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## In situ evidence for renitrification in the Arctic lower stratosphere during the polar aura validation experiment (PAVE)

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[1] In-situ measurements of nitric acid (HNO<sub>3</sub>), ozone (O<sub>3</sub>), and nitrous oxide (N<sub>2</sub>O) were made from the NASA DC-8 during the Polar Aura Validation Experiment in January/February 2005. In the lower stratosphere (9–12.5 km, potential temperature 300–350 K) characteristic compact relationships were observed between all three gases. The ratio HNO<sub>3</sub>/O<sub>3</sub> averaged 3.5 (±0.7) ppt/ppb. Samples with enhanced HNO<sub>3</sub>/O<sub>3</sub> (>4.0) were most abundant under the edge of the Arctic Polar vortex in air masses with enhanced mixing ratios of both gases (>400 ppb O<sub>3</sub> and >2000 ppt HNO<sub>3</sub>) and reduced mixing ratios of N<sub>2</sub>O (<305 ppb), indicating air from higher levels in the stratosphere. Relationships to N<sub>2</sub>O in the anomalous samples under the vortex edge indicate that increases in HNO<sub>3</sub>/O<sub>3</sub> reflect renitrification at DC-8 flight levels, with no indication of significant O<sub>3</sub> loss. Renitrified air was only observed at potential temperatures above 340 K, and was most abundant on the PAVE flights on 27 and 29 January. **Citation:** Dibb, J. E., E. Scheuer, M. Avery, J. Plant, and G. Sachse (2006), In situ evidence for renitrification in the Arctic lower stratosphere during the polar aura validation experiment (PAVE), *Geophys. Res. Lett.*, 33, L12815, doi:10.1029/2006GL026243.

### 1. Introduction

[2] The Polar Aura Validation Experiment (PAVE) made in situ and remote sensing measurements in the Arctic stratosphere from the NASA DC-8 to help validate measurements made from the EOS Aura satellite. Six missions were conducted from Portsmouth, NH to the north and east under the Arctic vortex between 27 January and 7 February, 2005. A lobe of the vortex extended to the southern shores of Hudson Bay (between 50–60 N) throughout this period [Schoeberl *et al.*, 2006]. All flights reached the vortex edge and several reached latitudes greater than 70 N (maximum 76 N) well within the vortex.

[3] Winter 2004/05 produced the lowest Arctic stratospheric temperatures on record [Manney *et al.*, 2006; C. Jimenez *et al.*, Dehydration in the 2004–2005 polar winters: A first look from EOS MLS, submitted to *Geophys. Res. Lett.*, 2006, hereinafter referred to as Jimenez *et al.*, submitted manuscript, 2006]. Temperatures low enough for formation of polar stratospheric clouds (PSCs) were observed for longer, and over a wider area, than any other

winter in the satellite era [Manney *et al.*, 2006]. PSCs (inferred to be predominantly nitric acid trihydrate (NAT)) were observed by MLS beginning in mid-December [Manney *et al.*, 2006]. Temperatures low enough for ice PSC formation were also occasionally observed; except for one event 25–27 January these were too short-lived to cause dehydration (Jimenez *et al.*, submitted manuscript, 2006). Indications of denitrification and ozone depletion were observed in MLS data between 420–460 K in January [Manney *et al.*, 2006; Schoeberl *et al.*, 2006]. Schoeberl *et al.* [2006] combine DC-8 lidar observations of PSCs with MLS observations of N<sub>2</sub>O and HNO<sub>3</sub> to suggest that vortex air at 18–20 km was denitrified by sedimentation of NAT between 25–31 January. This event coincided with the nucleation of ice PSCs, which greatly enhance the growth rate of NAT, thereby increasing the NAT sedimentation velocity and irreversibly removing HNO<sub>3</sub> from the altitude regions of PSC formation [e.g., Fahey *et al.*, 2001].

[4] We present in situ observations of O<sub>3</sub>, HNO<sub>3</sub>, and N<sub>2</sub>O between 9 and 12.5 km in the lowermost Arctic stratosphere. The HNO<sub>3</sub> – N<sub>2</sub>O – O<sub>3</sub> relationships are examined for evidence of descent of PSC-processed air (depleted in O<sub>3</sub> and HNO<sub>3</sub> relative to N<sub>2</sub>O) down to DC-8 flight levels, as well as renitrification from evaporation of NAT crystals that settled and evaporated.

