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Photochemistry in the arctic free troposphere: NO\textsubscript{x} budget and the role of odd nitrogen reservoir recycling

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Abstract

The budget of nitrogen oxides (NO\textsubscript{x}) in the arctic free troposphere is calculated with a constrained photochemical box model using aircraft observations from the Tropospheric O\textsubscript{3} Production about the Spring Equinox (TOPSE) campaign between February and May. Peroxyacetic nitric anhydride (PAN) was observed to be the dominant odd nitrogen species (NO\textsubscript{y}) in the arctic free troposphere and showed a pronounced seasonal increase in mixing ratio. When constrained to observed acetaldehyde (CH\textsubscript{3}CHO) mixing ratios, the box model calculates unrealistically large net NO\textsubscript{x} losses due to PAN formation (62 pptv/day for May, 1–3 km). Thus, given our current understanding of atmospheric chemistry, these results cast doubt on the robustness of the CH\textsubscript{3}CHO observations during TOPSE. When CH\textsubscript{3}CHO was calculated to steady state in the box model, the net NO\textsubscript{x} loss to PAN was of comparable magnitude to the net NO\textsubscript{x} loss to HNO\textsubscript{3} (NO\textsubscript{2} reaction with OH) for spring conditions. During the winter, net NO\textsubscript{x} loss due to N\textsubscript{2}O\textsubscript{5} hydrolysis dominates other NO\textsubscript{x} loss processes and is near saturation with respect to further increases in aerosol surface area concentration. NO\textsubscript{x} loss due to N\textsubscript{2}O\textsubscript{5} hydrolysis is sensitive to latitude and month due to changes in diurnal photolysis (sharp day–night transitions in winter to continuous sun in spring for the arctic). Near NO\textsubscript{x} sources, HNO\textsubscript{4} is a net sink for NO\textsubscript{x}; however, for more aged air masses HNO\textsubscript{4} is a net source for NO\textsubscript{x}, largely countering the NO\textsubscript{x} loss to PAN, N\textsubscript{2}O\textsubscript{3} and HNO\textsubscript{3}. Overall, HNO\textsubscript{4} chemistry impacts the timing of NO\textsubscript{x} decay and O\textsubscript{3} production; however, the cumulative impact on O\textsubscript{3} and NO\textsubscript{x} mixing ratios after a 20-day trajectory is minimal.

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1. Introduction

Nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2} + NO\textsubscript{3}) play a critical role in the oxidizing capacity of the troposphere through their impact on the production, loss and partitioning of radical species (OH, HO\textsubscript{2} and RO\textsubscript{2}) (Levy II, 1972; Crutzen, 1974, 1979). Furthermore, NO\textsubscript{x} not only affects the concentration and partitioning of radical species, but also directly participates in the reactions leading to the production and distribution of ozone (O\textsubscript{3}), i.e. reactions of peroxy radicals with nitric oxide (Chameides and Walker, 1973). Sources of NO\textsubscript{x} in the free troposphere include convective transport from surface sources, lightning, stratospheric injection, aircraft emissions and recycling reactions from reactive odd nitrogen reservoir species such as nitric acid (HNO\textsubscript{3}) and
peroxycetic nitric anhydride (PAN) (Roberts, 1990; Jacob et al., 1996; Levy II et al., 1999). A 3-D modeling study by Moxim et al. (1996) showed that the magnitude and seasonal cycle of the global tropospheric integral of NOy are barely affected by the inclusion of PAN chemistry; the global emissions of NOy balance formation of HNO3. However, as pointed out by Moxim et al. reservoir species such as PAN can regionally provide an efficient mechanism for redistributing the NOy far from source regions, and thus can perturb regional O3 photochemistry. As an illustration, Moxim et al. estimate that PAN decomposition can increase the monthly mean NOx mixing ratios in the remote lower troposphere over the North Atlantic and North Pacific by a factor of 5.

Direct measurements of total reactive odd nitrogen (NOy) and its suspected dominant components (NO2, HNO3, PAN) show good agreement at most continental sites at ppbv levels, i.e. components comprise greater than 90% of observed NOy (Parrish et al., 1993; Sandholm et al., 1994). At remote locations, NOx measurements and the NOy sum have disagreed by 30–50% (Ridley, 1991; Atlas et al., 1992; Crosley, 1996; Kondo et al., 1997); however, the recent SONEX study in the North Atlantic upper troposphere showed that the sum of the speciated NOy could account for greater than 90% of measured NOy (Talbot et al., 1999). Modeled peroxynitric acid (HNO4) accounted for the majority of the remaining NOy speciation.

In this study, we quantify the NOy budget in the arctic free troposphere during the Tropospheric O3 Production about the Spring Equinox (TOPSE) 2000 campaign using a chemical box model constrained by aircraft observations. The major goal of TOPSE was to study the late winter-to-spring transition in arctic photochemistry in order to assess the importance of the springtime increase in tropospheric photochemical O3 production with regard to the observed springtime maximum in high-latitude tropospheric O3. In this remote environment, it is expected that convection, lightning and aircraft sources of NOx are minimal so that recycling reactions from reservoir species dominate the NOy production and loss. Observations of the partitioning of the NOy species in the arctic free troposphere are sparse. Knowing the distribution of NOy and how recycling reactions redistribute NOy in the arctic free troposphere indicates whether the arctic free troposphere simply transports NOy, as PAN or whether the arctic free troposphere is a region of permanent removal of odd nitrogen from the global atmosphere as HNO3. If a large fraction of the NOy accumulates as PAN in the arctic free troposphere, then subsequent episodic transport of these air masses to mid-latitudes along subsiding trajectories would provide large sources of NOy which could shift the O3 budget to net O3 production in impacted regions (Beine et al., 1997; Hamlin and Honrath, 2002). Here, we also explore the importance of other reactive odd nitrogen species, such as N2O5 and HNO4 which rapidly inter-convert with NOy on intermediate time scales (on the order of a day), and thus impact how efficiently NOy is converted to either PAN or HNO3 in arctic air masses.

