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Authors
Wang, Y
Ridley, B
Fried, A
et al.

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Springtime photochemistry at northern mid and high latitudes

Yuhang Wang,1 Brian Ridley,2 Alan Fried,2 Christopher Cantrell,2 Douglas Davis,1 Gao Chen,1 Julie Snow,3 Brian Heikes,3 Robert Talbot,4 Jack Dibb,4 Frank Flocke,2 Andrew Weinheimer,2 Nicola Blake,5 Donald Blake,5 Richard Shetter,2 Barry Lefer,2 Elliot Atlas,2 Michael Coffey,2 Jim Walega,2 and Brian Wert2

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[1] Physical and chemical properties of the atmosphere at 0–8 km were measured during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiments from February to May 2000 at mid (40°–60°N) and high latitudes (60°–80°N). The observations were analyzed using a diel steady state box model to examine HOx and O3 photochemistry during the spring transition period. The radical chemistry is driven primarily by photolysis of O3 and the subsequent reaction of O(1D) and H2O, the rate of which increases rapidly during spring. Unlike in other tropospheric experiments, observed H2O2 concentrations are a factor of 2–10 lower than those simulated by the model. The required scavenging timescale to reconcile the model overestimates shows a rapid seasonal decrease down to 0.5–1 day in May, which cannot be explained by known mechanisms. This loss of H2O2 implies a large loss of HOx resulting in decreases in O3 production (10–20%) and OH concentrations (20–30%). Photolysis of CH3O2, either transported into the region or produced by unknown chemical pathways, appears to provide a significant HOx source at 6–8 km at high latitudes. The rapid increase of in situ O3 production in spring is fueled by concurrent increases of the primary HOx production and NO concentrations. Long-lived reactive nitrogen species continue to accumulate at mid and high latitudes in spring. There is a net loss of NOx to HNO3 and PAN throughout the spring, suggesting that these long-term NOx reservoirs do not provide a net source for NOx in the region. In situ O3 chemical loss is dominated by the reaction of O3 and HO2, and not that of O(1D) and H2O. At midlatitudes, there is net in situ chemical production of O3 from February to May. The lower free troposphere (1–4 km) is a region of significant net O3 production. The net production peaks in April coinciding with the observed peak of column O3 (0–8 km). The net in situ O3 production at midlatitudes can explain much of the observed column O3 increase, although it alone cannot explain the observed April maximum. In contrast, there is a net in situ O3 loss from February to April at high latitudes. Only in May is the in situ O3 production larger than loss. The observed continuous increase of column O3 at high latitudes throughout the spring is due to transport from other tropospheric regions or the stratosphere not in situ photochemistry. INDEX TERMS: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0324 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: springtime, ozone, HOx, oxidation, reactive nitrogen


1School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.
2National Center for Atmospheric Research, Boulder, Colorado, USA.
3Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, USA.
4Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, New Hampshire, USA.
5Department of Chemistry, University of California at Irvine, Irvine, California, USA.

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1. Introduction

[2] Oxidation processes in the troposphere are important pathways that mitigate the effects of human activities on the environment. These processes are intertwined in a tightly coupled photochemical system that involves among others HOx (OH + HO2), O3, NOx (NO + NO2), CO, and hydrocarbons. Spring at northern mid and high latitudes is a particularly interesting and challenging time to study the system because of the rapidly changing photochemical environment driven in part by increasing solar insolation.
Previous understanding for the spring period is largely based on surface measurements and ozonesondes. Logan [1985] showed on the basis of ozonesonde measurements a ubiquitous springtime O$_3$ maximum in the lower troposphere at remote northern mid and high latitude sites. The springtime O$_3$ maximum at rural sites is in contrast to the summertime O$_3$ maximum at polluted sites. Two factors have been attributed to the observed springtime ozone maximum, O$_3$ transport from the stratosphere [Logan, 1985; Levy et al., 1985] and O$_3$ production within the troposphere [Penkett and Brice, 1986; Liu et al., 1987]. Measurements in the Swiss Alps (at an altitude of 3.6 km) from the Free Tropospheric Experiment (FREETEX’96 and 98) suggested that the net in situ chemical production of O$_3$ from the Free Tropospheric Experiment (FREETEX’96 and Measurements in the Swiss Alps (at an altitude of 3.6 km) contributed significantly to the observed spring-summer maximum in the region [Crawford et al., 2000; Zanis et al., 2000]. Among global 3-D modeling studies of tropospheric O$_3$, Wang et al. [1998] and Yienger et al. [1999] investigated in detail the sources of the observed springtime O$_3$ maximum. While the former study showed that both factors contributed to the simulated springtime O$_3$ maximum with one peaking in early spring and the other peaking in early summer, the latter study emphasized the effect of net O$_3$ chemical production at midlatitudes. Possible accumulation of pollutants at high latitudes in winter [Honrath and Jaffe, 1992; Jobson et al., 1994; Novelli et al., 1994; Bottenheim and Shepherd, 1995; Honrath et al., 1996] may also enhance photochemistry in spring at mid and high latitudes.

The Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment took place in February–May 2000 (E. Atlas et al., The TOPSE experiment: Introduction, submitted to Journal of Geophysical Research, 2002, hereinafter referred to as Atlas et al., submitted manuscript, 2002). Forty two C-130 flights (including 4 test flights) in between Jeffco, Winnipeg, Churchill, and Thule were conducted in 7 deployments, 1–2 weeks apart. A broad suite of in situ measurements of meteorological parameters, trace gases, and aerosols were made from near the surface up to 8 km. The seasonal span of the experiment allows for analyzing the springtime evolution of photochemistry at northern mid and high latitudes.

We describe in section 2 the model and data processing procedures used in this work. In section 3 we examine various aspects of HO$_3$ chemistry. Contributions of primary HO$_3$ production and NO$_x$ concentrations to in situ O$_3$ production are investigated in section 4. Budgets of reactive nitrogen and O$_3$ are studied in section 5 to explore the sources of observed O$_3$ and NO$_x$. We summarize our findings in section 6.

2. Model Description and Data Processing

A box model is applied in the analysis of in situ photochemistry. The model has been used previously in analyzing observations from other aircraft missions [Davis et al., 1996, 2001; Crawford et al., 1997, 1999; Chen et al., 2001]. The kinetics data for O$_3$-NO$_x$-CO-hydrocarbon reactions are taken from DeMore et al. [1997] and Atkinson et al. [1997]. Crawford et al. [1999] listed the reaction rate constants used in the model. Photolysis rate coefficients are first computed using the DISORT 4-stream NCAR Tropospheric Ultraviolet-Visible (TUV) radiative transfer code (by S. Madronich). The quantum yield and absorption cross-section data are those reported by DeMore et al. [1997]; the quantum yield of O(1D) is from Talukdar et al. [1998]. The photolysis rates are then constrained by the observed J values [Shetter et al., 2002] to account for cloud and surface reflectivity.

The model is constrained by the observations of O$_3$, NO, CO, nonmethane hydrocarbons (NMHCs), temperature, and water vapor. Concentrations of H$_2$O$_2$, CH$_3$OOH, and CH$_2$O are constrained in some simulations (see figure captions for details). All model parameters except NO and photolysis rates are held constant in multiple-day runs. The concentrations of NO$_2$ (NO + NO$_2$) are held at constant values that give the observed NO concentrations at the time of the observation. The model converges and results are reported when the diurnal cycles of calculated concentrations do not vary from day to day.

