Evolution of Ozone and Peroxyacetyl Nitrate Along Air Parcel Trajectories Sampled During TOPSE in Spring 2000

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0. ABSTRACT

The major goal of the Tropospheric Ozone Production about the Spring Equinox (TOPSE) field campaign (2000) was to study the cause of the spring Arctic ozone maximum in the free troposphere. Sources for tropospheric ozone (O$_3$) are transport of O$_3$ from the stratosphere and in-situ photochemical production. Peroxyacetyl Nitrate (PAN) can be used as a tropospheric indicator, since it is formed photochemically along with ozone and there are no sources of PAN in the stratosphere. This study focused on examining the evolution of O$_3$ and PAN along air mass trajectories, calculated using the HYSPLIT© model, from the source region of the air mass to the point of observation in the Arctic on board the C-130 aircraft. By step-wise “backwards” modeling along sections of the air mass trajectory, NCAR’s Master Mechanism could be utilized to estimate initial conditions in the source area, which were within the expectations for a typical urban air mass. The Master Mechanism was then used to model the photochemistry along the trajectory forward to the point of observation. The observed O$_3$ to PAN ratio and the modeled ratio were within 5%. Thus, it was concluded that the modeling approach was successful. Based on the evolution of the O$_3$ to PAN ratio from a city mix at the source to a value very close to that observed, it was also concluded that no stratospheric O$_3$ input was needed for the trajectory case studied. The comparison of more trajectories and source regions will help to further constrain the Arctic ozone budget.

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1. INTRODUCTION

1.1 Ozone

Today, most people know about the ozone hole and how ozone in the stratosphere protects living beings on earth from harmful UV rays. Another important, less known, consequence of stratospheric ozone depletion is the alteration of tropospheric chemistry (Madronich, 1993). This depletion allows more UV rays to penetrate into the troposphere and thus increase the photolysis of tropospheric ozone. The result is an increase in the production of OH radicals and thus an increase in stratospheric “detergent”. In the stratosphere, from about 20 to 50 km above the ground depending on latitude, ozone is produced by oxygen photolysis:

\[ O_2 + hv (\lambda < 240 \text{ nm}) \rightarrow O + O \]  
\[ O + O_2 + M \rightarrow O_3 + M \]

where M is any molecule that will stabilize the reaction complex by removing excess energy.

In contrast, tropospheric ozone plays an important role in oxidation chemistry by being the primary producer of OH radicals (Wayne, 1991). First, ozone is photolysed yielding an excited oxygen atom, which is capable of reacting with water vapor to produce OH radicals:

\[ O_3 + hv (\lambda < 310 \text{ nm}) \rightarrow O^* + O_2^* \]  
\[ O^* + H_2O \rightarrow OH + OH \]

where only about 10% of the excited oxygen react, the rest gets quenched. Ozone in the troposphere, from ground level up to about 10 km depending on temperature, also plays a crucial role in the radiative balance of the atmosphere possibly enhancing climate change (Brausseur, et al, 1999). Exposure to ozone may cause permanent lung damage as well as aggravate respiratory diseases (EPA, 1999). Ground level ozone is also harmful to plants and is responsible for at least $500 million in crop loss every year in the U.S. (EPA, 1997). Because of its effects on humans and the biosphere, there has been extensive research to improve our understanding of the processes that control ozone.

1.1.a Sources of Tropospheric Ozone

There are two known sources of tropospheric ozone: injection of ozone from the stratosphere, and as the by-product of “photochemical smog” (Brasseur, et al, 1999). The relative importance of each of these tropospheric ozone sources is still being debated.

The first source, the injection of ozone from the stratosphere, involves mixing between the tropopause and the stratosphere. Although inhibited by the temperature increase at the tropopause, stratospheric air still mixes with the troposphere when meteorological conditions breakdown the temperature discontinuity at the tropopause (Finlayson-Pitts & Pitts, 1986). When stratospheric mixing occurs, ozone mixing ratios change very rapidly, producing peaks that are at times inconsistent with expected photochemical smog. Also, high concentration of the isotope \(^7\text{Be}\) has been used as a tracer of stratospheric air (Browell, et al, 2000). The increase of the ozone mixing ratio with increasing altitude, usually associated with low water vapor, also implies the ozone is of stratospheric source.