2. Model description

2.1. Data sorting

The TOPSE campaign was composed of a series of seven round-trip deployments between 4 February 2002 and 23 May 2002 with missions generally sampling the mid-to-high latitude troposphere over North America in the corridor originating in Colorado, traversing over Manitoba and Hudson Bay before ending north of Greenland and returning back to Colorado. A C-130 aircraft was used to probe the composition of the troposphere between 0 and 8 km. We based our analysis on a merged time series of the aircraft observations where the measurements were averaged over a common time interval of 1 min. We sorted the observations based on latitude (40–50°N, 50–58°N, 58–85°N), altitude (0–1, 1–3, 3–6, 6–8 km) and month (2 February deployments, 2 March deployments, 2 April deployments, 1 May deployment) and derived statistics (mean, 1σ standard deviation about the mean, median) for sorted cases. Tables 1 and 2 list statistics for many of the critical chemical species over the springtime transition in the arctic (58–85°N), separated for the 1–3 and 3–6 km altitude layers. Descriptions of the analytical measurement techniques and references can be found in a TOPSE overview paper (Atlas et al., 2003). Canister-GC/MS measurements of CH3CHO were performed, but mixing ratios are considered preliminary (D. Blake, personal communication) because canister sampling for CH3CHO has not been validated (factor of two uncertainty). Interestingly, prior informal comparisons between canister and airborne in situ CH3CHO measurements during PEM-Tropics-B (Singh et al., 2001) and Trace-P showed significant point-by-point variability, but overall reasonable agreement for median values.

2.2. Model approach

Our general approach in quantifying the NOy budget was to calculate 24-h average NOy production and loss rates for odd nitrogen recycling reactions for different months and altitudes by using a photochemical box model constrained by the measured medians listed in Tables 1 and 2. The photochemical box model was run for repetitive diurnal solar cycles to diel steady state with photolysis frequencies (j values) calculated using...
Table 1
Statistics generated from sorted aircraft data in the arctic mid-troposphere (58–85°N, 3–6 km)

| Parameter          | February | March | April       | May        |
|--------------------|----------|-------|-------------|------------|
| Latitude (°)       | 65 ± 5   | 64    | 71 ± 8      | 71 ± 8     |
| Altitude (km)      | 5.1 ± 0.8| 5.5   | 5.0 ± 0.9   | 5.0 ± 0.8  |
| Temperature (K)     | 237 ± 8  | 236   | 239 ± 8     | 238 ± 7    |
| Water vapor (g/kg)  | 0.23 ± 0.33| 0.08  | 0.29 ± 0.37 | 0.15       |
| j(O¹D) (s⁻¹)       | 9 ± 7 × 10⁻⁷| 7 × 10⁻⁷| 3 ± 1 × 10⁻⁶| 3 × 10⁻⁶    |
| Surface Albedo      | 0.82 ± 0.08 | 0.84 | 0.87 ± 0.03 | 0.87       |
| Cloud Factor       | 0.93 ± 0.19 | 0.98 | 0.97 ± 0.16 | 1.01       |
| O₃ (ppbv)          | 20 ± 16  | 18    | 25 ± 22     | 21         |
| NO₂ (pptv)         | 117 ± 37 | 111   | 199 ± 96    | 177        |
| HNO₃ (pptv)        | 39 ± 24  | 34    | 58 ± 70     | 32         |
| RONO₂ (pptv)       | 2.4 ± 2.2| 2.4   | 28.7 ± 6    | 24         |
| NO (pptv)          | 283 ± 89 | 279   | 352 ± 150   | 326        |
| NO₂ Deficit (pptv) | 60 ± 53  | 73    | 1.5 ± 54    | 37         |
| CH₄ (ppmv)         | 1.8 ± 0.01 | 1.81 | 1.83 ± 0.02 | 1.83       |
| CH₃O (ppmv)        | 100 ± 88 | 90    | 91 ± 92     | 73         |
| H₂O₂ (ppmv)        | 82 ± 81  | 58    | 115 ± 77    | 105        |
| CH₃OOH (pptv)      | 113 ± 113| 72    | 184 ± 121   | 157        |
| CO (ppmv)          | 145 ± 11 | 146   | 154 ± 12    | 151        |
| C₆H₆ (ppmv)        | 589 ± 159| 543   | 626 ± 255   | 607        |
| CH₃CHO (pptv)      | 112 ± 42 | 104   | 140¹       | 165 ± 101  |
| CH₃C(OH)₂ (pptv)   | 381 ± 98 | 382   | 550²       | 692 ± 218  |

¹ RONO₂ included methyl, ethyl, 1-propyl, 2-propyl, and 2-butyl nitrate.
² Only coincident data considered. Mean RONO₂/NOₓ ratio applied to NOₓ observations to expand RONO₂ database.
³ A highly uncertain value due to lack of data.

The TUV module was initialized for the various cases with measured median values for latitude, Julian day, altitude, O₃ column and albedo. Cloud correction factors were calculated by comparing the TUV clear-sky results run on individual aircraft points and individual j value measurements. Median values of the sorted cloud correction factors were then applied to all j values calculated by TUV within the photochemical box model. The median j(NO₂) and j(O¹D) cloud correction factor ranged between 0.82–1.06 and 0.92–1.00, respectively, for the arctic free troposphere sampled during TOPSE. The TUV module was updated with cross section and quantum yields from recent evaluations for inorganic species (DeMore, 1997, 2000) and organic species (Atkinson, 1997b; Atkinson et al., 2000). The photodissociation of HNO₃ in the near-IR was incorporated into TUV based on the recent measurements of Roehl et al. (2002). The clear sky photodissociation rate for HNO₃ is on the order of 10⁻⁵ s⁻¹ at 240 K, largely invariant with changes in solar zenith angle.

NCAR’s master mechanism was used as the chemical scheme within the model (Madronich and Calvert, 1990). The inorganic chemistry has undergone updates since then with the most recent recommendations taken from (DeMore, 1997, 2000). The hydrocarbon chemistry in the master mechanism is treated explicitly and includes the photo-oxidation of partly oxygenated organic species. Alkanes up to C₆, alkenes up to C₃ and aromatics up to C₅ were observed in the arctic free troposphere and were considered as initial hydrocarbon reagents in the gas-phase mechanism. The chemistry of the methyl peroxy radical is treated explicitly; a counter scheme is used for the other organic peroxy radicals (Madronich and Calvert, 1990). The rate coefficients for organic peroxy radical reactions were updated based on recent recommendations (Tyndall et al., 2001; Mereau et al., 2000). Alkox radical reactions were also updated based on the latest DeMore et al. recommendation (for CH₃O) and the specific studies in Atkinson (1997a) and Mereau et al. for the larger alkoxy radicals. Rate coefficients for hydrocarbons reactions with OH were updated based on the latest JPL compilations (DeMore, 1997, 2000) and the Atkinson (1994) review. The OH-initiated ethene oxidation mechanism was modified to include multiple branching for the β-hydroxy ethoxy radical reaction with NO (Orlando et al., 1998). OH-initiated rate coefficients for oxygenated hydrocarbons were updated from the Atkinson (1994) compilation.
Table 2
Statistics generated from sorted aircraft data in the arctic lower free troposphere (58–85°N, 1–3 km)