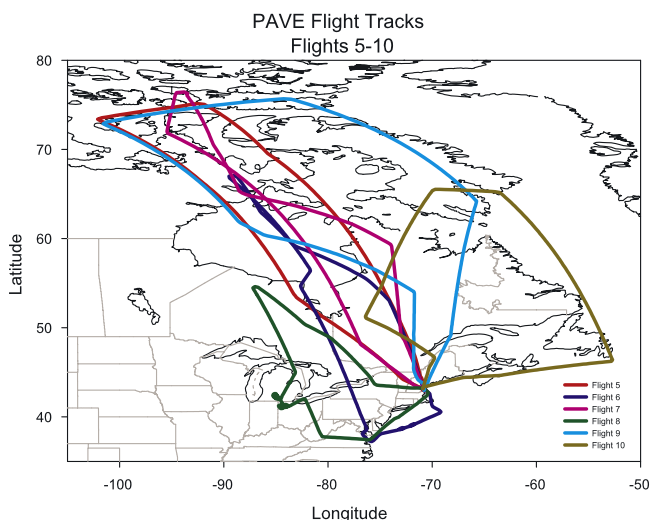
### 2. Methods

[5] Nitric acid (HNO<sub>3</sub>) was measured with the mist chamber/ion chromatography technique [Scheuer *et al.*, 2003], with 100 second sample integration. Ozone (O<sub>3</sub>) was measured by chemiluminescence at 1 second resolution (M. A. Avery *et al.*, FASTOZ: An accurate, fast-response in situ ozone measurement system for aircraft campaigns, in preparation for *J. Oceanic Atmos. Tech.*, 2006). Nitrous oxide (N<sub>2</sub>O) was measured at 1 second resolution by differential absorption spectrometry [Collins *et al.*, 1993]. We focus on interrelationships between HNO<sub>3</sub>, O<sub>3</sub>, and N<sub>2</sub>O on the 6 flights from Portsmouth, NH northward beneath the polar vortex (Figure 1). All plots and analyses use a merged data file where the faster measurements were averaged over the mist chamber integration interval. Potential vorticity (PV) from NASA's Global Modeling and Assimilation Office GEOS-4 model [Bloom *et al.*, 2005] was used for this analysis. Equivalent latitude calculations (EqL: the latitude which encloses a poleward area equal to that of a given potential vorticity contour) were performed using the GEOS-4 PV interpolated to isentropic surfaces, with EqL then interpolated to the DC-8 flight tracks.

[6] PAVE flight tracks were chosen to align with the ground track of one or more of the sensors on Aura (Figure 1). The DC-8 flew at the highest altitude that it could

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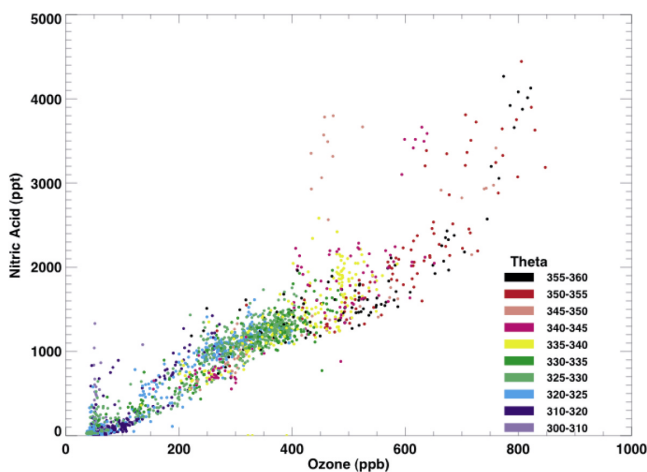


**Figure 1.** Flight tracks for PAVE flights 5–10 from Portsmouth, NH.

maintain, which increased through each flight as the fuel load was burned off. We focus on data obtained above 9 km pressure altitude.

