Photochemistry in the Arctic Free Troposphere: Ozone Budget and Its Dependence on Nitrogen Oxides and the Production Rate of Free Radicals

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Abstract. Local ozone production and loss rates for the arctic free troposphere (58–85° N, 1–6 km, February–May) during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) campaign were calculated using a constrained photochemical box model. Estimates were made to assess the importance of local photochemical ozone production relative to transport in accounting for the springtime maximum in arctic free tropospheric ozone. Ozone production and loss rates from our diel steady-state box model constrained by median observations were first compared to two point box models, one run to instantaneous steady-state and the other run to diel steady-state. A consistent picture of local ozone photochemistry was derived by all three box models suggesting that differences between the approaches were not critical. Our model-derived ozone production rates increased by a factor of 28 in the 1–3 km layer and a factor of 7 in the 3–6 km layer between February and May. The arctic ozone budget required net import of ozone into the arctic free troposphere throughout the campaign; however, the transport term exceeded the photochemical production only in the lower free troposphere (1–3 km) between February and March. Gross ozone production rates were calculated to increase linearly with NO\textsubscript{x} mixing ratios up to ~300 pptv in February and for NO\textsubscript{x} mixing ratios up to ~500 pptv in May. These NO\textsubscript{x} limits are an order of magnitude higher than median NO\textsubscript{x} levels observed, illustrating the strong dependence of gross ozone production rates on NO\textsubscript{x} mixing ratios for the majority of the observations. The threshold NO\textsubscript{x} mixing ratio needed for net positive ozone production was also calculated to increase from NO\textsubscript{x} ~ 10 pptv in February to ~25 pptv in May, suggesting that the NO\textsubscript{x} levels needed to sustain net ozone production are lower in winter than spring. This lower NO\textsubscript{x} threshold explains how wintertime photochemical ozone production can impact the build-up of ozone over winter and early spring. There is also an altitude dependence as the threshold NO\textsubscript{x} needed to produce net ozone shifts to higher values at lower altitudes. This partly
explains the calculation of net ozone destruction for the 1–3 km layer and net ozone production for the 3–6 km layer throughout the campaign.

**Key words:** global atmospheric chemistry, TOPSE, arctic photochemistry, ozone production, peroxide, radical chain length.

### 1. Introduction

The seasonal cycle of ozone (O₃) in the free troposphere has been an area of continued interest in atmospheric chemistry over the past several decades (Logan, 1985; Levy et al., 1985; Muller and Brasseur, 1995; Yienger, 1999; Reeves et al., 2002). Measurements from surface stations and ozonesondes in the remote northern hemisphere have shown a distinct springtime maximum in tropospheric O₃ (Otlmans et al., 1996; Monks et al., 2000). Junge (1962) suggested that the mixing ratio of tropospheric O₃ is determined by transport of O₃ from the stratosphere and destruction at the ground. This theory was questioned by Chameides and Walker (1973) and Crutzen (1974) and it is now generally believed that photochemical production in the troposphere and transport from the stratosphere both have important roles in shaping the tropospheric distribution of O₃ (Levy et al., 1985; Follows and Austin, 1992; Jacob et al., 1996; Roelofs and Lelieveld, 1995; Mauzerall et al., 1996; Levy et al., 1997; Tanimoto et al., 2002). O₃ photochemistry in the troposphere is highly sensitive to the mixing ratios of O₃ precursor gases (such as nitrogen oxides NOₓ = NO + NO₂, H₂O, CO and hydrocarbons) whose distributions are highly variable in space and time. The 2000 Tropospheric Ozone Production about the Spring Equinox (TOPSE) aircraft campaign took place over the North American continent at mid-to-high latitudes, characterizing the distribution of O₃ and O₃ precursor gases during the winter-to-spring transition (Atlas et al., 2002). A major goal of TOPSE was to assess our understanding of the tropospheric O₃ budget, and in particular to quantify the *in situ* O₃ production rates.

Constrained photochemical box models have been used successfully to understand how local photochemistry responds to environmental conditions and the concentrations of longer-lived species. For example, Chameides et al. (1987) presented sensitivity studies to show how O₃ production would change if mixing ratios of H₂O, CO, NO and O₃ were doubled. Models can also give estimates of the mixing ratios of species that react quickly and thus should be in steady-state with their environment. If measurements of the precursor gases and the reactive species are made, then model-measurement comparisons of the reactive species provide a test of our understanding of fast photochemistry (Ridley et al., 1992; Crawford et al., 1999; Frost et al., 1999; Zanis et al., 1999; Jaegle et al., 2000). Models can also give estimates of species that are difficult to measure. For example, Levy (1971) used a steady-state photochemical model to estimate the concentrations of intermediate radical species (OH, HO₂), which have only recently been measured...
quantitatively in the atmosphere (Eisele et al., 1997; Brune et al., 1995; Cantrell et al., 2000; Kanaya et al., 2001).

Here, we first evaluate the detailed photochemistry in a box model by making model-measurement comparisons for radical and non-radical intermediates. We address the assumption of steady-state and the applicability of steady-state model-measurement comparisons for peroxide intermediates, H$_2$O$_2$ and CH$_3$OOH. We then calculate the seasonal dependence of in situ gross O$_3$ production and loss rates during TOPSE using our photochemical box model constrained by median observations and compare our model results with two other box modeling approaches (Cantrell et al., 2003; Wang et al., 2003). We focus our analysis on air masses sampled in the arctic free troposphere (58–85° N, 1–6 km) during the winter to spring transition (February–May). We also look at the dependence of the gross O$_3$ production (P$_{O_3}$) and the in situ chemical cycling (radical chain length) on total radical production rates (P$_{RO_2}$) and NO$_x$ mixing ratios. We conclude by giving our assessment of the importance of the local tropospheric photochemical O$_3$ production to the seasonal trends in O$_3$ observed in the arctic free troposphere.

2. Methodology

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. The National Center for Atmospheric Research C-130 aircraft was used to probe the chemical composition of the troposphere between 0–8 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 minute. We sorted the observations based on latitude (40–50, 50–58, 58–85° N), altitude (0–1, 1–3, 3–6, 6–8 km) and month (February, March, April, May) and derived statistics (mean, 1σ standard deviation about the mean, median) for sorted cases. We assume that sampled air masses are representative of the region and month of the flights. Tables I and II list the mean ±1σ standard deviation and the median for many of the critical chemical species over the springtime transition in the arctic (58–85° N), separated for the 1–3 km 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., 2002).

2.2. MODEL APPROACH

Our major objective in this paper is to present the chemical budget for O$_x$ ([O$_x$] = [O] + [O$_3$] + [NO$_2$]) during the springtime transition in the arctic free troposphere. Our general approach was to calculate 24-hr average O$_x$ production and loss rates
Table I. Statistics generated from sorted aircraft data in the arctic mid-troposphere (58–85° N, 3–6 km)