| Parameter | February | March | April | May |
|-----------|----------|-------|-------|-----|
|           | Mean ± std. | Median | Mean ± std. | Median | Mean ± std. | Median | Mean ± std. | Median |
| Latitude (°) | 67 ± 7 | 65 | 70 ± 9 | 74 | 68 ± 8 | 68 | 69 ± 9 | 72 |
| Altitude (km) | 2.0 ± 0.6 | 2.1 | 2.1 ± 0.6 | 2.2 | 2.1 ± 0.6 | 2.1 | 1.9 ± 0.5 | 1.8 |
| Temperature (K) | 252 ± 7 | 249 | 255 ± 8 | 253 | 258 ± 7 | 256 | 264 ± 5 | 266 |
| Water vapor (g/kg) | 0.68 ± 0.81 | 0.43 | 1.0 ± 1.1 | 0.57 | 0.89 ± 0.79 | 0.70 | 1.0 ± 0.6 | 0.93 |
| j(O1D) (s) | 4.2 ± 4 × 10⁻⁷ | 3 ± 10⁻⁷ | 3 ± 3 × 10⁻⁶ | 2 × 10⁻⁶ | 6 ± 5 × 10⁻⁶ | 6 × 10⁻⁶ | 1 ± 1 × 10⁻⁵ | 1 × 10⁻⁵ |
| Surface Albedo | 0.82 ± 0.08 | 0.84 | 0.87 ± 0.03 | 0.87 | 0.86 ± 0.06 | 0.86 | 0.78 ± 0.10 | 0.79 |
| Cloud Factor | 0.94 ± 0.16 | 0.98 | 0.96 ± 0.15 | 1.01 | 0.97 ± 0.14 | 1.00 | 0.96 ± 0.16 | 1.01 |
| O₃ (pptv) | 46 ± 4 | 45 | 53 ± 5 | 53 | 55 ± 6 | 54 | 56 ± 12 | 57 |
| NO₂ (pptv) | 11 ± 15 | 7 | 25 ± 30 | 15 | 18 ± 17 | 13 | 28 ± 17 | 27 |
| PAN (pptv) | 158 ± 135 | 117 | 210 ± 106 | 197 | 199 ± 83 | 170 | 195 ± 98 | 172 |
| HNO₃ (pptv) | 69 ± 230 | 34 | 65 ± 61 | 39 | 81 ± 80 | 52 | 103 ± 52 | 96 |
| RONO₂ (pptv) | 31 ± 7.8 | 27 | 31 ± 5.3 | 28 | 21 ± 2.9 | 21 | 11 ± 0.9 | 11 |
| NO Deficit (pptv) | 34 ± 50 | 35 | 30 ± 59 | 11 | −39 ± 52 | −32 | −56 ± 55 | −66 |
| NO₃ (pptv) | 301 ± 168 | 255 | 342 ± 161 | 310 | 309 ± 137 | 272 | 294 ± 142 | 265 |
| CH₄ (ppmv) | 1.84 ± 0.02 | 1.84 | 1.84 ± 0.01 | 1.84 | 1.84 ± 0.01 | 1.84 | 1.84 ± 0.01 | 1.83 |
| CH₃O (pptv) | 143 ± 160 | 106 | 160 ± 193 | 91 | 121 ± 150 | 48 | 93 ± 71 | 84 |
| H₂O₂ (pptv) | 45 ± 58 | 12c | 152 ± 118 | 124 | 261 ± 151 | 235 | 340 ± 209 | 314 |
| CH₂O (pptv) | 94 ± 108 | 70 | 145 ± 78 | 140 | 187 ± 103 | 168 | 253 ± 115 | 251 |
| CO (ppbv) | 164 ± 19 | 161 | 156 ± 11 | 153 | 156 ± 5 | 156 | 144 ± 8 | 144 |
| C₂H₆ (pptv) | 920 ± 248 | 909 | 806 ± 176 | 780 | 448 ± 162 | 464 | 175 ± 43 | 166 |
| CH₃CHO (pptv) | 122 ± 43 | 107 | 153 ± 69 | 138 | 155 ± 61 | 140 | 218 ± 140 | 205 |
| CH₃CO(O)CH₃ (pptv) | 426 ± 164 | 385 | 543 ± 203 | 502 | 621 ± 170 | 582 | 772 ± 140 | 732 |

*aRONO₂ included methyl, ethyl, 1-propyl, 2-propyl, and 2-butyl nitrate.

*bOnly coincident data considered. Mean RONO₂/NO₃ ratio applied to NO₃ observations to expand RONO₂ database.

*cHalf the estimated detection limit.

The kinetics of the HO₂ self-reaction were recently measured (Christensen et al., 2002) to be lower than the current recommendation. As discussed by Stroud et al. (2003), the impact of these new data on HO₂, H₂O₂, and CH₂O mixing ratios was not significant for TOPSE conditions.

3. Results and discussion

3.1. Lifetime considerations for odd nitrogen species in the arctic free troposphere

In the remote troposphere, NO₃ is observed to be a small fraction of the total oxidized nitrogen budget due to the rapid processing of NO₃ to its reservoir species during transport from NO₂ sources. Fig. 1 illustrates the seasonal changes in lifetimes for odd nitrogen species in the arctic middle troposphere (3–6 km). Actual median latitudes and altitudes used in the TUV calculations are shown in Tables 1 and 2. NO₂ has a lifetime less than a week in the arctic free troposphere. The increase in photochemical activity between February and May results in the NO₂ lifetime decreasing from 6 to 2 days. In contrast, PAN and HNO₃ are more stable species with lifetimes on the order of a month (May) to a year (February). PAN photolysis dominates PAN thermal decomposition in the arctic middle troposphere, while OH oxidation and photolysis contribute comparably to
HNO₃ loss. Median temperatures in the arctic mid-
troposphere showed little change between winter and 
spring (from 237 to 243 K); as a result, PAN thermal 
decomposition changes were small. HNO₄ and N₂O₅ 
have shorter lifetimes, comparable in magnitude to 
NOₓ. HNO₃ thermal decomposition and IR photolysis 
are the important loss mechanisms for HNO₃ in the 
arctic free troposphere. Our calculations result in IR 
photodissociation contributing 20% and 37% to the 
total HNO₃ loss in February and May, respectively. 
Hydrolysis is the most important loss process for N₂O₅ 
throughout the winter to spring transition. N₂O₅ 
photolysis makes a smaller but important contribu-
tion in the winter (sensitive to February median 
latitude). Similarly, N₂O₅ thermal decomposition makes 
an important contribution in the spring (sensitive to 
May median temperature). The steady-state assumption 
should be a reasonable approximation for HNO₄ and 
N₂O₅ considering both have relatively short lifetimes 
given the remote location of the observations. 