The second source of tropospheric ozone is through photochemical smog. The ingredients of photochemical smog include reactive nitrogen (NO\(_x\)), volatile organic compounds (VOC), and sunlight (Brasseur, 1999). Nitric oxide (NO) and nitrogen dioxide (NO\(_2\)) are often treated combined as NO\(_x\) because of the fast interconversion between them. NO\(_x\) comes from fossil fuel combustion, and biomass burning as well as from natural sources such as lightning, and microbial activity in the soils and oceans. The sources of VOCs are from the biosphere as well as...
from fossil fuels and biomass burning. However, over the Arctic region, there are no significant biological sources of VOCs since there is little or no vegetation. Photochemical production of $O_3$ begins with the oxidation of the VOCs, carbon monoxide (CO), and methane (CH4) represented by RH:

$$RH + OH \rightarrow R + H_2O \quad [1.5]$$

where $R$ denotes an alkyl radical. Through further oxidation $R$ is converted into a peroxy radical, $RO_2$:

$$R + O_2 + M \rightarrow RO_2 + M \quad [1.6]$$

Now the NOx comes into play by reacting with $RO_2$:

$$RO_2 + NO \rightarrow RO + NO_2 \quad [1.7]$$

producing a NO2 that will photolyze releasing an atomic O:

$$NO_2 + hv (\lambda < 240 \text{ nm}) \rightarrow O + NO \quad [1.8]$$

The oxygen atom combines with molecular oxygen to form ozone [1.2]. However, the NO produced in reaction [1.8] can destroy ozone:

$$NO + O_3 + M \rightarrow NO_2 + O_2 + M \quad [1.9]$$

so that when reactions [1.9], [1.2] and [1.8] are added together they cancel each other out forming the null reaction series. Nonetheless, if NO is not produced through reaction [1.9], but through a different mechanism, such as reaction [1.7] or the following reaction:

$$HO_2 + NO \rightarrow OH + NO_2 \quad [1.10]$$

then there will be a net production of photochemical ozone. With HO2 being primarily produced per CO oxidation:

$$OH + CO \rightarrow CO_2 + H \quad [1.11]$$

$$H + O_2 \rightarrow HO_2 \quad [1.12]$$

Ozone production is also controlled by the $[NO]/[NO_2]$ ratio, which at higher tropospheric altitudes is larger because of the temperature dependence of reaction [1.9]. Diurnal variance the temperature is lower (Wayne, 1991). There are also other alternative methods of producing ozone that still use NO2 photolysis [1.8], which are supplied by the oxidation of carbon monoxide and various hydrocarbons.

1.1.b Spring Ozone Maximum

A feature of tropospheric ozone is the observed springtime maximum in the free troposphere of the Northern Hemisphere. The origin of this maximum is still being discussed in the literature. It has been attributed to both stratospheric mixing and photochemical processes (TOPSE, 1998). Using a 0-D model, Wang et al. argue that in-situ chemistry cannot explain the observed springtime ozone maxima at northern mid- and high- latitudes and that transport processes play an important role (Wang). On the other hand, because some important ozone and peroxyacetyl nitrate precursors accumulate in winter and early spring, when insolation increases they produce photochemical ozone. This process is used as an argument in favor of photochemical production of ozone in the Arctic spring (Browell, et al, 2000).

1.2 Peroxyacetyl Nitrate

The presence of peroxyacetyl nitrate, CH3C(O)OONO2, (PAN) has been observed throughout the world, in urban, rural, and remote atmospheres (Finlayson-Pitts & Pitts, 1986). PAN is a powerful lachrymator and a plant phytotoxicant (Finlayson-Pitts & Pitts, 1986). When some hydrocarbons, both from natural and anthropogenic sources, are photo-oxidized they sometimes form acetaldehyde, CH3CHO. Acetaldehyde is further oxidized:
CH₃CHO + OH + O₂ → CH₃(O)OO + H₂O  \[1.13\]
and makes peroxyacetyl radical, CH₃(O)OO, which is the precursor of PAN. It is important to note that CH₃(O)OO reacts with NO₂ therefore acting as a NOx sink:

CH₃C(O)OO + NO₂ ⇄ CH₃C(O)OONO₂ \[1.14\]

however, the rate constant for PAN decomposition \[-1.14\] is very strongly temperature dependent, \( k_{-11} = 1.95 \times 10^{16} \ e^{-13.543/T} \ s^{-1} \) (Finlayson-Pitts & Pitts, 1986). For example, at -30°C PAN can live up to 2.6 years, compared to only 11 minutes at 35°C. Thus, temperature can greatly determine the fate of PAN and consequently of NO₂ and ozone in the atmosphere.

PAN is an important trace gas in the atmosphere because it is a reservoir of NO₂, which plays an important role in the formation of photochemical smog. When the temperature is low and/or the ratio of [NO₂]/[NO] is high, then the reverse reaction \[-1.14\] is inhibited and PAN builds up. However, when the temperature rises or there is a high concentration of NO, then PAN decomposes following \[-1.14\]. PAN may be transported long distances at higher altitudes in the troposphere, for example after convective lifts take place, downwind of urban areas. Subsequent while air mass subsidence causes the release of NOx through PAN decomposition, which can produce ozone following reactions \[1.8\] and \[1.2\].

