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

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1. Introduction

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.

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 N₂O and HNO₃ 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 HNO₃ from the altitude regions of NAT formation [e.g., Fahey et al., 2001].

2. Methods

Nitric acid (HNO₃) was measured with the mist chamber/ion chromatography technique [Scheuer et al., 2003], with 100 second sample integration. Ozone (O₃) was measured by chemiluminescence at 1 second resolution by (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 (N₂O) was measured at 1 second resolution by differential absorption spectrometry [Collins et al., 1993]. We focus on interrelationships between HNO₃, O₃, and N₂O relative to N₂O between 9 and 12.5 km in the lowermost Arctic stratosphere. The HNO₃ – N₂O – O₃ relationships are examined for evidence of descent of PSC-processed air (depleted in O₃ and HNO₃ relative to N₂O) down to DC-8 flight levels, as well as renitrification from evaporation of NAT crystals that settled and evaporated.
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

Mixing ratios of HNO₃ and O₃ were tightly correlated when O₃ was greater than 100 ppb but less than about 450 ppb (Figure 2). Enhanced HNO₃ at low O₃ 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 HNO₃ per ppb of O₃, which is similar to the average value of the HNO₃/O₃ ratio in all samples shown in Figure 2 (3.5 ± 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 HNO₃/O₃ 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 NOₓ/O₃ to be consistently in the range 2.5–4.0 ppt/ppb in the extratropical lower stratosphere. Redistribution of HNO₃ by evaporation of nitric acid trihydrate (NAT) that had sedimented from higher altitudes was suggested as the dominant cause of enhanced HNO₃/O₃ 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 HNO₃/O₃ is similar to all previous reports of HNO₃/O₃ and NOₓ/O₃ 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 HNO₃/O₃ ratio of 3.5 ppt/ppb.

Time series of O₃ and HNO₃ on PAVE flight 6 (29 January) are scaled so that when HNO₃/O₃ = 3.5 ppt/ppb the points fall on top of each other (Figure 3). In the strato-

![Figure 1. Flight tracks for PAVE flights 5–10 from Portsmouth, NH.](image)

![Figure 2. Scatter plot of HNO₃ vs O₃, color coded by potential temperature. The slope of a linear regression suggests a stratospheric HNO₃/O₃ ratio of 3.7 ppt/ppb.](image)

![Figure 3. (top and bottom) Time series of O₃ (grey), HNO₃ (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 HNO₃/O₃ equals 3.5 ppt/ppb the points fall on top of each other.](image)
enhancements of HNO$_3$ and O$_3$, and especially HNO$_3$/O$_3$, the DC-8 was able to fly about a km higher. Sustained depletions are largest on the southbound legs of flights 5 and 6 when deformation at higher altitude (prior to descent), or sedimentation and subsequent re-evaporation of NAT in PSCs, redistributing HNO$_3$ to lower altitudes.

4. Discussion and Tracer Relationships

[9] In the stratosphere, N$_2$O 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$_2$O in the lower stratosphere. Departures from trends of O$_3$/N$_2$O, HNO$_3$/N$_2$O and NO$_y$/N$_2$O 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$_2$O was linear and very compact (Figure 4). Scattered around the trend decreased as N$_2$O mixing ratios decreased and O$_3$ increased deeper into the stratosphere. The linear regression slope (21.4 ppb O$_3$/ppb N$_2$O) 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$_2$O relationship shows more scatter, particularly at N$_2$O 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 × N$_2$O) (mixing ratios in ppb). Neuman et al. [2001] reported a shallower slope (0.049 ppb HNO$_3$/ppb N$_2$O) in the lower stratosphere on a flight over the central US; this is the only published example relating HNO$_3$ and N$_2$O we are aware of. However, NO$_y$/N$_2$O 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$_2$O 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$_y$/N$_2$O 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 O3 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 HNO3 at DC-8 flight levels are consistent with MLS and lidar observations of denitrification and PSC’s during the PAVE mission. Relationships between HNO3, O3 and N2O show that HNO3 was permanently redistributed from higher in the stratosphere, while O3 loss was not observed. Enhancements of HNO3 in the lowermost stratosphere were largely restricted to the region below the vortex edge, where descent was significant throughout the winter, O3 and HNO3 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 HNO3.

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