However, PAN and HNO₃ mixing ratios are likely 
impacted by chemistry as well as transport.

### 3.2. Observed seasonal trends in individual NOₓ species 
mixing ratios

Fig. 2 presents the observed seasonal dependence to 
the partitioning of the NOₓ budget in the lower (1–3 km, 
panel a) and middle (3–6 km, panel b) free troposphere. 
Mean mixing ratios with measurement uncertainties 
are shown for months between February and May with all 
the observations north of 58°N. Table 3 lists how the 
measurement uncertainties were estimated for each of 
the odd nitrogen species (columns 1 and 2). The mean 
NOₓ mixing ratios show a weak seasonal increase from 
February to May in both altitude ranges (from 11 to 
28 pptv for 1–3 km; from 20 to 30 pptv for 3–6 km). 
Surface measurements at Zeppelin mountain, Svalbard 
(78°N, 11°E, 474 m asl) generally ranged between 10 
and 40 pptv with no apparent seasonal trend between 
February and May (Beine et al., 1996). Surface 
measurements by Beine et al. (1997) at Poker Flat, 
Alaska showed a weak NOₓ trend with daytime NOₓ 
medians increasing from 5 to 15 pptv between March 
and May. These other surface observations are similar in 
magnitude and trend to the TOPSE observations. Thus, 
the TOPSE observations reinforce our understanding of 
the temporal NOₓ distribution near the surface while 
enhancing our understanding of the vertical and spatial 
NOₓ distribution.

The mixing ratios of the reservoir species, PAN and 
HNO₃, show a strong upward seasonal trend, with PAN 
showing the largest increase from a mean value of 
117 pptv in February to 319 pptv in May for the 3–6 km 
layer. HNO₃ increased from 39 to 76 pptv over this time 
period while PPN showed no significant seasonal trend

| Species | Measurement uncertainty | Mixing ratios for median NOₓ deficit point (in pptv) | Uncertainty (in pptv) |
|---------|-------------------------|--------------------------------------------------|----------------------|
| NO      | 2 pptv +5% (1 min)      | 5                                                | 2                    |
| NO₂     | 4 pptv +5% (1 min)      | 9                                                | 5                    |
| PANs    | 15%                     | 125                                              | 19                   |
| HNO₃    | 15%                     | 66                                               | 9.9                  |
| RONO₂   | 20%                     | 17                                               | 3.4                  |
| NO₃     | 5 pptv +10% (1 min)     | 286                                              | 34                   |
| NOₓ Deficit | 64a                   |                                                   | 41b                  |

*C* Calculated from the median of [NOₓ]–[NOₓ]–[PANs]–
[HNO₃]–[RONO₂] coincident points.

*b* Calculated from the sum of uncertainties in column added 
in quadrature.
with mean mixing ratios between 32 and 35 pptv in the 3–6 km layer. The pronounced seasonal increase in PAN and HNO$_3$ in Fig. 2 is an indication of the springtime growth in photochemical activity. The observed increase in PAN mixing ratios is consistent with the weak seasonal increase in observed CH$_3$CHO and NO$_x$ mixing ratios, the strong seasonal trend in observed OH and the persistence of cold temperatures (long PAN thermal decomposition lifetime). Changes in transport also play a role as supported by the concurrent increase in NO$_x$. Similar trends were seen for PAN and HNO$_3$ in the lower free troposphere (panel 2b) with the exception of the decrease in PAN between April and May. This is likely a reflection of the significant warming trend (median $T = 256–266$ K) between April and May in the 1–3 km layer.

3.3. In situ NO$_x$ cycling in the arctic free troposphere

3.3.1. Introduction

Numerous studies have examined the role of NO$_x$ reservoir species in NO$_x$ recycling in remote environments (Schultz et al., 2000; Jacob et al., 1996; Kotchenruther et al., 2001; Hamlin and Honrath, 2002). The importance of HNO$_3$ and PAN as a sink/source for NO$_x$ has been observed to vary with season and location. For example, during SUCCESS in the upper troposphere over the US, HNO$_3$ was the dominant NO$_x$ species and the principal sink for NO$_x$ (Jaegle et al., 2000). Similarly, over the North Atlantic during SONEX, HNO$_3$ composed the largest fraction of NO$_x$ (median ratio of 0.35) in the upper troposphere (Talbot et al., 1999). In urban areas, PAN is a net sink for NO$_x$ (Roberts et al., 2002); however, in remote areas PAN has been calculated to be a net source for NO$_x$. For example, Schultz et al. (1999) showed that the NO$_x$ responsible for O$_3$ production within the South Pacific below 4 km can largely be explained by the decomposition of PAN transported into the region from biomass burning plumes at higher altitudes. Kotchenruther et al. (2001) showed that PAN decomposition contributed significantly to NO$_x$ mixing ratios in the eastern Pacific troposphere off the coast of the US, especially for subsiding air masses originating from Asia. Hamlin and Honrath (2002) also showed that springtime NO$_x$ in air masses transported from the arctic to the North Atlantic can largely be attributed to PAN decomposition along the subsiding trajectories. The common feature among these studies is the enhanced levels of PAN in the upper troposphere (from biomass burning convection, from Asian outflow convection and arctic wintertime accumulation) followed by decomposition and release of NO$_x$ along subsiding trajectories.