### 3. Results

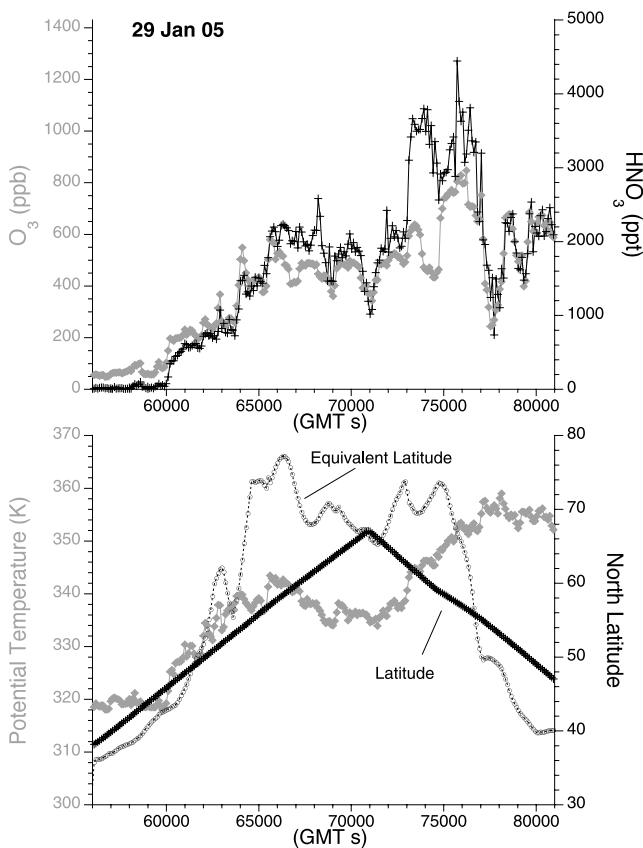
[7] Mixing ratios of  $\text{HNO}_3$  and  $\text{O}_3$  were tightly correlated when  $\text{O}_3$  was greater than 100 ppb but less than about 450 ppb (Figure 2). Enhanced  $\text{HNO}_3$  at low  $\text{O}_3$  reflects tropospheric samples at lower latitudes. The samples above the general trend at high mixing ratios of both gases are the focus of discussion below. Linear regression yields a slope of 3.7 ppt of  $\text{HNO}_3$  per ppb of  $\text{O}_3$ , which is similar to the average value of the  $\text{HNO}_3/\text{O}_3$  ratio in all samples shown in Figure 2 ( $3.5 \pm 0.7$  ppt/ppb). These ratios are similar to the mean (3.3 ppt/ppb) in the lower stratosphere over the Gulf of Mexico and the south eastern US during the pre-AVE and Houston AVE campaigns in Fall 2004 and Spring 2005 (P. Popp, personal communication, 2005). Measurements of



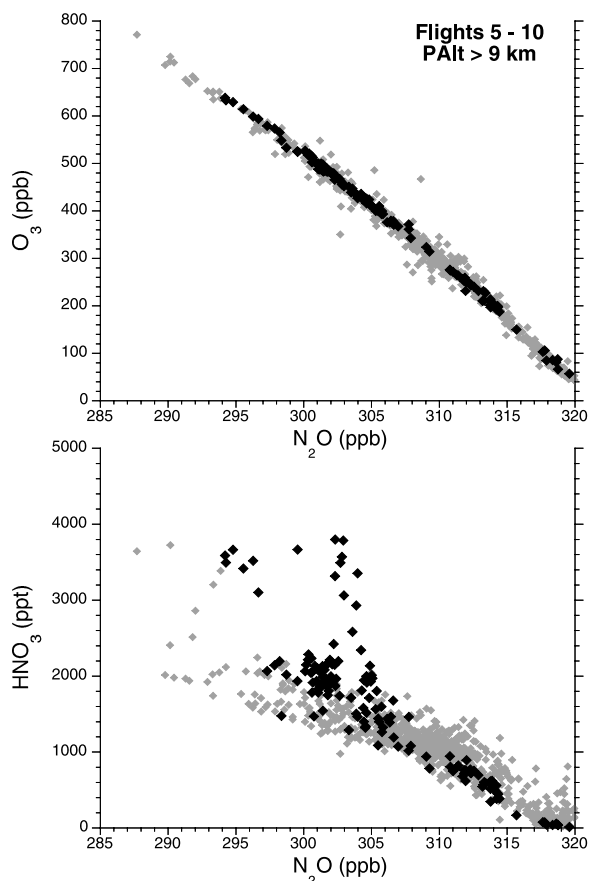
**Figure 2.** Scatter plot of  $\text{HNO}_3$  vs  $\text{O}_3$ , color coded by potential temperature. The slope of a linear regression suggests a stratospheric  $\text{HNO}_3/\text{O}_3$  ratio of 3.7 ppt/ppb.