Measurement techniques and related data issues are discussed in the companioning papers in the special issue (see Atlas et al. (submitted manuscript, 2002) for a guide). The 1-min merged data file (courtesy of L. Emmons) is used except the data for CH$_3$O. The updated data [Fried et al., 2002], where the interference from CH$_3$OH was removed, are used. Observations that show the imprints of Br and Cl chemistry are removed by eliminating data points with O$_3$ concentrations <20 ppbv or depleted C$_2$H$_2$ relative to benzene [Jobson et al., 1994]; these data were found at altitudes of <1 km above the surface. Data points with O$_3$ concentrations > 100 ppbv are also eliminated to remove the influence of stratospheric air masses.

Concentrations of CO were measured with two different instruments. The whole air samples were collected and analyzed later using gas chromatographic apparatus [Blake et al., 2002] (hereafter UCI CO). The sampling frequency is 1–5 min. A fast-response 1 Hz tunable diode laser system from NCAR (hereafter NCAR CO) was also employed. The sensitivity of the instrument is about 1 ppbv for the 30-sec averages reported. Measurements of this instrument are in good agreement with limited whole air canister samples analyzed by gas chromatography at NCAR (M. T. Coffey, personal communication, 2001). However, the UCI CO data are on average 8 ppbv lower than NCAR CO measurements. The root mean square of the difference is 14 ppbv. The reasons for the discrepancies between the two measurements are unclear. In our analysis, we use both measurements to increase the available pool of measured data. When both measurements are available, averages are used.

Acetone was not measured during TOPSE. We applied the observed acetone-CO correlations during the SONEX experiment [Singh et al., 2000]. A least squares fit of SONEX observations at 2–7 km gives [acetone] = 8 + 6.8 ([CO] – 10), where acetone is in pptv and CO is in ppbv. NMHCs and CO were measured using the whole air samples [Blake et al., 2002]. The relatively low sampling frequency of NMHCs reduced the available data points by half in the photochemical analysis. We made use of the faster-response NCAR CO measurements to estimate NMHC concentrations in a similar manner as in estimating acetone concentrations. We first find the least squares fits of NMHCs to NCAR CO and then interpolate NMHC concentrations.
concentrations for the NCAR CO data that do not overlap with the NMHC measurements. The fitting and interpolation are conducted for each month in two regions (40°–60°N and 60°–80°N) for each 2-km altitude bin from 0 to 8 km since much of our analysis in the following sections focuses on the monthly and regional characteristics. The procedure doubles the availability of measurement points, providing better statistical significance of the median values of key variables discussed in the following sections. The uncertainties introduced in these procedures will be taken into account in the analysis.

3. Odd Hydrogen

[11] Hydroxyl radicals are central to oxidation chemistry in the troposphere. Their chemical cycles are intrinsically connected to those of O₃. Carbon monoxide, CH₄, and NMHCs are oxidized by OH and peroxy radicals are produced. Peroxy radicals are recycled back to OH by NO, which is oxidized to NO₂. The oxidation cycle leads to O₃ production by NO₂ photolysis. Generally speaking, higher concentrations of O₃ and NO tend to increase OH concentrations and higher concentrations of CO and hydrocarbons tend to decrease OH concentrations. Figure 1 shows the observed monthly median profiles of O₃, NO, C₂H₂, and CO for mid (40°–60°N) and high latitudes (60°–80°N). Median concentrations of O₃ are comparable between mid and high latitudes. The increase of 10–30 ppbv O₃ from February to May is more pronounced at high latitudes. Concentrations of NO are much higher at midlatitudes, where the seasonal increase is about a factor of 2 (10–30 ppbv); the seasonal increase of NO at high latitudes is a factor of 3–5 (about 10 ppbv). In comparison, concentrations of C₂H₂ show a large seasonal decrease by a factor of 2–3 from February to May. This decrease was also observed for the concentrations of other NMHCs. There is a general decreasing trend for CO; however the trend is much smaller than that of C₂H₂, reflecting in part that photochemistry is both a source and sink for CO but only a sink for NMHCs. The dichotomy in the seasonal trends of O₃ and NO as compared to those of NMHCs and CO signifies the rapid increase of photochemical activity in springtime.

[12] Figure 2 shows simulated monthly median profiles of 24-hour average OH at mid and high latitudes. The model is constrained by observed peroxy concentrations. Only model results are shown because available OH measurements are limited to altitudes below 3 km and the overlapping measurement and simulation data points are few. The concentrations of OH increase significantly through the spring. Their values at high latitudes are significantly less than at midlatitudes reflecting in part the regional difference in solar irradiance and NO concentrations.

[13] Observed and simulated concentrations of total peroxy radicals (RO₂ = HO₂ + organic peroxy radicals) show a similar seasonal trend as OH (Figure 3). Simulated RO₂ concentrations are generally in good agreement with the observations although the model results are too high at midlatitudes in March. Among peroxy radicals, HO₂ and CH₂O₂ are the major components. Detailed analysis of peroxy radical chemistry is carried out by Cantrell et al. [2002]. Comparison between simulated and observed HO₂ concentrations is not made since <20 observational data points are available.

3.1. Slowdown of HOₓ Cycles: Heterogeneous Loss of H₂O₂

[14] We use the model to examine the cycling of odd hydrogen. The largest primary source of HOₓ in the troposphere is by photolysis of O₃ and the subsequent reaction of O(¹D) and H₂O [Logan et al., 1981]. This source is considered a primary source because its magnitude is largely independent of the HOₓ cycling. In comparison, H₂O₂, CH₂OOH, and other peroxides are produced chemically from the reaction of HO₂ and another peroxy radical, both of which are produced during OH oxidation of CO and hydrocarbons. Their photolysis cycles peroxides back to HOₓ and provides large HOₓ sources. They are generally considered secondary HOₓ sources because of their large dependence on OH oxidation. Photolysis of CH₂O is generally considered a secondary source because CH₂O is largely produced from hydrocarbon oxidation, whereas photolysis of acetone is generally a primary source [McKeen et al., 1997].

[15] Figure 4 shows the seasonal profiles of main HOₓ sources (24-hour averages) at mid and high latitudes. The three dominant HOₓ sources are O(¹D) + H₂O and photolysis of CH₂O and CH₂OOH. The latter two sources are particularly important at high altitudes. The large seasonal increase in the rate of O(¹D) + H₂O is due the increase of solar insolation, O₃ concentrations (Figure 1), and H₂O content of the atmosphere (not shown). The last factor is associated with the seasonal warming of the atmosphere, which increases the saturation vapor pressure. We will show that most of CH₂O and CH₂OOH concentrations are produced by in situ photochemistry. Therefore these two photolysis sources are largely secondary. As a result, the activation of photochemistry in early spring at midlatitudes and in late spring at high latitudes, as evidenced in the seasonal increase of OH and RO₂ concentrations (Figures 2 and 3), is largely driven by the radical source of O₃ photolysis followed by the reaction of O(¹D) and H₂O.