From our modeling analysis, we address the in situ partitioning of NO$_x$ to its oxidized products in the arctic free troposphere. Tables 4 and 5 present the 24-h Table 4

| Reactions considered | February | March | April | May |
|----------------------|----------|-------|-------|-----|
| OH + NO$_2$ → HNO$_3$ |          |       |       |     |
| HNO$_3$ + OH → H$_2$O + NO$_3$ | −0.5 | −1.2 | −0.8 | −4.4 |
| HNO$_3$ + hv → OH + NO$_2$ |          |       |       |     |
| CH$_3$CO$_3$ + NO$_2$ → PAN | −3.4$^a$ | −8.6$^a$ | −9.3$^a$ | −31$^a$ |
| PAN + M → CH$_3$CO$_3$ + NO$_2$ | −0.5$^b$ | −1.1$^b$ | −1.0$^b$ | −3.8$^b$ |
| PAN + hv → CH$_3$CO$_3$ + NO$_2$ |          |       |       |     |
| NO$_2$ + NO$_2$ → N$_2$O$_5$ |          |       |       |     |
| N$_2$O$_5$ + M → NO$_2$ + NO$_3$ | −2.9 | −2.0 | −0.9 | −0.05 |
| N$_2$O$_5$ + hv → NO$_2$ + NO$_3$ |          |       |       |     |

A negative value indicates net NO$_x$ loss (pptv/day). Species constrained at measured medians. Calculated from the 5th day of a constrained box model simulation (fixed NO$_x$, HNO$_3$ and PAN at measured medians). Model run at observed monthly median latitudes of 64°N, 71°N, 72°N, and 73°N.

$^a$Model was constrained by estimated median CH$_3$CHO measurement.

$^b$Model calculated CH$_3$CHO to steady state.

Table 5

| Reactions considered | February | March | April | May |
|----------------------|----------|-------|-------|-----|
| OH + NO$_2$ → HNO$_3$ |          |       |       |     |
| HNO$_3$ + OH → H$_2$O + NO$_3$ | −0.1 | −0.8 | −1.1 | −7.0 |
| HNO$_3$ + hv → OH + NO$_2$ |          |       |       |     |
| CH$_3$CO$_3$ + NO$_2$ → PAN | −2.5$^a$ | −7.4$^a$ | −14$^a$ | −62$^a$ |
| PAN + M → CH$_3$CO$_3$ + NO$_2$ | −0.4$^b$ | −0.7$^b$ | −1.2$^b$ | −2.2$^b$ |
| PAN + hv → CH$_3$CO$_3$ + NO$_2$ |          |       |       |     |
| NO$_2$ + NO$_2$ → N$_2$O$_5$ |          |       |       |     |
| N$_2$O$_5$ + M → NO$_2$ + NO$_3$ | −1.8 | −4.5 | −2.1 | −0.1 |
| N$_2$O$_5$ + hv → NO$_2$ + NO$_3$ |          |       |       |     |

A negative value indicates net NO$_x$ loss (pptv/day). Species constrained at measured medians. Calculated from the 5th day of a constrained box model simulation (fixed NO$_x$, HNO$_3$ and PAN at measured medians). Model run at observed monthly median latitudes of 65°N, 74°N, 65°N, and 72°N.

$^a$Model was constrained by estimated median CH$_3$CHO measurement.

$^b$Model calculated CH$_3$CHO to steady state.

The average NO$_x$ budget in the arctic free troposphere due to localized reservoir recycling in the 3–6 and 1–3 km layers. Net NO$_x$ fluxes were calculated from constrained box model simulations run to steady state where NO$_x$,
PAN and HNO₃ were fixed at measured medians. In these simulations, hydrocarbons, CH₄, CO, O₃, H₂O, CH₂O, H₂O₂ and CH₃OOH were also constrained at their measured medians. Two simulations were performed for Tables 4 and 5, with CH₃CHO either fixed at its measured median or calculated. Two simulations were necessary due to significant model-measurement differences for CH₃CHO. The following section summarizes the model results with CH₃CHO constrained, while the remainder of the paper relies on CH₃CHO calculated from the model photochemistry.

3.3.2. In situ NOₓ cycling with acetaldehyde constrained

Modeled steady-state CH₃CHO in the arctic free troposphere underestimated observations by an order of magnitude for all months during the campaign. For example, in May, modeled steady-state CH₃CHO underestimated observations by a factor of 20 (measured 160 pptv vs. model 8 pptv). Tables 4 and 5 illustrate that constraining CH₃CHO in the model results in a net NOₓ loss to PAN dominating other NOₓ chemical losses for all months and altitude ranges. However, a closer inspection of the net NOₓ loss to PAN suggests the magnitudes are unrealistically large. For example, in May, net NOₓ loss rates are calculated as large as −31 and −62 pptv/day for 3–6 and 1–3 km, respectively. Given that NOₓ median mixing ratios in May are 27 and 30 pptv for the 3–6 and 1–3 km, the NOₓ loss rates would imply significant regional sources of NOₓ in the arctic free troposphere. While some localized NOₓ sources are possible, at times, due to lightning or aircraft emissions, it does not seem feasible that for median conditions, over wide regions of the arctic free troposphere, there are NOₓ sources of this magnitude. Similarly, these net PAN production rates imply that in a relatively short time period, air masses in the arctic may have significantly more PAN than observed. For example, a 5-day simulation using constrained CH₃CHO resulted in an enhancement of modeled PAN by 67% from its initial median measured mixing ratio (323–539 pptv).

Several arguments may be postulated to explain these model-measurement differences for CH₃CHO: (1) widespread surface emissions (Domine and Shepson, 2002) and efficient transport into the arctic free troposphere, (2) incomplete distribution of measured hydrocarbons and an initialization of reactive hydrocarbons at observed values instead of some representative concentration along the arrival trajectory, (3) incomplete understanding of model organic oxidation pathways, (4) CH₃CHO artifact formation during sampling procedures or other instrumental errors. However, upon further inspection, several of these postulates should be discarded. In May, the CH₃CHO lifetime due to photolysis and OH reaction is only 0.9 day. Despite the potential for a surface source of CH₃CHO, this lifetime is significantly shorter than the timescale for mixing into the arctic free troposphere. Thus, mixing from surface sources should be discarded as an explanation for over an order magnitude model underestimation. Domine and Shepson (2002) also report an [HCHO]/[CH₃CHO] ratio of 2.5. However, the TOPSE observations show CH₃CHO mixing ratios consistently being larger than HCHO for all months and altitude ranges considered here. For example, a median [HCHO]/[CH₃CHO] ratio of 0.34 was observed for May conditions in the 3–6 km range. This behavior of CH₃CHO mixing ratios greater than HCHO mixing ratios does seem unusual given that typically lower molecular weight species are observed at higher mixing ratios than higher molecular weight analogs (CH₄ > C₂H₆, CH₃OH > C₃H₇OH). Given a lifetime for CH₃CHO of less than a day in May, the steady-state assumption for CH₃CHO should be a reasonable approximation. A simulation was performed to calculate the equivalent ethane-mixing ratio necessary to sustain CH₃CHO at 160 pptv for May conditions. An unrealistically large ethane-mixing ratio (40 ppbv) was necessary to photochemically sustain CH₃CHO at 160 pptv for May conditions. Cumulatively, these arguments shed uncertainty to the measurements of CH₃CHO during TOPSE. Interestingly, applying the ratio of [HCHO]/[CH₃CHO] observed by Domaine and Shepson to the HCHO observations yields CH₃CHO mixing ratio estimates (22 pptv for May, 3–6 km) closer to the model steady-state CH₃CHO mixing ratios (8 pptv for May, 3–6 km). Given these arguments, CH₃CHO was calculated to steady state in the model for the remainder of the NOₓ budget results reported here.