| Parameter                  | February Mean ± Std | Median | March Mean ± Std | Median | April Mean ± Std | Median | May Mean ± Std | Median |
|----------------------------|---------------------|--------|------------------|--------|------------------|--------|----------------|--------|
| Latitude (°)               | 65 ± 5              | 64     | 71 ± 8           | 71     | 71 ± 8           | 71     | 71 ± 7         | 73     |
| Altitude (km)              | 5.1 ± 0.8           | 5.5    | 5.0 ± 0.9        | 5.4    | 5.0 ± 0.8        | 5.1    | 4.8 ± 0.9      | 5.2    |
| Temperature (K)            | 237 ± 8             | 236    | 239 ± 8          | 238    | 238 ± 7          | 237    | 246 ± 8        | 243    |
| Water vapor (g/kg)         | 0.23 ± 0.33         | 0.08   | 0.29 ± 0.37      | 0.15   | 0.22 ± 0.24      | 0.14   | 0.32 ± 0.47    | 0.19   |
| \( J_{\text{O}_3D} \) (sec\(^{-1}\)) | \( 9 \times 10^{-7} \) | \( 7 \times 10^{-7} \) | \( 3 \times 10^{-6} \) | \( 3 \times 10^{-6} \) | \( 6 \times 10^{-6} \) | \( 6 \times 10^{-6} \) | \( 1.3 \times 10^{-5} \) | \( 1.2 \times 10^{-5} \) |
| Surface albedo             | 0.82 ± 0.08         | 0.84   | 0.87 ± 0.03      | 0.87   | 0.84 ± 0.06      | 0.85   | 0.77 ± 0.09    | 0.78   |
| Cloud factor               | 0.93 ± 0.19         | 0.98   | 0.97 ± 0.16      | 1.01   | 0.96 ± 0.07      | 0.97   | 0.95 ± 0.07    | 0.95   |
| O\(_3\) (ppbv)             | 55 ± 7              | 54     | 63 ± 13          | 60     | 67 ± 10          | 65     | 75 ± 11        | 78     |
| NO\(_2\) (ppbv)            | 20 ± 16             | 18     | 25 ± 22          | 21     | 17 ± 13          | 15     | 30 ± 13        | 30     |
| PAN (ppbv)                 | 117 ± 37            | 111    | 199 ± 96         | 177    | 263 ± 195        | 222    | 319 ± 86       | 323    |
| HNO\(_3\) (pptv)           | 39 ± 24             | 34     | 58 ± 70          | 32     | 51 ± 57          | 37     | 76 ± 42        | 68     |
| NO\(_3\) (pptv)            | 283 ± 89            | 279    | 352 ± 150        | 326    | 385 ± 234        | 332    | 436 ± 112      | 446    |
| CH\(_4\) (ppmv)            | 1.81 ± 0.01         | 1.81   | 1.83 ± 0.02      | 1.83   | 1.83 ± 0.01      | 1.86   | 1.83 ± 0.01    | 1.82   |
| CH\(_2\)O (pptv)           | 100 ± 88            | 90     | 91 ± 92          | 73     | 47 ± 82          | 41     | 64 ± 68        | 55     |
| H\(_2\)O\(_2\) (pptv)      | 82 ± 81             | 58     | 115 ± 77         | 105    | 165 ± 67         | 168    | 180 ± 74       | 174    |
| CH\(_3\)OOH (pptv)         | 113 ± 113           | 72     | 184 ± 121        | 157    | 126 ± 66         | 120    | 130 ± 64       | 125    |
| CO (ppbv)                  | 145 ± 11            | 146    | 154 ± 12         | 151    | 154 ± 9          | 154    | 145 ± 10       | 147    |
| C\(_2\)H\(_6\) (pptv)      | 589 ± 156           | 543    | 626 ± 255        | 607    | 398 ± 121        | 397    | 186 ± 43       | 179    |
| CH\(_3\)CHO (pptv)         | 112 ± 42            | 104    | 140 \(^a\)       | 165    | 101              | 141    | 183 ± 97       | 160    |
| CH\(_3\)C\(_2\)OCH\(_3\) (pptv) | 381 ± 98           | 382    | 550 \(^a\)       | 692    | 218              | 674    | 860 ± 214      | 839    |

\(^a\) Estimate due to lack of data.
### Table II. Statistics generated from sorted aircraft data in the arctic lower free troposphere (58–85° N, 1–3 km)

| Parameter            | February Mean ± Std | March Mean ± Std | April Mean ± Std | May Mean ± Std | Median       |
|----------------------|---------------------|------------------|------------------|----------------|--------------|
| Latitude (°)         | 67 ± 7              | 70 ± 9           | 68 ± 8           | 69 ± 9         | 72           |
| Altitude (km)        | 2.0 ± 0.6           | 2.1 ± 0.6        | 2.1 ± 0.6        | 2.1 ± 0.5      | 1.8          |
| Temperature (K)      | 252 ± 7             | 255 ± 8          | 258 ± 7          | 264 ± 5        | 266          |
| Water vapor (g/kg)   | 0.68 ± 0.81         | 1.0 ± 1.1        | 0.89 ± 0.79      | 1.0 ± 0.6      | 0.93         |
| $\text{H}_2\text{O}_2$ (sec$^{-1}$) | 4 ± 4 × 10$^{-7}$ | 3 ± 3 × 10$^{-6}$ | 6 ± 5 × 10$^{-6}$ | 1 ± 1 × 10$^{-5}$ | 1 × 10$^{-5}$ |
| Surface albedo       | 0.82 ± 0.08         | 0.87 ± 0.15      | 0.97 ± 0.14      | 0.96 ± 0.16    | 1.01         |
| Cloud factor         | 0.94 ± 0.16         | 0.96 ± 0.15      | 0.55 ± 0.6       | 0.56 ± 12      | 57           |
| $\text{O}_3$ (ppbv)  | 46 ± 4              | 53 ± 5           | 54 ± 5           | 56 ± 12        | 57           |
| $\text{NO}_2$ (ppbv) | 11 ± 15             | 25 ± 30          | 18 ± 17          | 28 ± 17        | 27           |
| PAN (ppbv)           | 158 ± 135           | 210 ± 106        | 199 ± 83         | 195 ± 98       | 172          |
| HNO$_3$ (ppbv)       | 69 ± 230            | 65 ± 61          | 81 ± 80          | 103 ± 52       | 96           |
| $\text{NO}_y$ (ppbv) | 301 ± 168           | 342 ± 161        | 309 ± 137        | 294 ± 142      | 265          |
| $\text{CH}_4$ (ppmv) | 1.84 ± 0.02         | 1.84 ± 0.01      | 1.84 ± 0.01      | 1.83 ± 0.01    | 1.83         |
| $\text{CH}_2\text{O}$ (ppbv) | 143 ± 160      | 166 ± 193        | 121 ± 150        | 93 ± 71        | 84           |
| $\text{H}_2\text{O}_2$ (ppbv) | 45 ± 58              | 152 ± 118        | 261 ± 151        | 340 ± 209      | 314          |
| $\text{CH}_2\text{OH}$ (ppbv) | 94 ± 108            | 145 ± 78         | 187 ± 103        | 253 ± 15       | 251          |
| CO (ppbv)            | 164 ± 19            | 156 ± 11         | 156 ± 5          | 144 ± 8        | 144          |
| $\text{C}_2\text{H}_6$ (ppbv) | 920 ± 248           | 806 ± 176        | 448 ± 162        | 175 ± 43       | 166          |
| $\text{CH}_3\text{CHO}$ (ppbv) | 122 ± 43            | 153 ± 69         | 155 ± 61         | 218 ± 140      | 205          |
| $\text{CH}_3\text{C(O)}\text{CH}_3$ (ppbv) | 426 ± 164          | 543 ± 203        | 621 ± 170        | 772 ± 140      | 732          |

*Half the estimated detection limit.*
for different months and altitudes by using the photochemical box model constrained by the measured medians listed in Tables I and II. A median value could not be calculated for several reactive hydrocarbons due to instrument detection limits and a value of half the detection limit was used as a model constraint (e.g., n-octane had a detection limit of 3 pptv and was above detection limit for 5% of the samples). The photochemical box model was run over repetitive diurnal solar cycles to diel steady-state with photolysis frequencies \( (j) \) values calculated using the Tropospheric Ultraviolet Visible (TUV) radiative transfer code (Version 4; Madronich and Flocke, 1998). The TUV module was initialized with measured median values for latitude, Julian day, altitude, O\(_3\) column and albedo. A standard aerosol vertical distribution was assumed to prescribe aerosol optical depths (Elterman, 1968). Cloud correction factors were calculated by comparing the TUV clear-sky modeled results run on individual aircraft points and individual \( j \) value measurements. Median values of the sorted cloud correction factors were then applied to all the \( j \) values calculated by TUV within the photochemical box model. The median \( j(\text{NO}_2) \) and \( j(\text{O}_1\text{D}) \) 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 et al., 1997; Sander et al., 2000) and organic species (Atkinson, 1997b; Atkinson et al., 2000).

NCAR’s master mechanism was used as the chemical scheme within the model (Madronich and Calvert, 1990). The inorganic chemistry has undergone updates since the original publication with the most recent recommendations taken from Demore et al. (1997); Sander et al. (2000). Hydrocarbon chemistry in the master mechanism is treated explicitly and includes the photo-oxidation of partly oxygenated organic species. Alkanes up to C\(_8\), alkenes up to C\(_3\) and aromatics up to C\(_8\) 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 the recommendations in Tyndall et al. (2001) and Mereau et al. (2000). Alkoxy radical reactions were also updated based on the latest Demore et al. recommendation (for CH\(_3\)O) and the specific studies in Atkinson (1997) and Mereau et al. (2000) for the larger alkoxy radicals. OH initiation rate coefficients for hydrocarbons were updated based on the latest JPL compilations (Demore et al. 1997; Sander et al. 2000) and the Atkinson (1994) review. The OH-initiated ethene oxidation mechanism was modified to include multiple branching for the \( \beta \)-hydroxy ethoxy radical reaction with NO (Orlando et al., 1998). OH-initiated rate coefficients for oxygenated hydrocarbons were updated from the Atkinson (1994) compilation.