[16] The relatively large HOₓ source from CH₂OOH photolysis stands in sharp contrast to the much smaller source from H₂O₂ photolysis. The contrast can be seen more clearly in the comparison of observed and simulated peroxide concentrations. Figure 5 compares observed and simulated H₂O₂ monthly median profiles at mid and high latitudes. Simulated H₂O₂ concentrations are a factor of 2–10 higher than the observations; the overestimates increase with decreasing altitude. In comparison, Figure 6 shows that simulated CH₂OOH concentrations are generally in agreement with the observations. Using the rate constant of the HO₂ self reaction suggested recently by Christensen et al. [2002], we find that simulated H₂O₂ concentrations decrease by 20–30% at 6–8 km and 5–15% at 0–4 km; the large model overestimates remain. The new rate constant has little effects on simulated OH and HO₂ concentrations.

[17] The measurement-model agreement of CH₂OOH at midlatitudes is, however, not as good as those found in the tropics [Wang et al., 2000, 2001]. Particularly noteworthy is that simulated CH₂OOH profiles have a consistent tendency of decreasing with altitude, which is in accordance with the observed profiles of RO₂ concentrations (Figure 3). The observed CH₂OOH profiles, however, show this altitude...
dependence in some months but not in others. In particular, the observed profile at midlatitudes in March shows increasing concentrations with altitude, opposite to the trend simulated in the model, resulting in large discrepancies between observed and simulated values. The model underestimate at 5–8 km is particularly large considering that the model overestimates peroxy radical concentrations in that month (Figure 3). The photochemical lifetime of CH$_3$OOH

Figure 1. Monthly median profiles of observed O$_3$, NO, C$_2$H$_2$, and CO concentrations at mid (40°–60°N) and high latitudes (60°–80°N). Data are binned vertically in 1-km intervals. A median value plotted represents a minimum of 10 data points.
is generally several weeks or longer during TOPSE. We examined the 10-day backtrajectories (courtesy of A. Wimmers and J. Moody). Above 4 km, the general flow is controlled by strong westerlies. Some enhancements of CH$_3$OOH are possible in the upper troposphere due to vertical transport in the upstream regions [e.g., Prather and Jacob, 1997]. Wang et al. [2001] estimated that the convective enhancement of CH$_3$OOH over the tropical Pacific during PEM-Tropics B is only 50–150 pptv (above 10 km) despite the short convective turnover timescale of 10 days.
The concentration of CH$_3$OOH in the tropical marine boundary is about 1 ppbv. In that work, concentrations of CH$_3$OOH are lowered by up to 100 pptv at 4–7 km due in part to the subsidence of lower concentrations from higher altitudes. Considering that boundary layer CH$_3$OOH concentrations in the TOPSE region are only 200–300 pptv, the likely source for high CH$_3$OOH air masses to the region is from convective transport over the Pacific. The backtrajectory analysis shows, however, flow patterns in April and May similar to that in March. We also examined other chemical tracers but did not find clear signals implicating strong influence by marine air masses in March. The overestimates at 0–4 km may reflect peroxy radical depletion by fresh NO emissions in the upstreamflow from western United States and Canada. A chemistry and transport model will be necessary to explore further the causes for the observed vertical trend of CH$_3$OOH at midlatitudes in March.

At first glance, the large overestimates of H$_2$O$_2$ concentrations but not CH$_3$OOH might be due to wet scavenging, which efficiently removes soluble H$_2$O$_2$ but not CH$_3$OOH. Wang et al. [2001] showed convective scavenging over the tropical Pacific decreases H$_2$O$_2$ concentrations by about 30%. Estimating the magnitude of wet scavenging on the basis of meteorological measurements during TOPSE is difficult. Instead we compare the degree of heterogeneous loss of two soluble tracers, H$_2$O$_2$ and HNO$_3$. Concentrations of HNO$_3$ are also overestimated in the model (not shown). Figure 7 shows the seasonal progression of photochemical lifetimes of the two species through the spring at mid and high latitudes. The photochemical lifetimes are getting shorter into the summer because of increasing photochemical activity. The photochemical lifetime of HNO$_3$ is generally about a factor 10 longer than H$_2$O$_2$. Furthermore, the solubility of HNO$_3$ is higher than H$_2$O$_2$, making HNO$_3$ concentrations more sensitive to wet scavenging and deposition loss.

Assuming gas phase oxidation (by OH), photolysis, and scavenging are the pathways for removal of H$_2$O$_2$ and HNO$_3$, we calculate the scavenging timescales necessary to match the observed concentrations in the model (Figure 8). The required timescales for HNO$_3$ scavenging are consistent with known rainout frequency and high solubility of HNO$_3$. The required scavenging is much faster at midlatitudes than at high latitudes, reflecting more frequent rainout at midlatitudes. The general trend of decreasing scavenging with altitude is also consistent with the distribution of rainout. The timescales of HNO$_3$ against scavenging loss are about 1 week at midlatitudes and 2–4 weeks at high latitudes. Our estimates of HNO$_3$ scavenging timescale are likely the upper limits since we do not take into account the heterogeneous production of HNO$_3$ by N$_2$O$_5$ hydrolysis on aerosols, which could be significant particularly at midlatitudes [Tie et al., 2002]. Nonetheless, the derived timescales are in line with the estimates derived from a global 3-D study of the observed $^{210}$Pb distributions by Balkanski et al. [1993].

The required timescales of H$_2$O$_2$ scavenging are more difficult to understand. First, the required scavenging...
frequency of $\text{H}_2\text{O}_2$ is up to a factor of 10 faster than that of $\text{HNO}_3$. In May, the loss by scavenging is about half a day at midlatitudes and 1 day at high latitudes. Second, the required scavenging frequency of $\text{H}_2\text{O}_2$ is more seasonal than that of $\text{HNO}_3$. The seasonal increase of the former is about a factor of 5 at mid and high latitudes. In contrast, the scavenging frequency of $\text{HNO}_3$ shows no clear seasonal change at midlatitudes and a much smaller increase (mostly

Figure 3. Monthly median profiles of observed and simulated total peroxy radicals ($\text{RO}_2$) at mid and high latitudes. The solid vertical lines show the observed medians in 1-km intervals. The solid horizontal lines and asterisks are the observed standard deviations and means, respectively. Simulated medians and standard deviations are shown in dashed lines. Model calculations are constrained by observed peroxide concentrations. Each observation data point has a corresponding simulated value and vice versa. A median value plotted represents a minimum of 10 data points. Not enough data are available for February.
from April to May) at high latitudes. Simple rainout that applies both to HNO₃ and H₂O₂ cannot explain the different characteristics in the required scavenging frequencies of the two species and the rapid rates of H₂O₂ removal at mid-latitudes. Similar results for H₂O₂ scavenging are obtained when using the rate constant of the HO₂ self reaction recommended by Christensen et al. [2002]. One possible pathway is heterogeneous removal of H₂O₂ by SO₂ oxida-

