flights shown in Figure 2. This inner vortex boundary will be used as the vortex edge in the following analysis. It can be seen that the VMRs of N_2O inside the vortex were below 100 ppb at 20 km altitude, in contrast to above 200 ppb for typical conditions outside the vortex, indicating that substantial descent of air masses had taken place inside the vortex. Considerable variability was observed for HNO_3 . There are regions of low HNO_3 at altitudes of 20–22 km, where VMRs drop below 6 ppb, in some measurements even below 4 ppb. In contrast, at ~ 16 km and below, patches of high HNO_3 values are found, with typical VMRs above 9 ppb but sometimes as large as ~ 14 ppb. It is noted that for the HNO_3 retrieval a zero a priori profile with constant a priori covariances has been used which makes it unlikely that peak values or peak altitudes in the retrieved profiles are influenced by the a priori.

3. Derivation of Denitrification

[5] To study the effect of denitrification the HNO_3 measurements during PAVE are compared to a profile that

represents the HNO_3 distribution before the onset of denitrification, denoted by HNO_3^* . As there are no measurements in early-winter 2004/2005, vortex averages of ASUR measurements of HNO_3 and N_2O taken between 2–5 Dec. 1999 are used [Kleinböhl et al., 2002]. The vortex averaged profiles of N_2O are shown in Figure 3 (left). It can be seen that N_2O mixing ratios during PAVE were located at altitudes about 3–4 km lower than the corresponding N_2O vortex average of early-Dec. 1999, indicating that considerable diabatic descent of air masses had occurred in the 2004/2005 Arctic vortex.

[6] For the vortex average of HNO_3 , measurements have been excluded when polar stratospheric clouds (PSCs) were observed around or above an altitude of 16 km to distinguish between temporary uptake in PSCs and irreversible denitrification. For this purpose aerosol measurements by the Langley Airborne Differential Absorption Lidar (DIAL) [Browell et al., 1998] were used, which was also operated on board the DC-8. A PSC was detected when the aerosol scattering ratio exceeded 0.6 in the infrared and 0.17 in the visible lidar channel at altitudes of about 18 km and above. Below this altitude PSC layers were identified by the depolarization of the aerosols with a total atmospheric depolarization of $>2\%$. To be conservative a margin of 300 seconds before and after each PSC detection has been excluded as well. In total 31% of the HNO_3 measurements inside the vortex during PAVE have been excluded due to these criteria. It is noted that there are cases where further layers of solid PSCs may be identified around 15 km

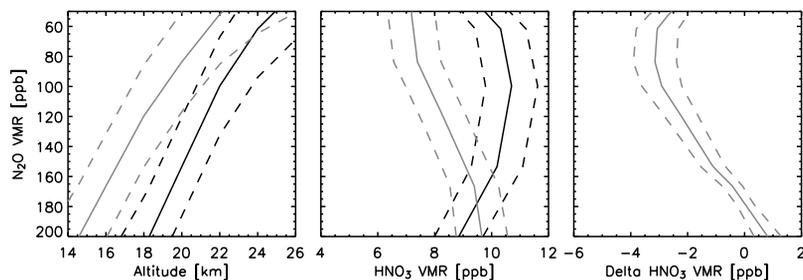


Figure 3. (left) Vortex averaged N_2O profile for 2–5 Dec. 1999 (black) and 24 Jan.–7 Feb. 2005 (gray). (middle) HNO_3^* (black) and vortex averaged HNO_3 for 24 Jan.–7 Feb. 2005 (gray). (right) Denitrification derived as $\text{HNO}_3 - \text{HNO}_3^*$, corrected for diabatic descent using the N_2O profiles. The dashed lines give the estimated accuracies in all cases.

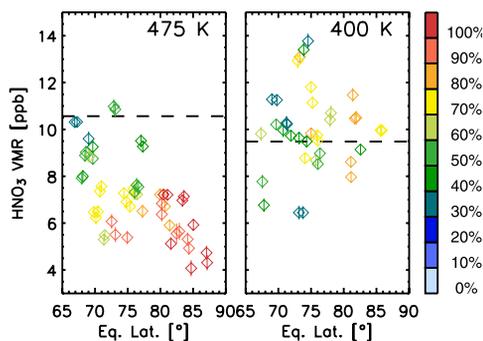


Figure 4. HNO_3 vs. EQL within the inner vortex boundaries (left) at 475 K and (right) at 400 K for measurements without PSC coverage, with the error bars giving the precision. The dashed line gives the HNO_3^* estimate inside the vortex. The colors indicate the fraction of time for which the airparcel had experienced temperatures below T_{NAT} along a 20-day back trajectory for each measurement.

altitude by applying the depolarization criterion in a reanalysis of the lidar data. Assuming that these layers contain HNO_3 as solid hydrates, the total HNO_3 at altitudes around 15–16 km might be larger than the gas-phase HNO_3 reported in this work. To obtain a more representative vortex average, the individual profiles were weighted with the area of the EQL band in which they were measured. This approach gives better comparability to areal measurements and is reasonable because the variations in the presented trace gases are dependent on EQL in the first approximation.

[7] To create an HNO_3^* profile, a vortex average of ClONO_2 derived from balloon borne measurements by the MkIV interferometer [Toon, 1991] and ground-based ClONO_2 measurements between 2 and 5 Dec. 1999 [Kleinböhl et al., 2002] is added to the HNO_3 average. We adopted this approach because no significant chlorine activation had been measured in early-Dec. 1999 but high chlorine activation was measured during PAVE (see auxiliary material¹).