3.3.3. In situ NOₓ cycling with acetaldehyde calculated

Tables 4 and 5 presents the net NOₓ fluxes due to PAN, HNO₃ and N₂O₅ in situ chemistry with CH₃CHO integrated to steady state and the odd nitrogen species constrained to their median measured mixing ratios. Since no direct measurement of HNO₃ was made during TOPSE, it is not possible to perform similar constrained calculations for HNO₃. Later, in Section 3.5, the role played by HNO₃ chemistry is highlighted with a series of time-dependent simulations.

HNO₃ is a net sink for NOₓ throughout the arctic free troposphere between February and May. In the 3–6 km layer, the net NOₓ sink due to HNO₃ formation varied from −0.5 to −4.4 pptv/day, increasing in magnitude in spring. Similarly, in the 1–3 km layer, the net NOₓ sink due to HNO₃ formation varied from −0.1 to −7.0 pptv/day. Net NOₓ loss rates to PAN show remarkable similarity to net NOₓ loss rates to HNO₃ throughout the winter to spring transition in the 3–6 km range (Tables 4 and 5). Between 1 and 3 km, net NOₓ loss to PAN is significantly larger than the net NOₓ loss to HNO₃ for February conditions. For March and April, similar net
NO₃ loss rates were calculated for both PAN and HNO₃. By May conditions, net NO₃ loss to HNO₃ dominates over loss to PAN for 1–3 km. This difference in seasonal trend between 1–3 and 3–6 km is likely a reflection of the difference in the seasonal temperature dependence for the two altitude ranges. For 1–3 km, significant warming occurred by May conditions (266 K) resulting in a shorter thermal decomposition lifetime for PAN (10 days) which, in part, explains the smaller net NO₃ loss rates to PAN compared to HNO₃. Seasonal changes in the [NO₂]/[NO] ratio also shorten the effective lifetime of PAN for springtime conditions.

N₂O₅ is expected to have a lifetime less than 1 day in the arctic free troposphere. At warmer temperatures (>245 K), thermal decomposition is the favored loss mechanism, while at cooler temperatures hydrolysis is expected to dominate. N₂O₅ is a net sink for NO₂ in the arctic free troposphere during the campaign; however, it behaves conversely to HNO₃ by decreasing in importance as a NO₂ sink over the course of the winter–spring transition. N₂O₅ hydrolysis was included in the chemical mechanism as a heterogeneous reaction. Its rate depends critically on aerosol surface area and (mostly light). Since our calculation of modeled NO₃ mixing ratios and, thus, slower N₂O₅ loss rates to PAN compared to HNO₃. Seasonal changes in the [NO₂]/[NO] ratio also shorten the effective lifetime of PAN for springtime conditions.

3.4. NO₃ deficit and its seasonal dependence

Another intriguing observation from Fig. 2 is a seasonal dependence to the NO₃ balance (defined here as (NO₃)–(PAN)–(PPN)–(HNO₃)–(RONO₂)–(NO₂)), which is a small deficit for February and systematically decreases to near balance in May for the 3–6 km layer and a small surplus in May for the 1–3 km layer. Limits for the mean NO₃ balance in Fig. 2 are measurement uncertainties added in quadrature. Since NO₃ is composed largely of PAN, then it should be noted that uncertainties in the NO₃ balance stem largely from the uncertainties in the NO₂ and PAN measurements. The NO₃ budget is in near balance for all months with the exception of February (3–6 km) where the NO₃ balance is significantly larger than zero when considering the combined measurement uncertainty (mean 60 ± 42 pptv). This is a positive result suggesting we can account for a large fraction (generally greater than 90%) of the observed NO₃. This is similar agreement to the NO₃ balance observed for the recent SONEX campaign (Talbot et al., 1999).

Table 3 lists the median NO₃ balance for February conditions. These observations support missing NO₂ species in the range 20–100 pptv for February conditions (3–6 km). A linear fit of mean NO₃ deficit vs. mean day of year for the data in Fig. 2, weighted by the inverse of the squared measurement uncertainties, yields slopes of −0.88 ± 0.85 pptv/day (3–6 km) and −1.00 ± 0.73 pptv/day (1–3 km).

Thus, the observations do support a marginal seasonal trend from a small deficit to small surplus. Fig. 3 also illustrates how the NO₃ deficit varies as a function of temperature, j(Ô¹D) and sulfate aerosol concentration for all the data in the arctic free troposphere between 3 and 6 km. A weak negative dependence is observed for temperature, j(Ô¹D), and sulfate aerosol concentration, although there is large atmospheric variability. One potentially important odd nitrogen species not considered in the NO₃ deficit calculations above is HNO₄. In the next section, the seasonal dependence for our modeled steady-state HNO₄ mixing
ratio is calculated and compared to the seasonal trend in the observed NO<sub>y</sub> balance.

3.5. Modeled HNO<sub>4</sub> chemistry

3.5.1. Lifetime considerations and steady-state HNO<sub>4</sub> mixing ratios

To calculate a steady-state HNO<sub>4</sub> and determine whether the steady-state assumption is reasonable, we performed four different time-dependent NO<sub>x</sub> simulations where NO<sub>x</sub> was initialized so that it decayed to its median measured mixing ratio in exactly 1–4 days (Figs. 4a and b, 3–6 km). In these simulations, HNO<sub>4</sub> mixing ratios were initialized at zero and hydrocarbons, CH<sub>4</sub>, CO, H<sub>2</sub>O, and O<sub>3</sub> were constrained at their median measured mixing ratios. CH<sub>3</sub>CHO was initialized at its predetermined steady-state value and calculated during the simulation. In Fig. 4, the time axis is plotted such that model time = 0 corresponds to the point where model NO<sub>x</sub> decayed to its median measured value. By comparing the HNO<sub>4</sub> at t = 0, we can estimate how long an air mass has to remain under these environmental conditions (i.e. temperature) for HNO<sub>4</sub> to reach steady state. For February conditions, the time for HNO<sub>4</sub> to reach steady-state is 3 days with a corresponding (HNO<sub>4</sub>)<sub>ss</sub> = 40 pptv (panel a and b). This relatively short induction time suggests that away from immediate NO<sub>x</sub> sources (e.g. aircraft exhaust, fresh convection) HNO<sub>4</sub> will be in steady state with NO<sub>x</sub>. The calculated steady-state methyl peroxy nitrate (CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>) mixing ratio was 5 pptv, suggesting the organic homologues play a minor role in the NO<sub>y</sub> budget compared to HNO<sub>4</sub>.