The kinetics of the HO\(_2\) self-reaction were recently measured by Christensen et al. (2002). The self-reaction proceeds via a complex potential energy surface and
displays pressure-dependent behavior. Demore et al. (1997) recommend separating the overall rate coefficient into two terms:

\[ k_1 = k_0 + k'[M], \]  

where \( k_0 \) and \( k' \) are the bimolecular and termolecular components. Christensen et al. (2002) recommend, \( k_0 = 1.5 \times 10^{-12} \exp(19/T) \), compared to the Demore et al. recommendation, \( k_0 = 2.3 \times 10^{-13} \exp(600/T) \). As a result, the HO\(_2\) self-reaction is considerably slower at the extreme cold temperatures found in the upper troposphere and stratosphere. Our photochemical box model results for arctic mid-troposphere (3–6 km) median conditions between February and May were compared. We found the impact of the new kinetic recommendation on HO\(_2\), H\(_2\)O\(_2\) and CH\(_3\)OOH mixing ratios was not significant for TOPSE conditions. At most, steady-state HO\(_2\) was higher by 7%, H\(_2\)O\(_2\) lower by 18% and CH\(_3\)OOH higher by 4% with the new recommendations.

Simulations were run for a time of 5 days, chosen in this study to allow sufficient initiation time for radical species to approach steady-state, but not so long as to allow several non-radical species in the model to reach unrealistic mixing ratios (e.g. H\(_2\)O\(_2\), HNO\(_3\)). 5 days also represents a reasonable estimate for the amount of time an air mass sampled in the arctic free troposphere would experience uniform conditions. For model-measurement comparisons of intermediate species (H\(_2\)O\(_2\), CH\(_3\)OOH and CH\(_2\)O), the species of interest was calculated while the other measured intermediates were constrained at their median values. For example O\(_3\), H\(_2\)O, CO, NO\(_x\), PANs, HNO\(_3\), VOCs, CH\(_3\)OOH, CH\(_2\)O and CH\(_3\)CHO were held fixed at their median measured values during H\(_2\)O\(_2\) time-varying simulations. Intermediate species mixing ratios after the 5-day simulations were then used for comparison with observations (Table III).

Several time-dependent NO\(_x\) simulations were also performed to assess how quickly the mixing ratio of intermediate species (H\(_2\)O\(_2\) and CH\(_3\)OOH) responded to model decays in NO\(_x\) (Figures 2 and 3). In these simulations, NO\(_x\) was calculated along with CH\(_2\)O, H\(_2\)O\(_2\), CH\(_3\)OOH while other longer-lived species were constrained (O\(_3\), CO, H\(_2\)O, VOCs, PANs, HNO\(_3\)). The goal of these simulations was to assess whether these intermediate species maintain steady-state for conditions in the arctic free troposphere.

24-hr average O\(_3\) production and loss rates were calculated from the model output at diel steady-state (Figures 5 and 6). The model was defined to be at diel steady-state when radical species were repeating their diurnal cycles within 5%. All measured species were initialized in the model at their median values. NO\(_x\) was also held constant at its median measured value during these simulations, while NO and NO\(_2\) were calculated. The mixing ratio of measured intermediate species (CH\(_2\)O, CH\(_3\)CHO, H\(_2\)O\(_2\), CH\(_3\)OOH, PAN, PPN, HNO\(_3\)) were also constrained at their observed medians. Measured CH\(_3\)CHO mixing ratios were highly uncertain, mainly due to issues involved in sampling oxygenated hydrocarbons. As a result, measured CH\(_3\)CHO mixing ratios should be considered as estimates (D. Blake,
Table III. Model results for intermediate species after the 5th day for a series of constrained simulations

| 58–85° N  | 5th day mixing ratios | February (pptv) | March (pptv) | April (pptv) | May (pptv) |
|-----------|-----------------------|------------------|--------------|--------------|-------------|
| 3–6 km    | CH$_2$O               | 29               | 49 SS        | 39 SS        | 64 SS       |
|           | H$_2$O$_2$            | 128              | 238          | 309          | 445         |
|           | CH$_3$OOH             | 66               | 109 SS       | 104 SS       | 119 SS      |
| 1–3 km    | CH$_2$O               | 33               | 49 SS        | 52 SS        | 111 SS      |
|           | H$_2$O$_2$            | 99               | 248          | 611          | 895         |
|           | CH$_3$OOH             | 87               | 140 SS       | 207 SS       | 268 SS      |

Simulations constrained at median measured NO$_x$, O$_3$, CO, H$_2$O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO$_3$, CH$_2$O, CH$_3$OOH, H$_2$O$_2$. The species of interest for a simulation (CH$_2$O, H$_2$O$_2$ or CH$_3$OOH) were calculated for that simulation. SS indicates the species reached steady-state.

personal communication). However, in comparing the observed free tropospheric CH$_3$CHO mixing ratios in Tables I and II with other \textit{in situ} measurements (Singh, 2001), we find similar ranges, generally between 100–200 pptv for the free troposphere. Simulations were also performed with calculated CH$_3$CHO; however, the assumption of constrained versus calculated CH$_3$CHO had a negligible impact on the O$_x$ photochemical production and loss rates.

3. Results and Discussion

3.1. MODEL EVALUATION: RADICAL SPECIES AND THEIR DEPENDENCE ON O$_3$ PHOTOLYSIS FREQUENCY

To evaluate how well the model constrained by medians represents the variability in observations, we compare the dependence of free radical species concentrations on the measured photolysis frequency, $j$(O$_1$D). Free radical species and families, such as OH and RO$_x$ ≡ (HO$_x$ + CH$_3$O$_x$ + higher analogs), have lifetimes on the order of seconds to minutes, and thus should be in chemical steady-state. As a result, their concentrations will adjust rapidly to local photolysis frequencies. Figure 1(a) compares the model and measurement dependence of log(OH) on log($j$(O$_1$D)) for March and May observations between 1–3 km and 58–85° N. Figure 1b compares the model and measurement dependence of log(RO$_x$) on log($j$(O$_1$D)) for February and May conditions between 3–6 km and 58–85° N. Here, modeled $j$(O$_1$D) was calculated from TUV and measured $j$(O$_1$D) taken from the aircraft observations. The solid points and vertical bars represent the mean and 1σ limits for data points binned into log($j$(O$_1$D)) = 0.25 intervals. The variability in observations is due to a combination of measurement imprecision and atmospheric sampling variability. The estimated uncertainties (2σ) in the OH and RO$_x$ measurements are ±46%.
Figure 1. Dependence of radical concentration (OH in panel a and RO\textsubscript{x} in panel b) against O\textsubscript{3} photolysis frequency. Open points are individual measurements and solid points are binned averages with one standard deviation limits. Points are separated by month and altitude for the 58–85° N latitude band. OH measurements were not available for February. The curves are modeled radical concentrations vs. modeled TUV \(j(O^1D)\) for a diurnal cycle at diel steady-state. TUV parameters were set at 58° N and the end of month to expand modeled TUV \(j(O^1D)\) so as to span all the individual points. Simulations constrained at median measured NO\textsubscript{x}, O\textsubscript{3}, CO, H\textsubscript{2}O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO\textsubscript{3}, CH\textsubscript{2}O, CH\textsubscript{3}OOH and H\textsubscript{2}O\textsubscript{2}.
(LOD = $2 \times 10^5$ molec/cm$^3$) and ±35% (LOD = $1 \times 10^7$ molec/cm$^3$), respectively. There was also evidence for atmospheric sampling variability in the radicals due to short-term changes in NO$_x$. Although the large variability in the observations does not provide a stringent test, it is encouraging that the box model, initialized with median observations for long-lived species, does yield modeled curves that generally reproduce the measured radical concentration dependence on $j$(O$^1$D), within the 1σ limits. This lends confidence in the box model and in its usefulness in representing the local chemistry for the various regimes observed during TOPSE.

Figure 1 also illustrates the springtime increase in photochemical activity. Measurements acquired during May have both the highest $j$(O$^1$D) frequencies and radical concentrations observed in the arctic free troposphere. This seasonal increase in RO$_2$ concentration is similar to the seasonal trend observed by Zanis et al. (2003) for a mountain site in the Swiss Alps. The average observed OH and RO$_x$ concentrations for the largest $j$(O$^1$D) bin in May were $2.5 \times 10^6$ and $1.4 \times 10^8$ molec/cm$^3$, respectively. This compares with modeled OH and RO$_x$ concentrations of $2.0 \times 10^6$ and $1.8 \times 10^8$ molec/cm$^3$ for the same $j$(O$^1$D) levels, respectively. The modeled curves and measurements in Figure 1(b) have a slope of $\sim 1/2$, which stems from the loss rate of RO$_2$ and its quadratic dependence on RO$_2$ concentration. Figure 1 also illustrates the asymmetry in the modeled radical diurnal profiles, which stems from the relatively long lifetime of the HNO$_4$ reservoir. In the model, HNO$_4$ builds in mixing ratio during the day and then slowly decays throughout the night. As a result, HNO$_4$ acts as a sink for radicals in the morning and a source of radicals in the evening.