Figure 4. Same as Figure 1 but for simulated 24-hour average HOₓ sources. The model is constrained with observed peroxide and CH₂O concentrations. The HOₓ yield of CH₂O photolysis is computed on line.
tion in droplets [e.g., Hoffmann and Edwards, 1975]. The observed monthly median profiles of SO₂ concentrations (not shown) peak in February and are lowest in May. The concentrations are generally in the range of 10–60 pptv, which are too low to account for significant H₂O₂ loss. Furthermore, considering that the average photochemical steady state concentrations of H₂O₂ are >1 ppbv at mid-latitudes from March to May and that the required scavenging lifetime is <1 day, the supply of SO₂ to the TOPSE region needs to be >1 ppbv/day. In terms of the sulfur

Figure 4. (continued)
Figure 5. Same as Figure 3 but for $\text{H}_2\text{O}_2$. The model is not constrained by observed peroxides.
Figure 6. Same as Figure 3 but for CH$_3$OOH. The model is constrained by observed H$_2$O$_2$ concentrations.
Figure 7. Same as Figure 1 but for simulated photochemical lifetimes of H₂O₂ and HNO₃.
Figure 8. Same as Figure 1 but for estimated scavenging timescales of H$_2$O$_2$ and HNO$_3$ necessary to explain the observed concentrations.
budget, it implies a $\text{SO}_2$ wet deposition rate for the TOPSE region of $>2.5 \text{ g S m}^{-2} \text{ yr}^{-1}$, a rate more than 1 order of magnitude larger than estimated by Langer and Rodhe [1991]. Other $\text{SO}_2$ like compounds are necessary to explain the derived scavenging rates.

[21] A survey of previous comparisons of simulated and observed $\text{H}_2\text{O}_2$ concentrations suggests that the rapid scavenging loss required for TOPSE observations is unique. The box models used in the analyses cited below are similar to the one used in this study and $\text{H}_2\text{O}_2$ was measured in a similar manner in those field experiments as during TOPSE. Davis et al. [1996] showed relatively good agreement between simulated and observed $\text{H}_2\text{O}_2$ during PEM-West A over the western Pacific (September–October). Heterogeneous removal of $\text{H}_2\text{O}_2$ was assumed in that model to have a timescale of 5 days below 4 km and longer at higher altitude. Jacob et al. [1996] found that the model could account for most of the observed $\text{H}_2\text{O}_2$ at 0–8 km during TRACE-A over the tropical South Atlantic (September–October). Schultz et al. [1999] found good simulation–measurement agreement at 2–8 km but the model was too high by a factor of 2 at 0–2 km during PEM-tropics A over the tropical Pacific (August–September). Jaegle et al. [2000] showed reasonable agreement between simulated and observed $\text{H}_2\text{O}_2$ during SONEX over the North Atlantic (October–November). Unlike in the work by Davis et al. [1996], no heterogeneous loss of $\text{H}_2\text{O}_2$ was included in the other three works. The latter two studies included heterogeneous production of $\text{H}_2\text{O}_2$ from $\text{HO}_2$ on aerosols. The rate of heterogeneous production used by Schultz et al. [1999] is $\text{H}_2\text{O}$ dependent with a $\gamma$ of 0.1 whereas that by Jaegle et al. [2000] depended only on $\text{HO}_2$ and aerosol surface area with a $\gamma$ of 0.2. Without the heterogeneous production, model results would be considerably lower than observations in the work by Jaegle et al. [2000]. It is unclear what effects heterogeneous production had in the work by Schultz et al. [1999], particularly how much it contributed to the model overestimates at 0–2 km. Wang et al. [2000] showed that a 1-D model with a column convective turnover timescale of 20 days could largely reproduce the observed profile of $\text{H}_2\text{O}_2$ during PEM-Tropics A.

[22] The required scavenging loss of $\text{H}_2\text{O}_2$ implies rapid removal of a large reservoir of $\text{HO}_2$ and consequently slows down the $\text{HO}_2$ cycles and $\text{O}_3$ production. Figure 9 shows the ratios of 24-hour average $\text{HO}_2$ production, $\text{OH}$ concentrations, and $\text{O}_3$ production in the simulations using observed versus simulated $\text{H}_2\text{O}_2$ concentrations. The relative effects are similar at mid and high latitudes and among different months. The decrease of $\text{HO}_2$ source from the photolysis of $\text{H}_2\text{O}_2$ leads to a loss of 20–40% in the production of $\text{HO}_2$. The decrease of 20–30% in $\text{OH}$ concentrations is larger than that of 10–20% for the peroxy radicals (not shown), which results in a similar decrease in $\text{O}_3$ production. The photochemical loss (and hence the net production or loss) also decreases in a similar proportion, reflecting the importance of the reaction of $\text{O}_3$ and $\text{HO}_2$ in $\text{O}_3$ loss (section 5).

3.2. $\text{CH}_2\text{O}$ as a Large Source of $\text{HO}_x$ at Northern High Latitudes

[23] Among the $\text{HO}_x$ sources shown in Figure 4, the photolysis of $\text{CH}_2\text{O}$ is particularly large. Relative to the total $\text{HO}_x$ source, it is larger at higher altitudes and latitudes where the decrease of $\text{H}_2\text{O}$ vapor concentrations with temperature reduces the source from the reaction of $\text{O}^{	ext{(1D)}}$ and $\text{H}_2\text{O}$. This $\text{HO}_x$ source often reflects the auto-catalytic nature of the $\text{HO}_x$ cycles since $\text{CH}_2\text{O}$ is largely produced during the OH oxidation of hydrocarbons.

[24] However, standard gas-phase photochemistry alone cannot explain the observed $\text{CH}_2\text{O}$ concentrations at high altitudes in northern high latitudes, where $\text{CH}_2\text{O}$ photolysis is of great importance to the $\text{HO}_x$ budget. Figure 10 compares model simulated median profiles of $\text{CH}_2\text{O}$ with observations. Simulated median $\text{CH}_2\text{O}$ concentrations are generally within the standard deviation of the observed concentrations. Whereas good agreement was found for midlatitude observations, simulated $\text{CH}_2\text{O}$ concentrations were much lower at high latitudes in March. These underestimates are particularly large at higher altitudes. Fried et al. [2002] further examined the model underestimates and investigated a number of possibilities that could increase $\text{CH}_2\text{O}$ production at high latitudes and altitudes, including direct production from the reaction of $\text{CH}_3\text{O}_2$ and $\text{HO}_2$ [Ayers et al., 1997], the decomposition of $\text{CH}_3\text{OONO}_2$ [Cantrell et al., 2002], and heterogeneous conversion of $\text{CH}_3\text{OH}$ to $\text{CH}_2\text{O}$ in aerosols [Singh et al., 2000]. They found no clear evidence attributing the observed excess $\text{CH}_2\text{O}$ to these pathways. Another hypothesis is mixing between mid and high latitude air masses enhances $\text{CH}_2\text{O}$ concentrations at high latitudes.