PAN has been used as an indicator of photochemical processes. Penkelt and Bryce (1986) observed a spring maximum coincident with an O₃ maximum at the north coast of Ireland. Although high tropospheric ozone concentration is also used as an indicator, there is more natural variability and the possibility of stratospheric ozone injection, which makes it a more uncertain indicator of photochemical ozone. Also, PAN homologues such as PeroxyMethAcrylyol (PMAN), PeroxyPropionyl Nitrate (PPN), etc can serve as indicators for the original hydrocarbon mix involved in the photochemical ozone production (Roberts, et al, 1997).

1.3 TOPSE

The Tropospheric Ozone Production upon the Spring Equinox (TOPSE) was a campaign conducted by the National Center for Atmospheric Research (NCAR), collaborating universities, and other research agencies funded by the National Science Foundation (NSF) between February and May of 2000 to study the chemical and dynamic evolution of tropospheric chemical composition over mid- to high-latitude continental North America during the winter/spring transition, with particular emphasis on the springtime ozone maximum in the troposphere (TOPSE, 1998). One of the primary scientific questions that motivated TOPSE was whether the widely observed spring maximum in ozone mixing ratios of the Northern Hemisphere free troposphere is primarily caused by increased mixing of stratospheric ozone into the troposphere or by in-situ photochemical production of ozone in the troposphere.

Seven missions of about 7-12 days duration each were conducted between Jeffco airport located in metro Denver, Colorado; Winnipeg, Manitoba, Canada; Churchill, Manitoba; and Thule, Greenland between 2/9 and 5/23 (Figure 1). An NCAR-NSF C-130 aircraft collected physical and chemical properties of the atmosphere from the surface up to 8 km and from 40 to 80°N. Data and further information about TOPSE is available online at http://topse.acd.ucar.edu/.
1.3.a PAN and Ozone During TOPSE

The goal of this project is to examine the evolution of individual ozone to PAN ratios measured during the TOPSE mission. PAN and ozone mixing ratios were observed to increase simultaneously with increasing insolation during the course of TOPSE, which is a clear indicator of photochemical ozone production. The average ratio of ozone to PAN observed during TOPSE was about 75 (Flocke, Weinheimer, 2000), as can be seen from the slope in Figure 2; whereas typical ozone to PAN ratios observed near fresh emission sources are around 25 (Flocke, Weinheimer, 2000). Blindly, this would mean that 2/3 of the ozone measured in TOPSE was of stratospheric origin. However, PAN is lost from the troposphere by thermal decomposition as well as by photolysis. As air parcels travel down from the upper to the lower troposphere they get compressionally heated and the equilibrium of reaction [1.13] is shifted towards the side of PAN decomposition. Thus, the temperature history of an air mass can greatly influence the ozone to PAN ratio observed in the troposphere.
2. METHODOLOGY

2.1 Backward Air Mass Trajectories

Backward trajectories from the point of observation during TOPSE to the source of emissions were calculated so that the meteorological conditions, such as temperature, humidity, and pressure, along the trajectory could be determined. The backward trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)\(^1\) model, March 2002 version, published and maintained by NOAA Air Resources Laboratory, which traces air parcels back in time and space using measured and interpolated meteorological data. Back trajectories for all TOPSE data points north of 58°N and between 2500 to 7000 m above ground level were calculated. An example of a back trajectory is shown in Figure 3. With these meteorological conditions known, the chemistry along the air parcel trajectory can now be modeled.

\[\text{Figure 3 Backward trajectory calculated with HYSPLIT. The star represents the point of observation during TOPSE. Top: Geographical coordinates. Bottom: Altitude coordinates}\]

\(^1\)Available at http://www.arl.noaa.gov/ss/models/hysplit.html
2.2 Source Regions and Coherent Trajectories

The air mass trajectories measured during TOPSE were sorted by Professor John Merrill at the Graduate School of Oceanography at the University of Rhode Island into 9 surface source emission regions summarized in Table 1. Surface source region codes are assigned based on where the air parcel traveled below 1500 m altitude closest to the end point of the trajectory, in this case where TOPSE took its measurements. When the air mass dips that far down into the lower troposphere, it is likely to pick up emissions from a variety of anthropogenic sources. Surface source codes were used to analyze the air parcels geographically. This was done with IGOR Pro © (by Wavemetrics) by mapping all the back trajectories of the same surface code on the same plot and then selecting similar or coherent trajectories. From these coherent trajectories, ambient conditions such as temperature, altitude, latitude, and longitude were averaged. This was done for each source region. An example using the Asian source region is shown in Figure 4. These averaged conditions were considered the typical conditions of the trajectory from each source region.