3.2. MODEL EVALUATION: NON-RADICAL SPECIES AND THE STEADY-STATE ASSUMPTION

To further validate our understanding of the photochemistry in the model and test the steady-state assumption for non-radical species, we made model-measurement comparisons for longer-lived intermediate species (H$_2$O$_2$, CH$_3$OOH and CH$_2$O). As outlined in the model methodology, we performed model simulations individually for CH$_2$O, H$_2$O$_2$ and CH$_3$OOH to derive time-dependent mixing ratios for each intermediate, i.e., all measured species constrained at medians except for the species of interest, which was initialized at its median mixing ratio and calculated. If the photochemical box model was run for extended periods of time (60 and 10 days for February and May conditions, respectively), these model simulations generated steady-state concentrations for the intermediate species (H$_2$O$_2$ was limiting). Table III lists the mixing ratios after five-day simulations. Species that reached steady-state in the model after 5 days are denoted with ‘SS’. In comparing these results with the measured medians in Tables I and II, we see that the general agreement between these intermediates improves when the species are denoted in diel steady-state. Our box modeling approach constrained with observed medians does not capture the atmospheric variability in observations. Given the large variabil-
ity in observed CH$_2$O throughout the campaign, our modeling approach did not enable a definitive CH$_2$O comparison. We refer the reader to Fried et al. (2003) for a detailed description of a point box model comparison with individual CH$_2$O observations. However, in looking at the peroxide mean mixing ratios and 1σ standard deviations in Tables I and II, the variabilities in the means decreases with season enabling a comparison between our modeling approach and the peroxide observations for April and May conditions. The simulations used to generate the modeled data in Table III illustrate that H$_2$O$_2$ has a time constant greater than 5 days to reach steady-state, while CH$_3$OOH reached steady-state in the model for all months except February. The lifetimes of H$_2$O$_2$ and CH$_3$OOH under February conditions (considering photolysis and reaction with OH) were calculated to be 15 days and 9 days, respectively. Atmospheric lifetimes will likely be shorter for the peroxides due to the additional heterogeneous loss mechanism, especially for the more water-soluble H$_2$O$_2$. Table III shows that modeled steady-state CH$_3$OOH mixing ratios are very similar to the measured medians for all months. H$_2$O$_2$ does not reach steady-state after 5 days, even in May, and as shown in Table III, its 5-day modeled mixing ratio in May is considerably higher than the measured H$_2$O$_2$ median by a factor of 2.6. In fact, while both the model and observations show a seasonal increase, the ratio of model-to-measurement does not show a significant change, even though the H$_2$O$_2$ lifetime decreases to 2.3 days.

Further simulations were performed to test the sensitivity of peroxides to NO$_x$ mixing ratios. Model H$_2$O$_2$ was shown to be largely insensitive to small changes in NO$_x$ about the median, dln[H$_2$O$_2$/dln[NO$_x$] = 0.035 (February, 3–6 km), while CH$_3$OOH did show a significant negative sensitivity toward NO$_x$, dln[CH$_3$OOH]/dln[NO$_x$] = –0.31. Additional time-dependent NO$_x$ simulations were also used to assess how the peroxide mixing ratios changed as NO$_x$ decreased over a 3-day period to the median measured NO$_x$. Figure 2 illustrates the time-dependent NO$_x$ simulations for May conditions, respectively. H$_2$O$_2$ showed a consistent increase during the simulation with H$_2$O$_2$ not reaching steady-state during the 6-day window. CH$_3$OOH initially decreased during the simulation consistent with the higher NO$_x$ mixing ratios and the negative CH$_3$OOH sensitivity towards NO$_x$; however, it then increased for the remainder of the simulation. At t = 3 days, modeled H$_2$O$_2$ is already considerably higher than the measured median, while CH$_3$OOH is consistent with the measured median. In comparing H$_2$O$_2$ and CH$_3$OOH, the H$_2$O$_2$ medians are likely impacted by heterogeneous loss to a greater extent than CH$_3$OOH. Thus, H$_2$O$_2$ is likely initialized considerably lower than our model steady-state value (no heterogeneous loss for peroxides in box model) in comparison to CH$_3$OOH. The long lifetime for the peroxides results in the modeled H$_2$O$_2$ not approaching its modeled steady-state during the 6-day window. In the Arctic free troposphere, after a heterogeneous loss process, there is a long time constant for H$_2$O$_2$ re-approaching steady-state with its longer-lived precursor species. This slow time constant hinders quantitative H$_2$O$_2$ model-measurement comparisons with a box model. However, while the intermittent nature of cloud encounter
Figure 2. Model-measurement comparison of peroxide species for May conditions. The points are median measured mixing ratios for CH$_3$OOH and H$_2$O$_2$ and are plotted at $t = 0$. Model curves represent results from a time-dependent NO$_x$ simulation where NO$_x$ was initialized higher and decreased over a three day initiation time to its median measured mixing ratio of 30 pptv at $t = 0$. Vertical bars are the 25 and 75 percentiles. Simulations constrained at median measured O$_3$, CO, H$_2$O, HCs, acetaldehyde, methanol, acetone, PAN, PPN and HNO$_3$.

and heterogeneous loss may explain episodic model-measurement differences, it does not seem likely that, in an average sense, H$_2$O$_2$ measurements over a wide area in the 3–6 km layer would be affected by heterogeneous loss by a factor more than 2. Uncertainties raised here in modeling H$_2$O$_2$ will need to be considered later in discussing the RO$_x$ and O$_x$ budget.

3.3. CHARACTERISTICS OF RADICAL POOL CYCLING

Radical species are produced, lost and inter-converted by numerous chemical channels. It is instructive to calculate diurnally averaged fluxes for critical reaction pathways with a photochemical model. Figure 3 illustrates the behavior of the
radical pool for May (panel a) and February conditions (panel b) in the arctic free troposphere. Diurnally averaged radical production rates in pptv/day are labeled for so-called primary photolysis reactions (O$_3$), secondary photolysis reactions (RCHO, H$_2$O$_2$, CH$_3$OOH and CH$_3$C(O)CH$_3$) and inter-conversion reactions. Several features in Figure 3 are prominent in importance due to the measurement location in the remote arctic free troposphere. OH is lost predominantly by reaction with CO for both May and February conditions. While the hydrocarbon reactions with OH have their greatest importance in winter, they still only contribute 5% to
OH loss in February while CO contributes 70%. The second largest contributor to OH loss is the sum of the aldehyde species (CH$_2$O and CH$_3$CHO were constrained at measured medians while other aldehydes were calculated from higher hydrocarbon chemistry in the model). H$_2$O and HNO$_3$ formation are terminal sinks for OH. H$_2$O formation dominated over HNO$_3$ formation in this low NO$_x$ environment. The result is an overall OH loss rate of 43 pptv/day (May) and 3.2 pptv/day (February); compared with an OH to peroxy radical conversion rate of 1660 pptv/day (May) and 233 pptv/day (February). This implies that for every OH radical that is terminated, 39 (May) and 73 (February) are inter-converted to the peroxy radical pool. The OH production also proceeds through recycling reactions from HO$_2$. It is interesting that in the arctic free troposphere, the reaction of HO$_2$ with O$_3$ is comparable (556 pptv/day in May and 92 pptv/day in February) to the reaction between HO$_2$ and NO (845 pptv/day in May and 122 pptv/day in February) in recycling OH. The primary source of OH from O$_3$ photolysis in February is very small (3.6 pptv/day). This is only 1.7% of the OH regeneration rate from HO$_2$. Furthermore, the photolysis of peroxides to produce OH is a factor of 2.9 times larger than O$_3$ photolysis in February. The differing sensitivities of peroxyde photolysis and O$_3$ photolysis on the low wintertime water vapor mixing ratios contributes to the importance of peroxyde photolysis in winter. While both the peroxyde photolysis rate and the O($^1$D) + H$_2$O reaction rate increase with water vapor, a further simulation with water vapor an order of magnitude larger for February conditions resulted in a factor of 11.5 increase in OH production from O$_3$ photolysis and a factor of 2.7 increase from H$_2$O$_2$ photolysis. This change in water vapor resulted in OH production now having a larger contribution from O$_3$ photolysis (42 pptv/day) compared to H$_2$O$_2$ photolysis (18 pptv/day). In May, the O$_3$ photolysis contribution to OH formation is larger than peroxyde photolysis; however, both terms are comparable. In May, the O$_3$ and peroxyde photolysis sources of OH are 12% and 10%, respectively, of the regeneration rate from HO$_2$. The model runs used in Figure 3 were performed with H$_2$O$_2$ constrained to observed medians. Results with H$_2$O$_2$ calculated by the model yield even larger estimates for H$_2$O$_2$ photolysis and OH production suggesting that our uncertainty in H$_2$O$_2$ translates into an uncertainty in understanding the OH budget.