[25] Simulated $\text{CH}_2\text{O}$ concentrations are affected by $\text{CH}_2\text{OOH}$ concentrations [Liu et al., 1992]. The sensitivity varies. The model underestimates at high altitudes are larger when model simulated $\text{CH}_2\text{OOH}$ concentrations are used instead of observed $\text{CH}_2\text{OOH}$ (Figure 11). The effect is particularly large at 6–8 km in March; using observed in place of simulated $\text{CH}_2\text{OOH}$ concentrations in the model increases $\text{CH}_2\text{O}$ concentrations by about 50–100% (20–30 pptv). In general, the enhancements are above 4 km; the increase is about 10–40% in April and May. The assumption used to calculate acetone concentrations by scaling to $\text{CO}$ concentrations is another factor contributing to the uncertainty in the simulated $\text{CH}_2\text{O}$ concentrations. Jacob et al. [2002] suggested that acetone concentrations are lower in winter and spring than in the fall due to the loss of acetone to the oceans. Reducing our estimated acetone concentrations by half matches the levels (300–600 ppbv) simulated by Jacob et al. [2002] for North America in January. The lowering of acetone concentrations decreases simulated $\text{CH}_2\text{O}$ concentrations by 10–20% above 5 km, which will increase the underestimates by the model.

[26] It is unclear if the additional $\text{CH}_2\text{O}$ beyond the level that can be sustained by the standard gas-phase photochemistry is a primary or secondary source of $\text{HO}_x$ at high altitudes since the nature of the model underestimate is unknown. However, we can examine the various hypotheses more closely. If the additional $\text{CH}_2\text{O}$ is due to transport or conversion of $\text{CH}_3\text{OH}$ in aerosols, its photolysis increases the primary $\text{HO}_2$ source. If it is due to production from the reaction of $\text{CH}_3\text{O}_2$ and $\text{HO}_2$ or from $\text{CH}_3\text{OONO}_2$ decomposition, the additional $\text{HO}_2$ source is secondary. Boosting the secondary $\text{HO}_2$ source implies more efficient yields of $\text{CH}_2\text{O}$ from hydrocarbon oxidation. Considering that $\text{CH}_4$ oxidation provides about 70–80% of the total $\text{CH}_2\text{O}$ source...
Figure 9. The monthly median ratios of simulated 24-hour average HO\textsubscript{x} production, OH concentrations, and O\textsubscript{3} production with relative to without constraining H\textsubscript{2}O\textsubscript{2} to the observed values in the model. A median value plotted represents a minimum of 10 data points.
and that the yield of CH$_2$O from this oxidation is already close to 1 in the box model (with no heterogeneous loss of CH$_3$OOH assumed), it is unlikely that these pathways will significantly increase CH$_2$O concentrations to make up for the large underestimates shown in Figure 10. Therefore, it is more likely that the additional HO$_x$ source from CH$_2$O photolysis is primary.

[27] Figure 12 shows the ratios of 24-hour average HO$_x$ production, OH concentrations, and O$_3$ production in the simulations using observed versus simulated CH$_2$O concentrations. The effects are significant at high latitudes above 6 km and are larger in March than in May. The largest effect is seen in the total production of HO$_x$, decreasing from a factor of 2 to 30% from March to May above 6 km at high latitudes. In the region, the concentrations of OH and HO$_2$ (not shown) and the production of O$_3$ increase by 20–50%. The seasonal decrease in the relative contribution of the “excess” CH$_2$O to HO$_x$ reflects in part the increasing contribution from the reaction O(1D) and H$_2$O to the HO$_x$ source with time and in part lesser underestimates by the model in late spring [Fried et al., 2002]. The effects are minimal at midlatitudes where simulated and observed CH$_2$O concentrations are in better agreement. Photolysis of acetone also affects HO$_x$ chemistry at high altitudes [e.g., McKeen et al., 1997]. During the TOPSE period, it is not the dominant HO$_x$ sources (Figure 4). Reducing acetone concentrations estimated in the model by half decreases HO$_x$ production by up to 12 and 20% at mid and high latitudes (>6 km), respectively. The effects on the concentration of OH and O$_3$ production are around 10% at altitude above 6 km. The effects are insignificant below 4 km where the source from the reaction of O(1D) and H$_2$O dominates HO$_x$ production.

4. Nitrogen Oxides and In Situ O$_3$ Production

[28] Figure 13 compares simulated and observed monthly median profiles of NO$_2$ at mid and high latitudes. Although the simulated median profiles of NO$_2$ at given altitude bins are within the observed monthly standard deviations, which are often larger than the scale of the plots and are hence not shown, simulated NO$_2$ concentrations tend to be lower than the observations. The underestimates are largest above 6 km (about 10 pptv). Some of the discrepancies can be attributed to the measurement uncertainty, which increases with altitude from 3 pptv to 8 pptv. The increasing measurement uncertainties with altitude are also reflected in the increasing proportion of data near the detection limits, reaching 50% at 6–8 km. The model overestimate at 1–2 km in February at midlatitudes is due to some high concentration plumes sampled by the C-130. On the basis of observed NO concentrations, the model predicts broader plumes than found in the NO$_2$ measurements. When model points with no corresponding NO$_2$ measurements are included, the median model value drops to 25 pptv and is in agreement with the observations. The seasonal increase of NO concentrations during TOPSE is shown in Figure 1. In comparison, the seasonal increase of NO$_2$ is much smaller, reflecting the shift of NO$_x$ partition toward NO as photolysis of NO$_2$ increases with time.
Figure 10. Same as Figure 3 but for CH$_2$O. A median value plotted represents a minimum of 5 data points.
[29] Jaeglé et al. [1999] mapped O₃ production as a function of the primary source of HOₓ and NOₓ concentration for the observations during SONEX. Figure 14 shows the mapping for TOPSE observations, where the primary HOₓ source is driven mostly by the reaction of O(1D) and H₂O. Compared with SONEX, two features stand out. First, there is a clear positive correlation between primary HOₓ production and NOₓ concentrations, whereas Jaeglé et al. [1999] found marine convected air masses (over the North Atlantic) with high primary HOₓ production but low NOₓ concentrations during SONEX. During TOPSE, the positive correlation reflects the convergence of favorable photochemical environment (Figure 4) and increasing NOₓ concentrations. Second, in the same range of primary HOₓ production rates and NOₓ concentrations, the O₃ production rates are similar between TOPSE and SONEX despite that our work is for 0–8 km in spring and the work by Jaeglé et al. [1999] is for 8–12 km in the fall.

A casual look of the first panel of Figure 14 would suggest that the primary HOₓ production does not play a significant role in the production rate of O₃. Part of the insensitivity of O₃ production to the primary HOₓ source is due to the rapid increase of NO/NO₂ ratio with altitude, which is driven by the temperature dependence of the NO + O₃ reaction and the altitude dependence of air density and photon flux. The same amount of NOₓ is therefore more effective in O₃ production at high altitudes where NO/NO₂ ratio is high since the production is driven by the reaction of NO with peroxy radicals. This effect combined with a decreasing trend of the HOₓ primary production with altitude tends to mask the contribution of the primary HOₓ source to O₃ production.

We therefore mapped O₃ production as a function of NO in Figure 14 as well. At NO levels above 10 pptv, it is clear that increasing the primary HOₓ source enhances O₃ production. Considering that the range of the primary HOₓ source spans about 4 orders of magnitudes, the efficiency of primary HOₓ production in boosting O₃ production ($\frac{\partial P(O_3)}{\partial P(HO_x)}$) is less than that of NOₓ (or NO). However, it should be noted that the increase of primary HOₓ production through the spring is much more rapid than that of NO (Figures 1 and 4). The large dependence of O₃ production on NO concentrations reflects a NOₓ-limited photochemical regime during TOPSE.