Table 1 Summary of surface source region codes

<table>
<thead>
<tr>
<th>Code</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>Asia</td>
<td>Europe &amp; Africa</td>
<td>USA &amp; Mexico</td>
<td>Canada</td>
<td>Western Pacific &lt; 30N</td>
<td>Western Pacific &gt; 30N</td>
<td>Eastern Pacific &lt; 30N</td>
<td>Eastern Pacific &gt; 30N</td>
<td>N Atlantic</td>
</tr>
</tbody>
</table>

Figure 4 Geographical distribution backward trajectories originated in Asia measured during TOPSE in Western Greenland.

2.3 Chemical Modeling

The chemical model used was NCAR’s Master Mechanism, which for TOPSE conditions included over 3000 gas phase reactions. The model is zero dimensional, so that it solves the chemistry at a single point in space. The goal is to find the initial chemical conditions for these trajectories at their source region, which is approximately seven days before the TOPSE measurements. TOPSE data gives the final chemical conditions of the air trajectories in the
troposphere. From the measured TOPSE data, we worked backwards. Since, the model cannot be run backwards in time, the trajectories were broken down into segments. Segments were selected depending on similar temperature, altitude, and latitude profiles. For example, Figure 5 shows the profile of the segments for the averaged coherent trajectory from the Asian source region.

![Figure 5: Averaged meteorological conditions for the average of coherent trajectories from Asia. The gray vertical lines show how the segments were divided. On the x-axis, time zero is the point of observation.](image)

Once the trajectories were broken down into segments, the average temperature, altitude, pressure, latitude, and albedo were calculated for each segment, as shown in Table 2 for the Asian case.

<table>
<thead>
<tr>
<th>Segment</th>
<th>Duration (days)</th>
<th>Altitude (m)</th>
<th>Temperature (K)</th>
<th>Pressure (mb)</th>
<th>Latitude (°N)</th>
<th>Albedo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5585</td>
<td>236</td>
<td>463</td>
<td>82.0</td>
<td>80</td>
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<td>1</td>
<td>5262</td>
<td>241</td>
<td>493</td>
<td>75.0</td>
<td>70</td>
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<tr>
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<td>4088</td>
<td>250</td>
<td>557</td>
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<td>789</td>
<td>61.0</td>
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<td>919</td>
<td>283</td>
<td>698</td>
<td>59.7</td>
<td>15</td>
</tr>
</tbody>
</table>

In order to work backwards, guesses were made about the initial NOx conditions of the last segment, the one closest to the point of observation. Then the model was run trying different steady concentrations, until the measured conditions were obtained. For the first run, all the chemical species, except NOx and HNO₄ were set constant at the measured values because of the low OH at high latitude and cold temperatures would slow the oxidation of VOCs and thus maintain them near measured values. HNO₄ was not measured during TOPSE, so in order to find...
what initial mixing ratio to use, the model was run for 15 days with everything constant except NOx and HNO₄. In order to check that the value of HNO₄ used is reasonable, an NOy calculation was made with the measured values at the end point.

\[
\text{HNO}_4 = \text{NOy} - \text{NO} - \text{NO}_2 - \text{HNO}_3 - \text{PAN} - \text{PPN} \quad [2.1]
\]

The measured allowed HNO₄ is 65.8 ppt in constrast to 340 ppt from the model. This is a big difference but acceptable nonetheless because of the uncertainties involved in the model as well as the measurements.

Once a value for HNO₄ was obtained, the initial NOx had to be guessed at until the model gave the target measured NOx value. The point where NOx matches its measured value is considered the end of the segment, and to find the beginning of the segment, we go back in time the duration of the particular segment.

The next step is to find the final conditions of the next segment, for which the final NOx will be the same as the initial conditions of the previous segment, as Figure 6 shows.