The sources and cycling of the peroxy radical pool are highly complex, even in a remote environment. RO$_2$ can be regenerated from OH recycling reactions. Secondary sources include the photolysis of intermediate VOC oxidation products such as aldehydes, ketones and peroxides. In looking at the sources to the total radical pool, the magnitude of the RO$_2$ photolysis sources are comparable with the OH photolysis sources in May (416 pptv/day vs. 318 pptv/day); however, in February, RO$_2$ photolysis sources dominate over OH photolysis sources (65 pptv/day vs. 14 pptv/day). Furthermore, an organic peroxy radical can react with NO via a complex series of intermediate steps involving alkoxy radical decomposition, O$_3$ abstraction or isomerization to form an HO$_2$ radical. As noted above, peroxy radicals can cycle back to OH by reactions with NO and O$_3$; however for low
NOx environments, peroxy radicals can also enter self-reactions forming peroxides. Under May conditions, HO2 is converted back to OH at a rate of 1400 pptv/day. This can be compared to an HO2 self-reaction loss equal to 312 pptv/day, an HO2 + CH3O2 reaction rate equal to 76 pptv/day and a HO2 + OH reaction equal to 36 pptv/day. Thus, for every HO2 radical that is terminated to form a peroxide or H2O, 3.0 are recycled back to OH. In February, this estimate changes only slightly with 3.7 HO2 radicals recycled back to OH for every HO2 terminated. This is in contrast to regions impacted by fresh emissions of NOx (VOC/NOx < 10) where the rate of the HO2 self-reaction is small compared to the rate of chain propagation by reaction of HO2 with NO (Seinfeld and Pandis, 1998).

It should be further emphasized that our uncertainty in modeling H2O2 translates to an uncertainty in the ROx budget. For example, the model overestimate of H2O2 could imply a model overestimate of ROx radical loss. Given the quadratic dependence of H2O2 formation on HO2 mixing ratios, a modeled steady-state H2O2 over-prediction by a factor of 3.6 for May conditions (from a 10 day simulation) could imply that modeled HO2 is being over-predicted by a factor of 1.9. However, these implications assume that steady-state is a reasonable assumption for H2O2 in May and that H2O2 loss is dominated by OH oxidation and photolysis, both of which are not strictly valid at all times in the springtime arctic free troposphere. Thus, our difficulty in modeling H2O2 adds uncertainty in our quantification of the ROx budget.

A parameter useful in understanding how the radical cycling in the arctic free troposphere varies with NOx and PROx (PROx is defined here as the total production rate of ROx considering O3, CH2O, H2O2 and CH3OOH photolysis) is the radical chain length, defined here as the production rate of OH through recycling reactions divided by the total loss rate of all radical species. Physically, the radical chain length represents the number of times an OH radical is recycled within the ROx family before being terminated. Figure 4 illustrates the dependence of the radical chain length on NOx, color-coded by PROx. Individual points are calculated by combining observations for NOx, ROx, O3, CH2O, H2O, j values, H2O2, CH3OOH with the point steady-state calculations Cantrell et al. (2003) used for the partitioning between the ROx family. Curves were calculated from the photochemical box model as a function of varying NOx. The individual points and modeled calculations lie between 0.2–6 with the points showing considerable scatter compared to the model. Points are binned for NOx in the range 10–30 pptv and 30–50 pptv and PROx between 0–200 pptv/day, 600–1000 pptv/day, and 1300–1800 pptv/day. The binning considerably reduces the scatter as the model now generally lies within the 1σ data limits, although comparing any modeled trend with the observations is beyond the measurement precision. In looking at the modeled dependence, intriguing relationships are observed for the range of NOx and PROx observed in the arctic free troposphere. At low PROx, the modeled radical chain length decreases with increasing NOx. This is the case for February conditions as radical concentrations are low, radical-radical reactions are slow and ROx + NOx reactions (PAN, HNO4 and
Figure 4. Dependence of radical chain length on NO\textsubscript{x} and P\textsubscript{RO\textsubscript{x}}. Chain length is defined as the recycling production rate of OH (reaction 1 + reaction 6) divided by the total loss of RO\textsubscript{x}. Points are calculated from measurements of NO, NO\textsubscript{2}, RO\textsubscript{x}, O\textsubscript{3}, H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, j(O\textsubscript{1D}) and steady-state calculations of OH, CH\textsubscript{3}C(O)O\textsubscript{2} \textsubscript{2} and the partitioning of RO\textsubscript{x} between HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2} \textsubscript{2} \textsubscript{[Cantrell et al., 2003]}. Data is binned based on NO\textsubscript{x} between 10–30, 30–60 pptv for PRO\textsubscript{x} in the ranges 0–200, 600–1000, 1300–1800 pptv/day. Curves are model-derived results for various cases, color-coded against model calculated P\textsubscript{RO\textsubscript{x}}. Simulations constrained at median measured O\textsubscript{3}, CO, H\textsubscript{2}O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO\textsubscript{3}, CH\textsubscript{2}O, CH\textsubscript{3}OOH, H\textsubscript{2}O\textsubscript{2} with varying NO\textsubscript{x}.

HNO\textsubscript{3} formation) become important with only modest increases in NO\textsubscript{x} mixing ratios. At higher P\textsubscript{RO\textsubscript{x}}, representative of May conditions, modeled chain lengths are nearly independent of NO\textsubscript{x}. The strongest dependence between chain length and P\textsubscript{RO\textsubscript{x}} is observed at low NO\textsubscript{x}. Here, radical chain lengths increase with decreasing P\textsubscript{RO\textsubscript{x}} because RO\textsubscript{x} sinks are quadratic in RO\textsubscript{x} mixing ratios. At higher P\textsubscript{RO\textsubscript{x}} rates, the observed points clearly show chain length increasing with NO\textsubscript{x}. Here, the increase in the chain length is driven by increases in the HO\textsubscript{2} + NO reaction with increasing NO\textsubscript{x}. These observations (blue points in Figure 4) generally correspond to mid-latitude observations later in spring.
3.4. SEASONAL DEPENDENCE OF THE O₃ PRODUCTION AND LOSS RATES

A key objective of TOPSE was to quantify the O₃ budget during the observed springtime maximum in tropospheric O₃. For our sorted data set (1–3 km, 58–85° N), median O₃ was observed to increase by 12 ppbv between February and May. The increase was even larger at higher altitudes in the free troposphere with an observed median O₃ increase of 24 ppbv between February and May (3–6 km and 58–85° N). Assessing the importance of the various source terms for O₃ is difficult with a 0-D photochemical box model. O₃ has a long lifetime; for TOPSE conditions, generally ranging between 10–100 days. As a result, transport in addition to chemistry can significantly impact measured O₃ mixing ratios. To assess the importance of the in situ O₃ production relative to transport for air masses in the arctic free troposphere, we used the box model to estimate gross O₃ production and loss rates for our defined regimes. Figure 5 presents the seasonal dependence in the diurnally-averaged gross O₃ production rate, \( P_{O_3} \), calculated with the box model constrained with data medians from 58–85° N and 1–3 km (panel a) and 3–6 km (panel b). \( P_{O_3} \) is divided into source terms from HO₂, organic peroxy radical (R'O₂) and organic peroxyacyl radical (R'C(O)OO) reactions with NO,

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{R'O}_2 + \text{NO} & \rightarrow \text{R'O} + \text{NO}_2 \\
\text{R'C(O)OO} + \text{NO} & \rightarrow \text{R'} + \text{CO}_2 + \text{NO}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

where reactions (1–3) are the rate-limiting steps in O₃ production. These two panels illustrate the strong seasonal increase in local O₃ production in the arctic free troposphere. The increase in O₃ production rates is driven, in large part, by a combination of increases in instantaneous actinic flux, integrated exposure to actinic flux (a unique feature of the high latitude winter-to-spring transition), ROₓ precursor compounds (water vapor, O₃, peroxides, aldehydes), and NOₓ. The reader is referred to Cantrell et al. (2003) for a detailed description of the peroxy radical budget and the relative importance of various precursor species throughout the springtime transition. Reaction (1) dominates over reactions (2–3) contributing between 66% (February, 1–3 km) and 69% (May, 1–3 km) to the gross O₃ production; note the importance of reaction (1) increases relative to reactions (2–3) with season. The slower rate of increase in O₃ production between March and April in the 3–6 km band stems from lower median water vapor and NOₓ in April compared to March. The modeled seasonal O₃ production rate increases more sharply in the lower free troposphere (a factor of 28 for 1–3 km between February and May) compared to the middle free troposphere (a factor of 7 for 3–6 km between February
Figure 5. Comparison of the seasonal dependence of the gross O\textsubscript{3} production rate (ppbv/day) between 3–6 km (panel a) and 1–3 km (panel b) for 58–85° N derived from both the model (run on medians) and observationally (using coincident RO\textsubscript{2} and NO observations). Rates are divided between contributions from HO\textsubscript{2}, R\textsuperscript{′}O\textsubscript{2} and R\textsuperscript{′}C(O)O\textsubscript{2}. Simulations constrained at median measured NO\textsubscript{x}, O\textsubscript{3}, CO, H\textsubscript{2}O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO\textsubscript{3}, CH\textsubscript{2}O, CH\textsubscript{3}OOH and H\textsubscript{2}O\textsubscript{2}.