Fig. 3. The dependence of the observed NO<sub>y</sub> deficit (defined as NO<sub>y</sub>-PANs-HNO<sub>3</sub>-NO<sub>x</sub>) on temperature (panel a), O<sub>3</sub> photolysis frequency, j(O<sub>1</sub>D) (panel b), and fine aerosol sulfate (panel c) for the 3–6 km layer and between 58° N and 85° N.
Other modeled NO\textsubscript{y} species (HONO, N\textsubscript{2}O\textsubscript{5} and NO\textsubscript{3}) were also at negligible concentrations compared to NO\textsubscript{y}; although it should be noted that the odd nitrogen flux through these species can be significant under cold, low light conditions. For the 1–3 km layer in the arctic, steady-state model HNO\textsubscript{4} was 0.5 pptv throughout the campaign.

An interesting paradox occurs when we compare the predicted steady-state HNO\textsubscript{4} mixing ratios with the median NO\textsubscript{y} balance for May. For the median NO\textsubscript{y} mixing ratio of 30 pptv (May, 3–6 km, 58–85° N) and \( T = 243 \) K, the model calculates a steady-state HNO\textsubscript{4} mixing ratio of 60 pptv. The steady-state assumption is surely valid for May conditions, as the induction time to reach steady state is less than a day. However, in comparing to the observed NO\textsubscript{y} remainder in May (3–6 km), there is no room in the budget for a 60 pptv missing species. Furthermore, the increase in HNO\textsubscript{4} from 40 to 60 pptv is opposite to the seasonal trend in the NO\textsubscript{y} balance. This suggests that there may be other unknown loss processes for HNO\textsubscript{4} in the spring. Recent laboratory studies show that HNO\textsubscript{4} can initiate the oxidation of S(IV) in aqueous particles (Amels et al., 1996; Warneck, 1999). HNO\textsubscript{4} is also known to react with HNO\textsubscript{2} (Logager and Sehested, 1993) and halide ions (Regimbal and Mozurkewich, 1997) in solution.

Murphy et al. (2002) discuss the temperature dependence of their indirect measurement of \([\text{HNO}_4] + [\text{RO}_2\text{NO}_2]\) during TOPSE. In their analysis, \([\text{HNO}_4] + [\text{RO}_2\text{NO}_2]\) is inferred as the difference between the measured sum of the peroxynitrates and the measured PANs, where they measured the sum of the peroxynitrates using a thermal dissociation laser-induced fluorescence technique. An even larger temperature dependence was observed for their inferred \([\text{HNO}_4] + [\text{RO}_2\text{NO}_2]\) mixing ratios with estimates of \(~100\) pptv at \( T < 240 \) K. These results clearly support the need for direct measurements of HNO\textsubscript{4} of sufficient precision and accuracy along with heterogeneous chemical modeling studies to shed further light on this apparent paradox in the NO\textsubscript{y} balance.

### 3.5.2. HNO\textsubscript{4} and its impact on the NO\textsubscript{x} lifetime

Since our modeling calculations and the measurements of Murphy suggest that HNO\textsubscript{4} can be a significant fraction of NO\textsubscript{y} in winter and there is some marginal evidence for an NO\textsubscript{y} deficit in winter, it is useful to study the role played by HNO\textsubscript{4} in the NO\textsubscript{x} budget in the arctic wintertime. Fig. 4c compares NO\textsubscript{x} decays for two simulations with and without HNO\textsubscript{4} chemistry. The solid curve is identical to the solid blue curve shown in Fig. 4a for the model simulation with a 3-day induction time and HNO\textsubscript{4} chemistry included. The dashed line in Fig. 4c is the corresponding NO\textsubscript{x} decay for a simulation with identical initial NO\textsubscript{x}, however no HNO\textsubscript{4} chemistry. The importance of HNO\textsubscript{4} to modeled NO\textsubscript{x} mixing ratios depends on the age of the NO\textsubscript{x} in the air mass. For ‘fresh’ air masses, NO\textsubscript{x} decays more quickly with the HNO\textsubscript{4} chemistry included due to the initial formation of HNO\textsubscript{4}. However, for more ‘aged’ air masses, the HNO\textsubscript{4} reservoir acts as a buffer replenishing NO\textsubscript{x}. The cross-over point where the addition of HNO\textsubscript{4} chemistry enhances NO\textsubscript{x} mixing ratios over the case with no HNO\textsubscript{4} chemistry occurs between 5 and 6 days and is largely independent of initial NO\textsubscript{x} mixing ratios. It is very likely that typical air masses sampled in the arctic free troposphere have NO\textsubscript{x} ages longer than 5–6 days and thus the presence of the HNO\textsubscript{4} reservoir can act as a source for NO\textsubscript{x} in the arctic. Here we considered a constant temperature history for the modeled air mass at the observed median temperature (February, 3–6 km). Given that thermal decomposition is the dominant loss process for HNO\textsubscript{4}, the cross-over point will be a strong function of the temperature history of an air mass.