[8] The derived HNO_3^* and measured HNO_3 profiles are shown in Figure 3. The HNO_3^* profile reveals a peak of 10.7 ppb at a level of 100 ppb N_2O , which corresponds to an altitude of 22 km if the N_2O profile from early-Dec. 1999 is considered, and 19 km if the N_2O profile for Jan./Feb. 2005 is taken into account. In contrast, the HNO_3 average from Jan./Feb. 2005 exhibits a minimum of 7.2 ppb at 50 ppb of N_2O , corresponding to an altitude of 22 km in Jan./Feb. 2005. Below an N_2O level of ~ 180 ppb (about 15.5 km in Jan./Feb. 2005), the HNO_3 profile from Jan./Feb. 2005 starts to exceed the HNO_3^* profile.

[9] Figure 3 (right) shows our estimate of denitrification, derived as $\text{HNO}_3 - \text{HNO}_3^*$, corrected for diabatic effects using the corresponding N_2O profiles. A maximum denitrification of 3.1 ± 0.8 ppb is found around an altitude of 20 km, with the error giving the estimated accuracy. Below about 15.5 km, $\text{HNO}_3 - \text{HNO}_3^*$ becomes positive, indicating that renitrification (evaporation of HNO_3 from sedimenting particles) had occurred at these altitudes.

[10] To further study the structure of the HNO_3 observed inside the vortex in Jan./Feb. 2005, the distribution of the VMRs at 475 K potential temperature (~ 19.5 km altitude) and 400 K potential temperature (~ 15.5 km altitude) vs. EQL are considered. This distribution is shown in Figure 4 for measurements inside the vortex at 475 K. A tendency of lower HNO_3 towards higher EQL is clearly evident at 475 K. Close to the vortex edge, around 65° to 70° EQL, HNO_3 VMRs around or only slightly below estimated HNO_3^* are observed, while around 85° EQL, close to the vortex center, observed HNO_3 reaches down to 4–5 ppb, about 6 ppb below HNO_3^* .

[11] We further investigate this situation by calculating 20-day back trajectories for every measurement using meteorological data from ECMWF. The color code in Figure 4 represents the fraction of time that the measured air mass had spent below the existence temperature of nitric acid trihydrate (T_{NAT}) during a 20-day back trajectory. T_{NAT} was calculated using HNO_3 from the HNO_3^* profile and H_2O from profiles measured during a previous winter [Schiller et al., 2002]. It can be seen that in the region where the strongest HNO_3 deficit is observed, north of about 80° EQL, the air masses had spent more than 80% of their time below T_{NAT} . In the region around 75° EQL this fraction was typically about 60–70%, while at the vortex edge, where little difference from HNO_3^* is observed, the fraction of time below T_{NAT} is below $\sim 50\%$. It is noted that along the trajectories the HNO_3 deficit showed no dependence on the minimum temperature, the attainment of the frost point, or the fraction of time below the frost point. This indicates that the major denitrification mechanism is likely to be based on the sedimentation of large NAT-particles [Fahey et al., 2001] that grow and fall in conditions when the temperature is below T_{NAT} for sufficiently long periods of time (typically several days) [Mann et al., 2002].

[12] On the 400 K potential temperature level the data scatter around or slightly above HNO_3^* , indicating no significant denitrification and perhaps slight renitrification. North of $\sim 70^\circ$ EQL there are airparcels which experienced temperatures below T_{NAT} at these altitudes, in some cases up to 60–80% of a 20-day trajectory. As suggested by preliminary analyses of the DIAL data, this indicates that PSC formation, and potentially also denitrification, is possible at these altitudes.

4. Summary and Conclusions

[13] We studied denitrification in one of the coldest Arctic winters of the recent years using measurements of the airborne submillimeter radiometer during the PAVE campaign. A vortex averaged denitrification, defined as $\text{HNO}_3 - \text{HNO}_3^*$, of 3.1 ± 0.8 ppb around 20 km altitude was derived for late-Jan./early-Feb. 2005, taking diabatic processes inside the vortex into account. Slight renitrification was observed below about 15.5 km altitude. The denitrification observed in this winter was comparable within the error bars with the winter of 1999/2000, so far the winter with the strongest Arctic denitrification observed [Popp et al., 2001], where a ΔNO_y of 4.0 ± 2.1 to 5.3 ± 2.7 ppb was derived at altitudes between 19 and 20.5 km in mid-March 2000 based on measurements with the same instrument [Kleinböhl et al., 2002]. The observed HNO_3 deficit is largest (~ 6 ppb) near the center of the

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2005GL023408>.

vortex, where the air masses had experienced temperatures below the NAT formation threshold for 80–100% of the last 20 days according to back trajectories. This suggests that the main denitrification mechanism is based on sedimenting NAT particles.

[14] Potential for further denitrification in the vortex of 2004/2005 after the time of the last ASUR measurements in early-Feb. exists, because considerable areas with temperatures below the NAT formation threshold continued to exist until late-February. The conditions of high chlorine activation, shown by the ASUR observations of high ClO, together with denitrification indicate that the vortex was primed for substantial ozone loss in the Arctic winter 2004/2005. As the stratosphere may cool in the changing climatic environment of the next decades [Rex *et al.*, 2004], severe denitrification might become a more frequent feature in the Arctic vortex, leading to increased potential for ozone loss.

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