$\text{HNO}_3/\text{O}_3$  in the lower stratosphere are sparse. *Neuman et al.* [2001] found a tight correlation with a slope of 2.3 ppt/ppb above the central US. Measurements in the Arctic range from 2–4 ppt/ppb [*Schneider et al.*, 1999] to significantly higher values of 10–12 ppt/ppb during STREAM I and II near Kiruna, Sweden [*Bregman et al.*, 1995; *Fischer et al.*, 1997]. The STREAM results are notably high and appear to conflict with the compilation of *Murphy et al.* [1993] who found  $\text{NO}_y/\text{O}_3$  to be consistently in the range 2.5–4.0 ppt/ppb in the extratropical lower stratosphere. Redistribution of  $\text{HNO}_3$  by evaporation of nitric acid trihydrate (NAT) that had sedimented from higher altitudes was suggested as the dominant cause of enhanced  $\text{HNO}_3/\text{O}_3$  during the STREAM flights, though heterogeneous chemistry on Pinatubo aerosol may have contributed [*Bregman et al.*, 1995; *Fischer et al.*, 1997]. Because the PAVE mean value of  $\text{HNO}_3/\text{O}_3$  is similar to all previous reports of  $\text{HNO}_3/\text{O}_3$  and  $\text{NO}_y/\text{O}_3$  in the lower stratosphere except those from STREAM, and agrees closely with the recent results from AVE, we consider that the unperturbed lower stratosphere above North America during PAVE was characterized by an  $\text{HNO}_3/\text{O}_3$  ratio of 3.5 ppt/ppb.

[8] Time series of  $\text{O}_3$  and  $\text{HNO}_3$  on PAVE flight 6 (29 January) are scaled so that when  $\text{HNO}_3/\text{O}_3 = 3.5$  ppt/ppb the points fall on top of each other (Figure 3). In the strato-



**Figure 3.** (top and bottom) Time series of  $\text{O}_3$  (grey),  $\text{HNO}_3$  (black) (Figure 1, top), potential temperature (grey), latitude (black crosses), and equivalent latitude (open circles) on PAVE flight 6. Axes in Figure 1 (top) are scaled so that when  $\text{HNO}_3/\text{O}_3$  equals 3.5 ppt/ppb the points fall on top of each other.



**Figure 4.** Scatter plots of (top)  $O_3$  and (bottom)  $HNO_3$  versus  $N_2O$ . Samples from flights 5 and 6 are shown in the black diamonds, all six flights from Portsmouth are shown in grey diamonds.

sphere, mixing ratios of these gases track each other over more than a 5-fold range in mixing ratios. Similar plots for all flights out of Portsmouth confirm the tight relationship at 100 second time scales, as does the correlation plot (Figure 2). Significant enhancements of  $HNO_3$  above the 3.5 ppt/ppb ratio tend to be clustered in time from 66–68 ksec and again from 73–77 ksec on flight 6 (Figure 3), when the DC-8 was passing under the edge of the vortex lobe. Nitric acid was similarly enhanced in the same region during flight 5 on 27 January. Mixing ratios of both gases and potential vorticity increase markedly beneath the vortex edge. Parallel increases in EqL suggest strongly descending air at the vortex edge, consistent with observations higher in the stratosphere [Schoeberl *et al.*, 2006]. Mixing ratios of both gases decreased when the DC-8 flew under the inner vortex, where MLS observations show relatively less  $O_3$  and  $HNO_3$ , and also less descent. The  $HNO_3$  enhancements are largest on the southbound legs of flights 5 and 6 when the DC-8 was able to fly about a km higher. Sustained enhancements of  $HNO_3$  and  $O_3$ , and especially  $HNO_3/O_3$ , are most frequent near 50–60 N, and at potential temperatures greater than 340 K. Elevated  $HNO_3/O_3$  in air that had recently descended to the lowermost stratosphere raise the question whether the increased ratio is primarily due to  $O_3$  depletion at higher altitude (prior to descent), or sedimen-

tation and subsequent re-evaporation of NAT in PSCs, redistributing  $HNO_3$  to lower altitudes.

#### 4. Discussion and Tracer Relationships

[9] In the stratosphere,  $N_2O$  decreases with time since injection from the troposphere. In contrast, mixing ratios of  $O_3$  and  $HNO_3$  increase with altitude above the tropopause, so they have tight inverse correlations with  $N_2O$  in the lower stratosphere. Departures from trends of  $O_3/N_2O$ ,  $HNO_3/N_2O$  and  $NO_y/N_2O$  in the unperturbed lower stratosphere have provided evidence for  $O_3$  depletion, as well as denitrification and renitrification, in both polar vortices [e.g., Bregman *et al.*, 1995; Fischer *et al.*, 1997; Koike *et al.*, 2002].