and May). This largely stems from a sharper increase in median NO\textsubscript{x} mixing ratios in the lower free troposphere (7–27 pptv) compared to the mid troposphere (18–30 pptv). Also included in Figure 5 is the P\textsubscript{O\textsubscript{3}} derived solely from observed RO\textsubscript{2} mixing ratios and observed NO mixing ratios, \(k[RO_2][NO]\), where \(k\) is approximated by the HO\textsubscript{2} + NO rate coefficient. While the observation-derived P\textsubscript{O\textsubscript{3}} is generally higher than the model-derived P\textsubscript{O\textsubscript{3}} (at most by a factor of 2), a similar seasonal dependence is noted for both altitude bands.
The gross O\textsubscript{x} production rates in the arctic free troposphere during TOPSE can be compared with rates from other recent missions over northern mid to high latitudes such as STRAT (Stratospheric Tracers for Atmospheric Transport), SUCCESS (Subsonic Aircraft: Contrail and Cloud Effects Special Study), SONEX (Subsonic Assessment: Ozone and Nitrogen Oxide experiment) and FREETEX (Free Tropospheric Experiment). The common feature among these other missions was an altitude range in the free troposphere. The STRAT mission took place over the North Pacific between California and Hawaii in three seasonal deployments (October–November, January–February and August). The SUCCESS mission took place over the central United States from April to May. The SONEX campaign took place over the North Atlantic region between October and November. FREETEX’96 resided on a mountain site in the Swiss Alps from April 15 to May 24, 1996. An additional study, TRACE A, had measurements throughout the troposphere but focused on the region in the South Atlantic east of Brazil in September and October. Table IV compiles the gross O\textsubscript{x} production rates calculated for these missions and can be compared to the results in Figure 5 for TOPSE. The initial deployments during TOPSE yield some of the lowest gross O\textsubscript{x} production rates reported in the troposphere (<0.2 ppbv/day for February, 58–85° N). The timing of the SONEX campaign in late fall coincides with similar actinic fluxes for the early spring during TOPSE; however, direct comparison should be made with TOPSE conditions in the 40–50° N band to coincide with the 39–54° N latitude band during SUCCESS. A box model simulation for median conditions in February between 3–6 km and 40–50° N resulted in a P\textsubscript{O\textsubscript{x}} of 0.43 ppbv/day, similar to the 0.54 ppbv/day median P\textsubscript{O\textsubscript{x}} observed during SONEX (Jaegle et al., 2000).

Figure 6 presents the seasonal dependence in the diurnally averaged production, loss and net production of O\textsubscript{x} in the arctic free troposphere. The results were generated from our box model constrained with median data between 58–85° N and for 1–3 km (panel a) and 3–6 km (panel b). Figure 6 also includes results from two
Figure 6. Comparison of the seasonal dependence of net O₃ production rate (ppbv/day) between 3–6 km (panel a) and 1–3 km (panel b) for 58–85° N with two other box modeling approaches (Wang et al., 2003; Cantrell et al., 2003). Our simulations were constrained at median measured NOₓ, O₃, CO, H₂O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO₃, CH₂O, CH₃OOH and H₂O₂.

point box models (Wang et al., 2003; Cantrell et al., 2003). The Wang et al. model was run to diel steady-state for each data point. The Cantrell et al. model was run to instantaneous steady-state using the observed j values for each data point. For both point models, O₃ rates from individual points were calculated, divided into the latitude, altitude and month bins in Tables I and II and then sorted to calculate the median POₓ, LOₓ and TOₓ. This differs from our modeling approach of constraining a box model based on the observed medians, integrating it for 5 days to diel steady-
PHOTOCHEMISTRY IN THE ARCTIC FREE TROPOSPHERE

state and then calculating rates for \( P_{O_3}, L_{O_3} \) and \( T_{O_3} \). While our approach is similar to the Wang \textit{et al.} model in that it calculates diurnally averaged rates, our model has the advantage of using a more explicit organic oxidation scheme while having the disadvantage of not being automated to run on individual points and thus cannot capture atmospheric variability. The three model approaches do provide a unique opportunity to compare the importance of the various assumptions in the models. Interestingly, all three models yield a consistent picture for the local \( O_3 \) photochemical rates in the arctic free troposphere. This suggests that the detailed organic chemistry in our box model is not critical to deriving \( O_3 \) rates for the remote arctic free troposphere and that atmospheric conditions are uniform enough for a box model constrained by median observations to capture the seasonal trends in the \( O_3 \) budget. Generally, the mid-troposphere shows a tendency for net \( O_3 \) production throughout the mission while the 1–3 km layer shows a small tendency for net loss of \( O_3 \). This combined with the generally increasing \( O_3 \) mixing ratio throughout the campaign directly imply the necessity for a net import of \( O_3 \) transported into the arctic lower free troposphere.

Our uncertainty in modeling \( H_2O_2 \) also adds uncertainty to the model-derived \( O_3 \) photochemical rates. To evaluate the sensitivity of the \( O_3 \) budget to our uncertainty in \( H_2O_2 \), we calculated \( P_{O_3}, L_{O_3} \) and \( T_{O_3} \) from a series of simulations where \( H_2O_2 \) was allowed to reach diel steady-state. For February conditions, this resulted in a 23% increase in \( P_{O_3} \) and a 22% increase in \( T_{O_3} \), compared to the simulations with \( H_2O_2 \) constrained by observations. For May conditions, this resulted in a 16% increase in \( P_{O_3} \) and a 10% increase in \( T_{O_3} \).

It would be advantageous to apply a simple method to estimate the relative importance of transport and local photochemical production to the observed \( O_3 \) mixing ratios during TOPSE. The local derivative of \( O_3 \) with respect to time can be expressed in terms of the local \( O_3 \) production rate (\( P_{O_3} \)), the local \( O_3 \) loss rate (\( L_{O_3} \)) and a term representing transport of \( O_3 \) into the arctic free troposphere (\( T \)):

\[
\frac{d[O_3]}{dt} = P_{O_3} - L_{O_3}[O_3] + T. \tag{2}
\]

Solution of Equation (2) leads to the following expression for \( O_3 \) (Klonecki and Levy, 1997; Cantrell \textit{et al.}, 2003):

\[
[O_3]_t = [O_3]_{ss} + ([O_3]_o - [O_3]_{ss}) \exp(-L_{O_3} t). \tag{3}
\]

where \([O_3]_{ss}\) is the steady-state \( O_3 \) concentration equal to \((P_{O_3} + T)/L_{O_3}\). An implicit assumption in using Equation (3) is that \([O_3] \) changes are small so that \( P_{O_3} \) and \( L_{O_3} \) remain reasonably constant. The transport term, \( T \), can be calculated by substituting the expression for \([O_3]_{ss}\) and rearranging Equation (3):

\[
T = \frac{L_{O_3}[O_3]_o - P_{O_3} - L[O_3]_o \exp(-L_{O_3} t) + P_{O_3} \exp(-L_{O_3} t)}{1 - \exp(-L_{O_3} t)}. \tag{4}
\]

Here, we compare our photochemical box modeled results run on median data with the point steady-state model (Cantrell \textit{et al.}, 2003) and a 3-D chemical-transport
model (Emmons et al., 2002) to see if similar answers to this important question are observed with various modeling approaches. From our modeled estimates of $P_{O_3}$ and $L_{O_3}$ for each month and the observed median $O_3$ mixing ratios and a time increment of 1 month, it is possible to estimate the magnitude of the transport term. A positive value for $T$ indicates net $O_3$ transport into the arctic free troposphere while a negative term indicates net $O_3$ transport out of the arctic free troposphere. The analysis implicitly assumes that the $P_{O_3}$ and $L_{O_3}$ values derived from the model are representative of the monthly period. Table V summarizes the results for $T$ for 1–3 km and 3–6 km between 58–85° N. In all cases, we calculate net transport of $O_3$ into the arctic free troposphere (positive values for $T$). Between February and March in the 1–3 km layer, transport of $O_3$ into the region dominates the local photochemical production (78% vs. 22%). After March, the transport term is a small percentage (<26%) of the local production term (>74%), as the effects of increased photochemical activity increase the local rates of $O_3$ production significantly. In the 3–6 km layer, the local production term always dominates the transport term with the transport term contributing a maximum percentage of 31% between February and March. These results are qualitatively consistent with the regional $O_3$ budget derived by a 3-D chemical-transport model (MOZART) for the vertically integrated, 60–90° N latitude band (Emmons et al., 2002). MOZART derived a $d[O_3]/dt$ for transport greater than $O_3$ production (5 Tg/mon vs. 1 Tg/mon) between February and March. Later in the season between April and May, MOZART derived a transport term that was less than the $O_3$ production (3 Tg/mon vs. 6 Tg/mon). The steady-state point model described in (Cantrell et al., 2003) also derived a net import of $O_3$ into the arctic troposphere between 0.1–0.4 ppbv/day compared to local production rates of 0.7–0.9 ppbv/day, similar to the magnitudes shown in Table V. The steady-state point model also derived a net export of $O_3$ from the 40–60° N latitude band of 2–3 ppbv/day compared to local production rates of 6–8 ppbv/day. These results are also consistent with Zanis et al. (2000) who suggest a photochemical origin for the springtime $O_3$ maximum at Jungfraujoch, Switzerland. Collectively, these studies suggest that in winter $O_3$ transport and local photochemical production both play comparable roles in the observed $O_3$ trend while the photochemical bloom later in the campaign results in local photochemical production dominating transport. While the box modeled results can infer a magnitude and sign for the transport term, it cannot discern the source of the $O_3$ being transported into the arctic free troposphere, i.e., transport from stratosphere or transport from the industrialized boundary layer farther south. The reader is referred to the 3-D model study by Emmons et al. (2002) for a further breakdown of the transport term into vertical and horizontal components.
Table V. Calculated O₃ photochemical production term and transport term needed to reproduce the monthly changes in median O₃ (58–85° N)