5. Budgets of Reactive Nitrogen and O₃

[32] Penkett and Brice [1986] used the rapid buildup and loss of peroxyacetyl nitrate (PAN) at a rural site in spring as a proxy to suggest that intensifying photochemistry activity contributes to the observed springtime O₃ maximum. Honrath et al. [1996] further suggested that the accumulation of reactive nitrogen at winter high latitudes and the subsequent decomposition of these reservoirs back to NOₓ in spring could contribute to the observed springtime maximum.
Figure 15 shows the monthly median profiles of total reactive nitrogen (NO\textsubscript{y}) and PAN concentrations at mid and high latitudes. The most abundant NO\textsubscript{y} component is PAN accounting for 40–80% of NO\textsubscript{y}. The PAN fraction in NO\textsubscript{y} decreases with season. The continually increasing concentrations of NO\textsubscript{y} and PAN in the most part of the troposphere show no evidence for wintertime accumulation at high latitudes followed by springtime transport to midlatitudes.

Figure 12. The monthly median ratios of simulated 24-hour average HO\textsubscript{x} production, OH, and O\textsubscript{3} production with relative to without constraining CH\textsubscript{2}O to the observed values in the model. Peroxides in the model are specified as observed. Each median value represents a minimum of 5 data points.
Free tropospheric measurements are particularly important in understanding the seasonality of reactive nitrogen species at mid and high latitudes because the seasonal trends are quite different near the surface from that in the free troposphere. Concentrations of NO\textsubscript{y} and PAN above 3 km continue to increase throughout the spring. The seasonal trend at lower altitudes is not as well defined as that at higher altitudes. The concentrations of NO\textsubscript{y} tend to peak in February near the surface; the seasonal maximum of PAN near the surface is shifted toward April particularly at midlatitudes.

The apparent disparity in the observed seasonal variations of NO\textsubscript{y} and PAN near the surface would imply that some major component of NO\textsubscript{y} decreases throughout the spring as NMHCs (Figure 1), particularly in light of the increasing HNO\textsubscript{3} concentrations with season (not shown). However, no such component is found. To illustrate the point, we show in Figure 15 the seasonal profiles of DNO\textsubscript{y}, defined as NO\textsubscript{y}/(NO + NO\textsubscript{2} + PAN + PPN + HNO\textsubscript{3} + 2N\textsubscript{2}O\textsubscript{5} + HNO\textsubscript{4}). Simulated N\textsubscript{2}O\textsubscript{5} and HNO\textsubscript{4} are used because these species were not measured. We also used model computed NO\textsubscript{2} concentrations to increase the availability of data points. Unlike in many tropospheric missions [e.g., Bradshaw et al., 2000], there is generally no need to invoke missing nitrogen species to account for measured NO\textsubscript{y} concentrations during TOPSE. The exception is in February when NO\textsubscript{y} concentrations are higher than the sums of individual components by 50–100 pptv. We note the extreme scarcity of overlapping reactive nitrogen data in February; the median profiles for that month are generated from 1–3 points at 1-km intervals. There is an opposite problem most of the time, i.e., measured NO\textsubscript{y} concentrations are not enough to match the sums of reactive nitrogen species. This shortfall from NO\textsubscript{y} measurements increases from March to May at both mid and high latitudes. Without counting model simulated HNO\textsubscript{4} concentrations, the shortfall can be largely eliminated at high altitudes but not at lower altitudes, where simulated HNO\textsubscript{4} concentrations are low due to relatively high temperatures. We note that DNO\textsubscript{y} carries the uncertainties in the measurements or model simulations of all the components. Detailed analysis of measurement uncertainties is carried out by F. Flocke et al. (The behavior of PAN and the balance of odd nitrogen during TOPSE, submitted to Journal of Geophysical Research, 2002). In particular, there is evidence for occasional interference of particulate and cloud nitrates in the HNO\textsubscript{3} measurements (Flocke et al., submitted manuscript, 2002).

We examine now the budget of reactive nitrogen during the TOPSE experiment. Among the reactive nitrogen reservoirs, PAN and HNO\textsubscript{3} concentrations are largest. Peroxypropionylnitrate is not simulated in the model. Its behavior follows closely that of PAN (Flocke et al., submitted manuscript, 2002); we hence expect its budget resembles that of PAN as well. Figure 16 shows the seasonal evolution of the net production rates for these two species at mid and high latitudes. Loss of NO\textsubscript{y} to HNO\textsubscript{3} is likely underestimated particularly at midlatitudes because heterogeneous conversion in aerosols via N\textsubscript{2}O\textsubscript{5} hydrolysis is not accounted for in the model. Loss of NO\textsubscript{y} to HNO\textsubscript{3} is much more significant at mid than high latitudes because of...
Figure 13. Same as Figure 5 but for NO₂. Line symbols are the same as Figure 3. Standard deviations are not shown because of the large data variability, which is reflected in the large differences between observed means and medians at mid latitudes.
higher OH concentrations at midlatitudes. The net loss of NO$_x$ to PAN is also more significant at about 2 pptv/day at midlatitudes than a rate of about 1 pptv/day at high latitudes. The loss is larger at higher altitudes because of the strong temperature dependence of PAN thermal decomposition. Unlike in the tropics where PAN decomposition provides the main NO$_x$ source in the lower troposphere [Schultz et al., 1999; Wang et al., 2001], PAN formation constitutes a net loss of NO$_x$ at all altitudes during TOPSE. Reducing acetone concentrations in the model by 50% decreases the net loss of NO$_x$ to PAN by 0.1–1 pptv/day at midlatitudes and <0.5 pptv/day at high latitudes. It appears clear that the decomposition of long-lived nitrogen reservoirs cannot explain the observed seasonal increase of NO$_x$ during TOPSE. Carpenter et al. [2000] also found that PAN decomposition did not contribute to NO$_x$ concentrations at the Jungfraujoch Observatory (3.6 km above sea level) in the Swiss Alps during FREETEX’98. These results are consistent with the finding by Wang et al. [1998] in a global 3-D model study that PAN formation and decomposition generally does not contribute significantly to the observed springtime O$_3$ maxima over northern mid and high latitude continents. More measurements are necessary to understand if and how the NO$_x$ source from PAN decom-

Figure 14. Numerical values of simulated 24-hour average O$_3$ production rates (ppbv/day) as a function of 24-hour average primary HO$_x$ production and NO$_x$ or NO concentrations. The primary HO$_x$ production is from the reaction of O(1D) and H$_2$O and photolysis of acetone. Constraining the model with observed peroxide and CH$_2$O concentrations would yield similar results but with much fewer data.
position in remote marine regions and lower latitudes contributes to the seasonal variability of ozone.