To further quantify the role played by HNO\textsubscript{4} in the NO\textsubscript{x} budget, we calculated diurnally averaged net NO\textsubscript{x}
loss/production rates from a time-dependent NO\textsubscript{x} simulation for February in the arctic mid-troposphere (February simulation the same as in Fig. 4; analogous simulation for May also performed). If we look at the diurnally averaged net NO\textsubscript{x} rates for the first 24h of these simulations we find significant net NO\textsubscript{x} loss rates to HNO\textsubscript{4} (\(-28\) and \(-69\) pptv/day for February and May) compared to the other odd nitrogen reservoirs (Table 6). Conversely, if we arbitrarily look at the model simulations for a more ‘aged’ air mass, after 4 days, we find that HNO\textsubscript{4} is a net source for NO\textsubscript{x} (\(+3.4\) and \(+5.4\) pptv/day for February and May) largely countering the net NO\textsubscript{x} losses to N\textsubscript{2}O\textsubscript{5}, PAN and HNO\textsubscript{3}. These results yield a consistent picture with Tables 4 and 5 for N\textsubscript{2}O\textsubscript{5}, PAN and HNO\textsubscript{3} and now show the additional role played by HNO\textsubscript{4}. For ‘fresh’ air masses, HNO\textsubscript{4} is a net sink for NO\textsubscript{x}. For more ‘aged’ air masses, HNO\textsubscript{4} is a net source for NO\textsubscript{x}, largely countering the NO\textsubscript{x} losses to N\textsubscript{2}O\textsubscript{3} in the winter and PAN and HNO\textsubscript{3} in the spring.

3.5.3. HNO\textsubscript{4} and its impact on O\textsubscript{3} production

The time evolution of modeled O\textsubscript{3} mixing ratios for the two scenarios discussed in the prior section (with and without HNO\textsubscript{4} chemistry) was also considered. The goal of these simulations was to evaluate the importance of HNO\textsubscript{4} chemistry on the amount of O\textsubscript{3} produced along a trajectory from a source region for NO\textsubscript{x}. The initial production of HNO\textsubscript{4} near NO\textsubscript{x} sources clearly slows the rate of O\textsubscript{3} production (after 5 days O\textsubscript{3} difference was 0.7 ppbv for February conditions). For more ‘aged’ air masses, the buffering impact of HNO\textsubscript{4} begins to narrow the difference between the two O\textsubscript{3} traces, however even after 20 days the modeled O\textsubscript{3} from the simulation with HNO\textsubscript{4} chemistry included still has slightly smaller O\textsubscript{3} mixing ratios (difference of 0.4 ppbv). Qualitatively, similar results were obtained for a simulation in May with maximum differences in O\textsubscript{3} of 2.3 ppbv after 5 days and 0.9 ppbv after 20 days. Thus, these simulations suggest that HNO\textsubscript{4} chemistry impacts the timing of O\textsubscript{3} production; however, the cumulative impact on O\textsubscript{3} mixing ratios after a 20-day trajectory is minimal.

4. Conclusions

In this paper, we evaluated the in situ recycling reactions for NO\textsubscript{x} in the arctic free troposphere using a constrained box model. In the winter, N\textsubscript{2}O\textsubscript{3} hydrolysis is the largest net sink for NO\textsubscript{x} (\(-2.9\) pptv/day in February); however, it reduces to negligible importance in spring due to the seasonal increase in the rate of NO\textsubscript{3} photolysis. NO\textsubscript{x} loss through N\textsubscript{2}O\textsubscript{3} is limited by the rate of the NO\textsubscript{2} + O\textsubscript{3} reaction for conditions in the winter-time arctic free troposphere. HNO\textsubscript{3} and PAN are also permanent net sinks for NO\textsubscript{x} in the arctic free troposphere during TOPSE. Modeled CH\textsubscript{3}CHO mixing ratios are an order of magnitude smaller than observations. Given our current understanding of atmospheric chemistry, constraining the model with observed CH\textsubscript{3}CHO yields unrealistic estimates for net NO\textsubscript{x} loss rates to PAN. Median observed CH\textsubscript{3}CHO mixing ratios...
were also larger than observed HCHO mixing ratios for arctic free troposphere cases; a rather unusual behavior. Thus, until the CH$_3$CHO canister measurements are fully characterized in the laboratory and formally inter-compared in the field, the TOPSE CH$_3$CHO observations are considered preliminary and suspect. Using simulations where CH$_3$CHO reached steady state, the net NO$_x$ loss to PAN was calculated to be of comparable magnitude to net NO$_x$ loss to HNO$_3$, with net PAN formation being larger in the wintertime lower free troposphere and net HNO$_3$ formation being larger in the springtime lower free troposphere. Overall, NO$_x$ loss due to N$_2$O$_5$ hydrolysis dominates in winter, whereas NO$_x$ loss due to PAN and HNO$_3$ formation dominates in the spring. These conclusions derived from an observationally constrained box model with explicit chemical study will be useful in future validation of NO$_x$ loss processes in 3D chemical-transport models.

The role of HNO$_4$ chemistry in impacting arctic free troposphere NO$_x$ mixing ratios depends on the age of the air mass. Near NO$_x$ sources, HNO$_4$ is a net sink for NO$_x$; however, HNO$_4$ decomposition and IR photolysis can be net sources of NO$_x$ for more ‘aged’ arctic air masses. Model simulations suggest the cross-over point to NO$_x$ enhancement due to the buffering impact of HNO$_4$ occurs after 5–6 days (dependent on temperature history of air mass). Given that the age of NO$_x$ in typical arctic free troposphere air samples is likely older than 5–6 days, HNO$_4$ chemistry tends to enhance remote NO$_x$ mixing ratios. These conclusions may change as our understanding of the HNO$_4$ heterogeneous chemistry improves in the future. While the presence of HNO$_4$ chemistry may locally enhance O$_3$ production rates for ‘aged’ air masses, the impact of HNO$_4$ over the entire air parcel trajectory is a slight decrease in O$_3$ mixing ratio.

The NO$_x$ budget is in near balance for all months with the exception of February (3–6 km) where a mean deficit of 60±42 pptv is observed. Thus, it is possible for the observed NO$_x$ deficit to support the modeled HNO$_4$ mixing ratio of 40 pptv in February (3–6 km). It is intriguing that the marginal seasonal trend in the NO$_x$ balance from small deficit to small surplus is not consistent with the seasonal trend in our modeled HNO$_4$ mixing ratios. The modeled HNO$_4$ of 60 pptv in May (3–6 km) is only supported if we consider the upper limits for the combined measurement uncertainties, −18±75 pptv. Thus, it is speculated that unknown HNO$_4$ chemistry may be important in the arctic springtime. Future measurements of HNO$_4$ in combination with modeling studies that incorporate heterogeneous laboratory studies are clearly warranted.

Finally, these observations and modeling results illustrate how NO$_x$ can accumulate as the PAN reservoir during the spring months in the northern free troposphere. As a result, air masses leaving the high latitude arctic free troposphere and following anti-cyclonic, descending trajectories will have high rates of PAN thermal decomposition, which can enhance O$_3$ production rates at impacted mid-latitude surface locations.

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