[10] During PAVE the in situ relationship between  $O_3$  and  $N_2O$  was linear and very compact (Figure 4). Scatter around the trend decreased as  $N_2O$  mixing ratios decreased and  $O_3$  increased deeper into the stratosphere. The linear regression slope (21.4 ppb  $O_3$ /ppb  $N_2O$ ) is within the narrow range reported from previous Arctic campaigns (20.0–24.4 [Murphy and Fahey, 1994; Koike *et al.*, 2002; Collins *et al.*, 1993]. Although  $O_3$  depletion was observed to start in mid-January at higher altitudes [Manney *et al.*, 2006], ozone loss was not observed by in situ measurements on any of the PAVE flights.

[11] The  $HNO_3 - N_2O$  relationship shows more scatter, particularly at  $N_2O$  mixing ratios below 305 ppb (Figure 4). Most points above the trend are the samples with high values of  $HNO_3/O_3$  observed on flights 5 and 6 (Figure 3). Recall that flight 5 occurred during, and flight 6 was two days after, the only dehydration event observed by MLS in the Arctic stratosphere during winter 2004/2005 (Jimenez *et al.*, submitted manuscript, 2006). The linear fit to PAVE stratospheric samples (excluding those with  $HNO_3/O_3 > 4.0$ ) yields the relationship  $HNO_3 = 20.6 - (0.063 \times N_2O)$  (mixing ratios in ppb). Neuman *et al.* [2001] reported a shallower slope (0.049 ppb  $HNO_3$ /ppb  $N_2O$ ) in the lower stratosphere on a flight over the central US; this is the only published example relating  $HNO_3$  and  $N_2O$  we are aware of. However,  $NO_y/N_2O$  has played an important role in many stratospheric sampling campaigns. In polar regions up to about 13 km altitude reported slopes range from 0.070 to 0.123 [Weinheimer *et al.*, 1993; Koike *et al.*, 2002]. Koike *et al.* [2002] found the  $NO_y/N_2O$  slope to increase from 0.07 to 0.12 between the December and March deployments during SOLVE and suggested the increase was due to redistribution of  $HNO_3$  via evaporation of NAT that had fallen from higher altitudes. At higher altitudes in the lower extratropical stratosphere (up to 20 km), the  $NO_y/NO_2$  ratio appears to be nearly constant at 0.062–0.065 ppb/ppb [Murphy and Fahey, 1994; Fahey *et al.*, 1990].

[12] The scatter plots in Figure 4 indicate that enhanced values of  $HNO_3/O_3$  beneath the vortex edge are due to elevated  $HNO_3$  mixing ratios, with no evidence for  $O_3$  depletion in the air masses that descended to DC-8 flight level. Sedimentation of NAT from higher altitudes with subsequent evaporation appears to have redistributed  $HNO_3$  to the lower stratosphere. Remote observations from the DC-8 on PAVE flight 7 (31 January), and also MLS profiles from Aura in the last week of January, found PSCs near the vortex edge and evidence for denitrification several km

above the DC-8 ceiling [Schoeberl *et al.*, 2006]. The dehydration event during this period (Jimenez *et al.*, submitted manuscript, 2006) may have caused formation of larger NAT particles [e.g., Fahey *et al.*, 2001], leading to the denitrification observed above DC-8 flight levels and the renitrification reported here.

## 5. Conclusions

[13] PAVE was conducted during a winter with unusually cold stratospheric temperatures, significant denitrification and O<sub>3</sub> depletion in the Arctic stratosphere, and at a time when a lobe of the polar vortex was quite far south over North America. Our observations of enhanced HNO<sub>3</sub> at DC-8 flight levels are consistent with MLS and lidar observations of denitrification and PSC's during the PAVE mission. Relationships between HNO<sub>3</sub>, O<sub>3</sub> and N<sub>2</sub>O show that HNO<sub>3</sub> was permanently redistributed from higher in the stratosphere, while O<sub>3</sub> loss was not observed. Enhancements of HNO<sub>3</sub> in the lowermost stratosphere were largely restricted to the region below the vortex edge, where descent was strongest throughout the winter, O<sub>3</sub> and HNO<sub>3</sub> were displaced downward relative to the vortex center, and PSC formation was observed at higher altitudes. Based on our observations, sedimenting NAT crystals rarely descended below potential temperatures of 340 K before evaporating and releasing HNO<sub>3</sub>.

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