[16] The seasonal increases of NO and primary HO\textsubscript{x} production (Figures 1 and 4) result in increasing chemical production of O\textsubscript{3} (Figure 14). Figure 17 shows the budgets of O\textsubscript{3} at mid and high latitudes. The model is not constrained by observed peroxides or CH\textsubscript{2}O because the restriction would reduce available data points so severely.
that no statistically meaningful column budget can be obtained. The comparison of the simulations with and without the constraints shows that the effect of the scavenging loss of H$_2$O$_2$ is larger than those of higher than simulated ("excess") CH$_3$OOH and CH$_2$O concentrations in the observations. The resulting effects are similar (10–20% overestimates) for O$_3$ production, loss, and net production (loss).

Figure 17 shows the rapid increase of O$_3$ production throughout the spring. The increase is more rapid at high latitudes (by a factor of 2–3 per month) than at midlatitudes (decreasing from a factor of 2 in February–March to 50% in April–May). By May, O$_3$ column production rates (0–8 km) are $3.2 \times 10^{11}$ and $2.3 \times 10^{11}$ cm$^{-2}$ s$^{-1}$ for mid and high latitudes, respectively. About 70% of O$_3$ production is due to the reaction of HO$_2$ and NO, and the rest is by the reactions of NO with CH$_3$O$_2$ and other organic peroxy radicals. The source from the reactions of NO and other organic peroxy radicals are significant compared to that from the reaction of NO and CH$_3$O$_2$ in early spring. The relative strengths of the two sources changes from 1:1 (1:2) in February to 1:3 (1:4) in May at high (mid) latitudes, reflecting the decrease of NMHCs with season (Figure 1). Our rate estimates are less than those calculated by Cantrell et al. [2002]; the former values are 24-hour averages while the latter ones are instantaneous rates at the time of the observations.

The ozone budget at midlatitudes can be compared with the estimates for the western north Pacific ($30^\circ$–$50^\circ$N) in February–March (1994) by Crawford et al. [1997]. They found much larger column O$_3$ production ($10.5 \times 10^{10}$ cm$^{-2}$ s$^{-1}$) than loss ($3.8 \times 10^{10}$ cm$^{-2}$ s$^{-1}$). Their production rate is similar to our estimate for March but their loss rate is similar to our estimate in February. As a result, their estimated column net production is much larger than our estimate. The discrepancy is due in part to higher O$_3$ concentrations ($\sim$20 ppbv) during TOPSE. One important similarity between the two studies is that the lower free troposphere (1–4 km) is a significant region of net O$_3$ production. Crawford et al. [1997] attributed the enhanced O$_3$ production at these altitudes to continental outflow to the western Pacific.

The dominant role that HO$_2$ plays in O$_3$ loss rates is shown in Figure 18. The largest loss of O$_3$ in the tropical and subtropical regions is due to photolysis of O$_3$ and the subsequent reaction of O($^1$D) and H$_2$O [e.g., Davis et al., 1996; Jacob et al., 1996]. In comparison, during TOPSE the largest loss of O$_3$ is from the reaction of O$_3$ and HO$_2$. At midlatitudes, that loss accounts for 70% of the total O$_3$ loss in February and a smaller 45% in May. Kotchenruther et al. [2001] reported a fraction of about 60% in April over the north eastern Pacific. The fractional contribution by the reaction of O$_3$ and HO$_2$ at high latitudes decreases from 90% in February to 70% in May. The highest contribution by the reaction of O($^1$D) and H$_2$O is 35% at midlatitudes in May. The small fractional contribution to O$_3$ loss by the reaction of O($^1$D) and H$_2$O reflects much drier air and less solar insolation over the TOPSE region compared to the lower latitudes. The crucial role played by HO$_2$ in both O$_3$ production and loss explains the similar sensitivities of these variables to a change in the HO$_x$ source.
Figure 16. Same as Figure 1 but for simulated 24-hour average net production rates of HNO₃ and PAN. The model is constrained by observed HNO₃ and PAN concentrations.
Figure 17. Simulated monthly medians of 24-hour average O$_3$ production and loss rates as a function of altitude at mid and high latitudes. A median value plotted represents a minimum of 10 data points. The column (0–8 km) O$_3$ production rates at mid (high) latitudes are 6.3 (0.8), 14 (2.7), 21 (8.0), and 32 (23) × 10$^{10}$ cm$^{-2}$ s$^{-1}$ for February, March, April, and May, respectively. The corresponding loss rates are 4.4 (0.9), 13 (2.7), 17 (9.0), and 31 (20) × 10$^{10}$ cm$^{-2}$ s$^{-1}$. 
The relatively small loss of O\(_3\) by the reaction of O\(^{1}\text{D}\) and H\(_2\text{O}\) helps limit O\(_3\) loss at northern mid and high latitudes in spring, resulting in a net chemical production of O\(_3\) at midlatitudes during TOPSE. At midlatitudes, the net column chemical production is \(2 \times 10^{10}\), \(1 \times 10^{10}\), \(4 \times 10^{11}\), and \(1 \times 10^{11}\) cm\(^{-2}\) s\(^{-1}\) for February, March, April, and May respectively. The corresponding values at high latitudes are \(-6 \times 10^{9}\), \(-4 \times 10^{9}\), \(-1 \times 10^{10}\), and \(3 \times 10^{10}\) cm\(^{-2}\) s\(^{-1}\). The net loss in February–April at high latitudes reflects the low NO\(_x\) concentrations (<5 pptv below 5 km) in the region (Figure 1). The net chemical production or loss is only 3–20% of the column O\(_3\) production or loss rate at
0–8 km. The combination of high NO concentrations and low H$_2$O content leads to net O$_3$ production at high altitudes. Including the net O$_3$ production in the region between 8 km and the tropopause will further increase the estimated net chemical production of O$_3$.

[41] Figure 19 shows that the median column O$_3$ concentration (defined as column moles of O$_3$/column moles of air) at midlatitudes is highest in April and that the most rapid O$_3$ increase occurs in March–April, a period when the springtime O$_3$ maxima were observed at lower altitudes at
mid and high latitudes [e.g., Logan, 1985; Levy et al., 1985]. The estimated net \(O_3\) production is also largest in April. In contrast, at high latitudes during TOPSE, column \(O_3\) concentrations continue to increase from February to May and there is an estimated chemical loss of \(O_3\) from February to April. To illustrate the different effects of in situ net \(O_3\) chemical production (loss) on column \(O_3\) concentrations at mid and high latitudes, we show in Figure 19 the column concentrations of \(O_3\) for March, April, and May if in situ chemistry is the only factor influencing the concentrations (see also the figure caption). The estimated column \(O_3\) at midlatitudes does not show a maximum in April
because the in situ chemical production is still larger than loss in May. Nonetheless, the estimated concentrations reach the observed levels at midlatitudes. In comparison, the estimated O₃ concentrations at high latitudes remain at about 50 ppbv due to the relatively small net production or loss in that region, whereas the observed column mixing ratio increases by 15 ppbv.

[42] In situ chemistry alone cannot explain the observed springtime O₃ maxima at northern mid and high latitudes; transport plays an important role. Wang et al. [1998] tagged O₃ transported from the stratosphere and that produced in transport plays an important role. Their simulated net chemical production at midlatitudes peaks in March, April, and May using simulated monthly medians of 24-hour average net production (loss) rates.