|          | February to March period | March to April period | April to May period |
|----------|--------------------------|-----------------------|---------------------|
| 3–6 km   | P₀ₓ (ppbv/day) 0.25 (69%) | 0.39 (87%)           | 0.80 (80%)          |
|          | T (ppbv/day) 0.11 (31%)   | 0.057 (13%)          | 0.20 (20%)          |
| 1–3 km   | P₀ₓ (ppbv/day) 0.10 (22%) | 0.32 (74%)           | 0.93 (76%)          |
|          | T (ppbv/day) 0.35 (78%)   | 0.11 (26%)           | 0.29 (24%)          |

In parenthesis are shown the percentages of the total for each term.
Simulations constrained at median measured NOₓ, O₃, CO, H₂O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO₃, CH₂O, CH₃OOH, H₂O₂.

3.5. SENSITIVITY OF Oₓ PRODUCTION AND LOSS RATES TO NOₓ MIXING RATIOS AND ROₓ PRODUCTION RATES

Since the local gross O₃ production rate in the arctic free troposphere plays a considerable role in the observed seasonal O₃ trend, especially later in the campaign, it is desirable to examine the factors that influence Oₓ production rates. Numerous prior studies have suggested that in the remote troposphere gross O₃ production increases linearly with NOₓ mixing ratios (so called NOₓ-limited regime). To determine the sensitivity of P₀ₓ to NOₓ, we calculated dln(POₓ)/dln(NOₓ) for each regime by using the model-derived change in P₀ₓ for small changes in NOₓ mixing ratios (±10%). We derived dln(POₓ)/dln(NOₓ) values between 0.86–1.02, generally independent of month in the arctic free troposphere. This means that a 1% increase in NOₓ mixing ratios will correspond to a 0.86–1.02% increase in gross Oₓ production rates. This implies that gross Oₓ production rates are strongly dependent on NOₓ mixing ratios (a value of unity would imply linearity) in the arctic free troposphere, as has been observed for other low NOₓ environments around the world (Ridley et al., 1992; Schultz et al., 1999; Jaegle et al., 2000; Kotchenruther et al., 2001). Similarly, we derived dln(LOₓ)/dln(NOₓ) values less than 0.2, independent of month in the arctic free troposphere. This suggests that the Oₓ loss rate is generally independent of small changes in [NOₓ]. Together these results imply that the net Oₓ tendency will also be strongly sensitive to small changes in NOₓ mixing ratios in the arctic free troposphere.

Numerous prior studies have shown that Oₓ production rates depend on NOₓ in a non-linear manner over a wide range of NOₓ mixing ratios. In Figure 7 are calculated gross Oₓ production rate points as a function of measured NOₓ mixing ratios for the entire TOPSE mission. P₀ₓ was calculated using measured ROₓ and NO mixing ratios. Point steady-state calculations (Cantrell et al., 2003) were used to partition the measured ROₓ into HO₂ and CH₃O₂ fractions. The data are also color-
Figure 7. Dependence of gross $O_3$ production rate (ppbv/day) on NO$_x$, color-coded against P$O_x$. Points are calculated from measurements of NO, NO$_x$, RO$_x$, H$_2$O, O$_3$, CH$_2$O, H$_2$O$_2$, CH$_3$OOH, $O_3$ and steady-state calculations of the partitioning of RO$_x$ between HO$_2$ and CH$_3$O$_2$ [Cantrell et al., 2003]. Data is binned based on NO$_x$ between 10–30, 30–60 pptv for P$O_x$ in the ranges 0–200, 600–1000, 1300–1800 pptv/day. Curves are model-derived results for various cases, color-coded against model calculated P$O_x$. Simulations constrained at median measured O$_3$, CO, H$_2$O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO$_3$, CH$_2$O, CH$_3$OOH, H$_2$O$_2$ with varying NO$_x$. 
coded as a function of the RO\textsubscript{x} production rate derived observationally considering O\textsubscript{3}, CH\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}OOH photolysis. Figure 7 clearly shows an increase in P\textsubscript{O\textsubscript{x}} with NO\textsubscript{x} for a given RO\textsubscript{x} production rate (linear for low NO\textsubscript{x}). For a given NO\textsubscript{x} mixing ratio, P\textsubscript{O\textsubscript{x}} also increases almost linearly with increasing P\textsubscript{RO\textsubscript{x}}. Also, included on Figure 7 are our photochemical model-derived curves corresponding to February (3–6 km) and May (1–3 km and 3–6 km) median conditions in the arctic free troposphere. Several model simulations were performed at constant RO\textsubscript{x} precursor concentrations (P\textsubscript{RO\textsubscript{x}} = 85 pptv/day for February (3–6 km), 770 pptv/day for May (3–6 km) and 1500 pptv/day for May (1–3 km)) and different NO\textsubscript{x} mixing ratios (spanning independent axis). The modeled lines are also color-coded based on the P\textsubscript{RO\textsubscript{x}} scale. The dependence of the modeled P\textsubscript{O\textsubscript{x}} curves on NO\textsubscript{x} mixing ratios is very similar to that of the individual data points for comparable P\textsubscript{RO\textsubscript{x}} rates. The modeled curves are linear in P\textsubscript{O\textsubscript{x}} vs. NO\textsubscript{x} at low NO\textsubscript{x}; however, do appear to fall off at higher NO\textsubscript{x}. Prior studies suggest that the optimum NO\textsubscript{x} mixing ratio to maximize P\textsubscript{O\textsubscript{x}} decreases with lower P\textsubscript{RO\textsubscript{x}} rates. Jaegle et al. (2002) showed that for the upper troposphere, the optimum NO\textsubscript{x} level is \sim 500 pptv for P\textsubscript{RO\textsubscript{x}} = 1000 pptv/day and decreases to \sim 200 pptv at P\textsubscript{RO\textsubscript{x}} = 10 pptv/day. Thornton et al. (2002) presented data for an urban, forested site during the 1999 Southern Oxidant Study (SOS) that showed P\textsubscript{O\textsubscript{x}} maximized at NO\textsubscript{x} levels between 4–5 ppbv at P\textsubscript{RO\textsubscript{x}} as high as 60 ppbv/day. From our model simulations in the arctic free troposphere, P\textsubscript{O\textsubscript{x}} maximized at NO\textsubscript{x} levels between 300 pptv (February, P\textsubscript{RO\textsubscript{x}} = 85 pptv/day) and 600 pptv (May, P\textsubscript{RO\textsubscript{x}} = 1500 pptv/day). These NO\textsubscript{x} ranges are very similar in magnitude to the results obtained by (Jaegle et al., 2000) for comparable P\textsubscript{RO\textsubscript{x}} in the upper troposphere during STRAT, SUCCESS and SONEX. In comparing the modeled curves with the observations, it is not possible to discern curvature due to the majority of the data lying at low NO\textsubscript{x} levels. The general agreement between the modeled curves and the observations lends further confidence in our understanding of the chemistry and its dependence on NO\textsubscript{x}; however, the argument is somewhat circular as point steady-state calculations were used, in part, to calculate the P\textsubscript{O\textsubscript{x}} term. Furthermore, our assignment of P\textsubscript{O\textsubscript{x}} as the sum of the rates of peroxy radical reactions with NO also prescribes a predetermined understanding of what chemistry limits O\textsubscript{3} production.

