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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$_3$), ozone (O$_3$), and nitrous oxide (N$_2$O) were made from the NASA DC-8 during 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$_3$/O$_3$ averaged 3.5 (±0.7) ppt/ppb. Samples with enhanced HNO$_3$/O$_3$ (>4.0) were most abundant under the edge of the Arctic Polar vortex in airmasses with enhanced mixing ratios of both gases (>400 ppb O$_3$ and >2000 ppt HNO$_3$) and reduced mixing ratios of N$_2$O (<305 ppb), indicating air from higher levels in the stratosphere. Relationships to N$_2$O in the anomalous samples under the vortex edge indicate that increases in HNO$_3$/O$_3$ reflect renitrification at DC-8 flight levels, with no indication of significant O$_3$ 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.


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., 2006]. 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$_2$O and HNO$_3$ 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$_3$ from the altitude regions of PSC formation [e.g., Fahey et al., 2001].

[4] We present in situ observations of O$_3$, HNO$_3$, and N$_2$O between 9 and 12.5 km in the lowermost Arctic stratosphere. The HNO$_3$ – N$_2$O – O$_3$ relationships are examined for evidence of descent of PSC-processed air (depleted in O$_3$ and HNO$_3$ relative to N$_2$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$_3$) was measured with the mist chamber/ion chromatography technique [Scheuer et al., 2003], with 100 second sample integration. Ozone (O$_3$) 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$_2$O) was measured at 1 second resolution by differential absorption spectrometry [Collins et al., 1993]. We focus on interrelationships between HNO$_3$, O$_3$, and N$_2$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...
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 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.

[8] 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.

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.

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.
enhancements of HNO₃ and O₃, and especially HNO₃/O₃, the DC-8 was able to fly about a km higher. Sustained are largest on the southbound legs of flights 5 and 6 when depletion at higher altitude (prior to descent), or sedimentation and subsequent re-evaporation of NAT in PSCs, redistributing HNO₃ to lower altitudes.

4. Discussion and Tracer Relationships

[9] In the stratosphere, N₂O decreases with time since injection from the troposphere. In contrast, mixing ratios of O₃ and HNO₃ increase with altitude above the tropopause, so they have tight inverse correlations with N₂O in the lower stratosphere. Departures from trends of O₃/N₂O, HNO₃/N₂O and NOₓ/N₂O in the unperturbed lower stratosphere have provided evidence for O₃ 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 O₃ and N₂O was linear and very compact (Figure 4). Scatter around the trend decreased as N₂O mixing ratios decreased and O₃ increased deeper into the stratosphere. The linear regression slope (21.4 ppb O₃/ppb N₂O) 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 O₃ 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 HNO₃ – N₂O relationship shows more scatter, particularly at N₂O mixing ratios below 305 ppb (Figure 4). Most points above the trend are the samples with high values of HNO₃/O₃ 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 HNO₃/O₃ > 4.0) yields the relationship HNO₃ = 20.6 – (0.063 × N₂O) (mixing ratios in ppb). Neuman et al. [2001] reported a shallower slope (0.049 ppb HNO₃/ppb N₂O) in the lower stratosphere on a flight over the central US; this is the only published example relating HNO₃ and N₂O we are aware of. However, NOₓ/N₂O 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 NOₓ/N₂O 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 HNO₃ via evaporation of NAT that had fallen from higher altitudes. At higher altitudes in the lower extratropical stratosphere (up to 20 km), the NOₓ/N₂O 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 HNO₃/O₃ beneath the vortex edge are due to elevated HNO₃ mixing ratios, with no evidence for O₃ 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 HNO₃ 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
dehdration event during this period (Jimenez et al., sub-
mitted 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
renitrfication 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
HNO₃ was permanently redistributed from higher in the
stratosphere, while O₃ loss was not observed. Enhance-
ments of HNO₃ in the lowermost stratosphere were largely
restricted to the region below the vortex edge, where
descent was strongest 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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