[43] Measurements were made onboard the NCAR/NSF C-130 aircraft in February–May during the TOPSE experiment at northern mid and high latitudes. The temporal and spatial span of the measurements allows for analysis of the rapid transition of photochemistry in springtime using a photochemical model. We have focused our work on photochemical factors driving HOₓ and O₃ chemistry.

[44] The continuously decreasing concentrations of NMHCs through spring, due in part to increasing OH oxidation, contrast to the observed increase in O₃ and NO concentrations. Both trends favor partitioning of HO₅ toward OH. Photochemical activity as measured by the sources of HO₂ increases rapidly at mid and high latitudes with season. The primary driving force for radical chemistry is photolysis of O₃ and the subsequent reaction of O(¹D) and H₂O, which benefits not only from the increasing solar insolation but higher H₂O content of the warming air. The concentrations of total peroxy radicals rise accordingly; observed and simulated concentrations are in good agreement.

[45] One feature that sets TOPSE apart from the other tropospheric field experiments is the observations of low H₂O₂ concentrations (by a factor of 2–10) compared to model estimates. The loss of HO₂ required to match observed H₂O₂ concentrations in the model implies a loss of 20–30% in HO₂ concentrations. Both trends favor partitioning of HO₂ toward OH. Photochemical activity as measured by the sources of HO₂ increases rapidly at mid and high latitudes with season. The estimated timescales of H₂O₂ against scavenging loss in May are about half a day and 1 day at mid and high latitudes, respectively. If the scavenging loss frequency of H₂O₂ is much faster. Furthermore, it increases rapidly with season. The estimated timescales of H₂O₂ against scavenging loss in May are about half a day and 1 day at mid and high latitudes, respectively. If the scavenging loss frequency of H₂O₂ was mostly due to its oxidation of SO₂ in droplets, the oxidation would imply a sulfate deposition rate of >2.5 g S m⁻² yr⁻¹, an order of magnitude larger than previous estimates. Unknown mechanisms need to be invoked to explain the rapid loss of H₂O₂ during TOPSE.

[46] Whereas observed and simulated CH₃OOH concentrations show good agreement in April and May at high latitudes, they differ significantly in March at midlatitudes. The model shows generally decreasing CH₃OOH concentrations with altitude; an opposite trend is observed in March at midlatitudes. Transport processes alone do not appear to explain the observed profile of increasing CH₃OOH concentrations with altitude. Using observed in place of simulated CH₃OOH concentrations in the model tends to increase CH₃O concentrations at high altitudes. The
relative enhancement is significant (50–100% or 20–30 pptv) at 6–8 km in March.

[47] Observed and simulated CH$_2$O concentrations show better agreement than in previous northern midlatitude missions. The consistent underestimates by the model in the upper troposphere at high altitudes imply a large source of HO$_x$ (by CH$_3$O photolysis) in the region. Likely sources are transport from midlatitudes or heterogeneous conversion from methanol or other species, in which case photolysis of CH$_2$O boosts the primary production of HO$_x$. This additional HO$_x$ source increases the total HO$_x$ production by 50–200% at 6–8 km at high latitudes resulting in 10–50% increases in OH concentrations and O$_3$ production.

[48] The source of NO$_x$ does not appear to come from the decomposition of long-lived reactive nitrogen species, among which PAN is the most dominant component. The tropospheric burden of NO$_x$ at mid and high latitudes continues to grow throughout the spring. This seasonal increase is clearly evident in the free troposphere. The seasonality is less clearly defined at 0–3 km. The concentrations of NO$_x$ near the surface decrease from February to May (particularly at high latitudes) as those of NMHCs. Similar difference of the seasonal trend with altitude is observed for PAN except that the seasonal peak of PAN near the surface shifts toward April. Budget studies of PAN and HNO$_3$ show a net loss of NO$_x$ to these reservoirs species throughout the spring. There appears to be a seasonal shift in the difference between NO$_x$ and the sum of individual components (NO + NO$_2$ + PAN + PPN + HNO$_3$ + 2N$_2$O$_5$ + HNO$_4$), among which NO$_2$, N$_2$O$_5$, and HNO$_4$ are computed in the model. The former is larger in February but becomes progressively smaller than the latter in later months. The shift shows little altitude dependence.

[49] The production of O$_3$ in the TOPSE region increases substantially from February to May, by factors of 5 and 25 respectively at mid and high latitudes. The rapid increase is driven by increasing primary HO$_x$ production and NO concentrations. The latter is due in part to the increasing partitioning of NO$_x$ toward NO with more intense solar irradiation in spring. Ozone production is less sensitive to an increase in the primary HO$_x$ production than that in NO concentrations. However, the former factor, driven by the reaction of O($^1$D) and H$_2$O, increases more rapidly than the latter. Ozone photochemistry is in the NO$_x$-limited regime during TOPSE.

[50] Peroxy radicals generally play the pivotal role in O$_3$ production. The reaction of HO$_x$ and NO accounts for about 70% of the total production. The contribution by the reaction of higher (≥C$_2$) organic peroxy radicals and NO is as large as that by the reaction of CH$_2$O and NO in early spring, reflecting the high concentrations of NMHCs at the time. Its relative importance decreases toward summer. During TOPSE, HO$_x$ is also the major component in O$_3$ loss through the reaction of HO$_2$ and O$_3$. The loss pathway accounts for 45–70% and 70–90% of the total loss at mid and high latitudes, respectively. The loss pathway by photolysis of O$_3$ and the subsequent reaction of O($^1$D) and H$_2$O, which dominates O$_3$ loss at lower latitudes, is highest (35%) at midaltitudes in May. As a result, the sensitivities of O$_3$ production and loss to a change in the primary HO$_x$ production are similar.

[51] We find net in situ column O$_3$ chemical production (0–8 km) at midlatitudes, 2 × 10$^{10}$, 1 × 10$^{10}$, 4 × 10$^{10}$, and 1 × 10$^{11}$ cm$^{-2}$ s$^{-1}$ for February, March, April, and May respectively. In contrast, there is a net in situ chemical loss of O$_3$ at high latitudes except in May. The corresponding values at high latitudes are −6 × 10$^9$, −4 × 10$^9$, −1 × 10$^{10}$, and 3 × 10$^{10}$ cm$^{-2}$ s$^{-1}$. The difference reflects lower NO concentrations and solar irradiation at high latitudes. At midlatitudes, the lower free troposphere (1–4 km) in addition to the upper troposphere is a region of significant net O$_3$ production. The observed O$_3$ column (0–8 km) shows a peak in April at midlatitudes but continues to increase from February to May at high latitudes. In situ chemistry alone cannot explain the observed seasonality of column O$_3$ during TOPSE. Nonetheless, in situ net chemical production is a significant contributor to the observed O$_3$ increase at midlatitudes, where both net O$_3$ production and column concentration peak in April. Net transport from other tropospheric regions or the stratosphere is necessary to explain the observed seasonal increase of column O$_3$ at high latitudes.

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D. Blake and N. Blake, Department of Chemistry, University of California at Irvine, Irvine, CA, USA.

G. Chen, D. Davis, and Y. Wang, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332-0340, USA. (ywang@eas.gatech.edu)

J. Dibb and R. Talbot, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH, USA.

B. Heikes and J. Snow, Graduate School of Oceanography, University of Rhode Island, Narraganset, RI, USA.