Figure 8 illustrates how the net O\textsubscript{3} production rate depends on NO\textsubscript{x} mixing ratios. Net O\textsubscript{3} production rates were calculated considering the following O\textsubscript{3} loss reactions:

\[
\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(R6)}
\]

\[
\text{O}^\text{I(D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(R7)}
\]

\[
\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2 . \quad \text{(R8)}
\]

Individual points were calculated from observations of RO\textsubscript{x}, NO, O\textsubscript{3}, J\textsubscript{O1D}, and H\textsubscript{2}O. Steady-state calculations (Cantrell et al., 2003) were used for OH and to
Figure 8. Dependence of net $O_3$ production rate (ppbv/day) on $NO_x$, color-coded against $P_{RO_x}$. Points are calculated from measurements of NO, NO$_x$, RO$_x$, H$_2$O, O$_3$, CH$_2$O, H$_2$O$_2$, CH$_3$OOH, $JO_{1D}$ and steady-state calculations of OH and the partitioning of RO$_x$ between HO$_2$ and CH$_3$O$_2$ [Cantrell et al., 2003]. Data is binned based on NO$_x$ between 10–30, 30–60 pptv for $P_{RO_x}$ in the ranges 0–200, 600–1000, 1300–1800 pptv/day. Curves are model-derived results for various cases, color-coded against model calculated $P_{RO_x}$. Simulations constrained at median measured O$_3$, CO, H$_2$O, HCs, acetaldehyde, methanol, acetone, PAN, PPN, HNO$_3$, CH$_2$O, CH$_3$OOH, H$_2$O$_2$ with varying NO$_x$. 

PHOTOCHEMISTRY IN THE ARCTIC FREE TROPOSPHERE 133

apportion HO2 and CH3O2. Curves represent the results of our photochemical box model run repeatedly over the range of NOx mixing ratios. Agreement between our modeled curves and observations is generally good for similar ranges of PROx.

For the low-light level conditions in February (PROx ≈ 80 pptv/day), the cross-over threshold to positive net O3 production occurs at NOx ≈ 10 pptv (58–85° N, 3–6 km); by May (PROx ≈ 1500 pptv/day), the threshold increases to NOx ≈ 30 pptv (58–85° N, 1–3 km). This observation suggests that in the arctic free troposphere in the winter, the NOx level needed to sustain net O3 production is considerably lower than in spring. There also appears to be a dependence on altitude as the NOx level needed to produce net O3 is shifted to higher NOx mixing ratios at lower altitudes. This may be an explanation for the altitude dependence seen in Figure 6, as NOx levels are not significantly different between the 1–3 km and 3–6 km layer, especially later in the campaign.

It is also interesting to compare the sensitivity of POx to NOx (dln(POx)/

ln(NOx)) with the sensitivity of POx to PROx (dln(POx)/dln(PROx)) for the arctic free troposphere. Model runs for observations between 58–85° N yield a range of values for dln(POx)/dln(PROx) between 0.50 in February and 0.38 in May, implying a fairly strong POx dependence of PROx. However, this sensitivity is lower than the values stated above for dln(POx)/dln(NOx) and suggests that in the arctic free troposphere while POx increases with both NOx and PROx, POx is more sensitive to the same relative change in NOx. This comparison illustrates the importance of understanding the NOx budget in the arctic free troposphere, as the lifetime of NOx and thus its persistence in the arctic strongly affects the atmosphere’s ability to produce O3. The reader is referred to a companion paper for details on the NOx budget during TOPSE (Stroud et al., 2003).

4. Conclusions

The goal of this paper was to characterize the seasonal dependence of the O3 budget in the arctic free troposphere so that the following two questions could be addressed: (1) what is the importance of local photochemistry compared to transport in creating the springtime maximum in high latitude O3 trends, and (2) what is the response of local gross and net O3 production rates to changes in PROx and NOx?

A photochemical box model was constrained by measured median mixing ratios based on the TOPSE observations and run to diel steady-state to calculate gross O3 production and loss rates. The box model was run for sorted data cases based on latitude, altitude and month. This methodology was validated by comparing modeled dependencies with individual measurement points. Curves generated with the box model generally reproduced the dependence seen in the individual data points, especially for species/quantities with short equilibration times (e.g., radicals vs. j(O1D) and O3 production rates vs. NOx).

The radical cycling in the arctic free troposphere is considerably different from other locations, especially in winter under low actinic flux and low water vapor
mixing ratios. The majority of radical species enter and leave the radical pool as peroxy radicals. Furthermore, when peroxy radicals are converted to OH, they are very efficiently converted back to peroxy radicals. The loss mechanism of OH radicals to form HNO$_3$ is not efficient at the low NO$_x$ mixing ratios typical of the arctic free troposphere. The radical production from the photolysis of aldehyde and peroxy species also dominates over O$_3$ photolysis. The efficiency of the radical cycling actually decreases with increasing NO$_x$ in February. This stems from the low water vapor and low actinic flux conditions which result in low radical concentrations. Under these conditions, RO$_x$ + NO$_x$ reactions play an important role in removing radicals with increasing NO$_x$. Overall, very small radical chain lengths ($\sim$1–3) were calculated suggesting that the concept of a radical chain is not appropriate for the low NO$_x$ conditions in the arctic mid-troposphere.

Prior modeling studies suggested a build up in the wintertime of hydrocarbons and NO$_x$ in the arctic free troposphere followed by a ‘spring cleaning’ where species mixing ratios decrease due to increased rates of OH oxidation. Interestingly, while hydrocarbons decreased throughout the winter-to-spring transition, NO$_x$ actually increased in mixing ratio between February and May, likely due to an increase in ventilation from the boundary layer. This increase in NO$_x$ in combination with increases in radical production rates (O$_3$, CH$_2$O and peroxy photolysis) led to the springtime bloom in photochemical production of O$_3$. In the lower free troposphere (1–3 km), O$_3$ transport into the arctic free troposphere dominated the observed O$_3$ trend between February and March while local O$_3$ photochemical production dominated transport between March and May. In the middle free troposphere (3–6 km), local O$_3$ photochemical production dominated transport between February and May. However, the transport term was always calculated to be positive meaning that net transport of O$_3$ into the arctic free troposphere was needed in combination with photochemistry to reproduce the observed monthly O$_3$ trend. Quantitatively, our calculated gross O$_3$ production and loss rates are similar to results from Cantrell et al. (2003) and Wang et al. (2003) suggesting that the differences in modeling approaches (explicit vs. lumped organic chemistry, instantaneous steady-state vs. diel steady-state, point vs. median constraint) were not critical for calculating O$_3$ production rates in the arctic free troposphere. However, our interpretation of the results is critically different from Wang et al. who conclude that a small net O$_3$ loss ($P_{O_3} - L_{O_3}[O_3] < 0$) implies that transport must dominate over in situ photochemistry in explaining the springtime increase in arctic free tropospheric O$_3$. Fundamentally, the ($P_{O_3} - L_{O_3}[O_3]$) term can remain negative while both $P_{O_3}$ and $L_{O_3}[O_3]$ increase significantly with season so that the $P_{O_3}$ term surpasses the transport, $T$, term. Essentially, Wang et al. compare the $T$ term to the ($P_{O_3} - L_{O_3}[O_3]$) term and we compare the $T$ term to the $P_{O_3}$ term to derive our differing conclusions.

Gross O$_3$ production rates were calculated to increase linearly with NO$_x$ throughout the range of NO$_x$ observed during TOPSE. In February, the optimum NO$_x$ mixing ratio to maximize $P_{O_3}$ occurs at NO$_x$ $\sim$ 300 pptv. This optimum NO$_x$
increased to NO$_x$ $\sim$ 500 pptv in May due to the higher P$_{RO}$ rates in spring. These optimum NO$_x$ levels are considerably lower than calculations for urban centers where [NO$_x$] $>$ 1 ppbv are necessary to maximize P$_O$; however, the range of NO$_x$ between 300–500 pptv is still more than a factor of 10 higher than the median measured values during TOPSE. The threshold for net positive O$_3$ production increased from NO$_x$ $\sim$ 10 pptv in February to NO$_x$ $\sim$ 25 pptv in May suggesting that the NO$_x$ levels needed to sustain net positive O$_3$ production are considerably lower in winter than spring. These higher minimum NO$_x$ levels in winter partly explain why wintertime photochemical O$_3$ production impacts the build-up of O$_3$ over winter and early spring. There is also a dependence on altitude as the NO$_x$ threshold needed to produce net O$_3$ shifts to higher NO$_x$ at lower altitudes. This likely explains why we calculate net O$_3$ destruction for the 1–3 km layer and net O$_3$ production for the 3–6 km layer. Overall, median NO$_x$ levels observed in the arctic free troposphere are considerably lower than the NO$_x$ levels associated with peak gross O$_3$ production rates. As a result, possible future increases in NO$_x$ in the arctic free troposphere will translate into greater O$_3$ production throughout the winter-to-spring transition.

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