For the remaining segments, the hydrocarbons were set constant at the values calculated following:

\[
[\text{HC}]_{\text{new run}} = [\text{HC}]_{\text{previous run}} \exp (k[\text{OH}]t) \quad [2.2]
\]

where \(k\) is the rate constant at the temperature and pressure of the segment, \([\text{OH}]\) is the average mixing ratio of OH during that segment of the model run, and \(t\) is the duration of the segment in seconds. The mixing ratio of HNO₄ is found again from a model run with everything constant but the NOx and itself. For all other species, such as O₃, PAN, CO, HNO₃, and nitrates, their new target or final mixing ratio for the second segment was determined by taking the difference of the points at the same time the NOx was selected. This difference is added to the initial mixing ratio of the previous segment to obtain the new target values. This calculation is expressed in the following formula:

---

Figure 6 Depiction of how initial conditions were found for each segment by guessing initial run NOx concentration until arriving at the measured NOx. From the measured NOx concentration one goes back the duration of the segment to arrive at the initial NOx for the segment. This initial NOx for the segment then becomes the final or target value for the next segment back in time. Again, one guesses the initial NOx until arriving at the target value. This process is repeated until the NOx at the time of source emission is arrived at.
\[ [X]_f = [X]_{\text{init}} - ([X]_{f\text{NOx}} - [X]_{\text{Init NOx}}) \]  \[2.3\]

where \([X]_f\) is the final concentration of the chemical species, \([X]_{\text{init}}\) is the initial concentration of the previous segment, \([X]_{f\text{NOx}}\) is the concentration of X at the point in the segment where NOx is at the final concentration, and \([X]_{\text{Init NOx}}\) is the concentration of X at the point in the segment where NOx is at the initial value.

This process is repeated until all segments have been modeled. When the last segment is done, then its initial conditions will be an estimate of those of the original air trajectory. Once the initial conditions are known, they were modeled again with the Master Mechanism, but this time in the forward direction, to the point of observation aboard the C-130. The forward modeling was also done by segments using the averaged meteorological conditions, but all chemical species were left unconstrained to see if assumptions used for the backwards modeling were valid.

The goal of using the model was to predict the chemical evolution of the ozone to PAN ratio. Finally, the model ozone to PAN ratios were compared to the measured ratios in an attempt to improve our understanding of the ozone budget in the Arctic free troposphere.

3. RESULTS AND DISCUSSION

Due to time constraints, only the Asian source region has been completely modeled. From Figure 7 one can see how the PAN and ozone behave during the trajectory from Asia. During both the backwards and forward run, the ozone increases during the first few days, due to the higher NOx closer to the source. Higher temperatures represent proximity to the source. The PAN decreases steadily during the first couple of days for both runs, while the air mass trajectory is warm. As PAN is destroyed, it releases NOx, which contributes to some additional production of photochemical ozone. Both ozone and PAN seem stable at the colder segments close to time 0, the point of observation, reinforcing our assumption that little chemistry occurs at these cold regions. However, if these two graphs in Figure 7 are looked at in detail, one can see that although the trends are the same, the mixing ratios are slightly different. Table 3 lists several chemical species of interest in photochemical ozone production. It can be seen

![Figure 7 PAN and ozone profiles from the forward (left) and backward (right) modeling of the Asian trajectory.](image)

![Table 3 Chemical conditions at the point of observation from model and measurements during TOPSE. All chemical species are in ppt, except for O3 and CO which are in ppb. Overall there is general agreement between measurements and models.](image)
<table>
<thead>
<tr>
<th>species</th>
<th>modeled</th>
<th>measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>773.9</td>
<td>648.9</td>
</tr>
<tr>
<td>O3</td>
<td>81.3</td>
<td>71.1</td>
</tr>
<tr>
<td>O3/PAN</td>
<td>105.1</td>
<td>109.5</td>
</tr>
<tr>
<td>NOx</td>
<td>6.2</td>
<td>24.1</td>
</tr>
<tr>
<td>HNO3</td>
<td>1173.9</td>
<td>100.0</td>
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<tr>
<td>HNO4</td>
<td>19.9</td>
<td>NM</td>
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<td>CH3CHO</td>
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<td>CH2O</td>
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<tr>
<td>H2O2</td>
<td>596.1</td>
<td>189.8</td>
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<table>
<thead>
<tr>
<th>species</th>
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<th>measured</th>
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</thead>
<tbody>
<tr>
<td>CO</td>
<td>201.5</td>
<td>189.1</td>
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<tr>
<td>Methyl-peroxide</td>
<td>166.2</td>
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<td>acetone</td>
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<td>99.7</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

that O3 and PAN are slightly overestimated. This is because in order to have reasonable initial conditions, PAN was increased in the first segment so that the ozone to PAN ratio would match that of a city mix. Because the ozone to PAN ratio modeled at the end is similar to that measured, it was concluded that this assumption was reasonable. NOx is underestimated by this model. However, this is a common feature among tropospheric chemical models not constraining NOx. Because the NOx is underestimated, it would have affected the mixing ratio of ozone and PAN. Table 3 also shows that the more reactive hydrocarbons are underestimated, while the less reactive ones have a better agreement.

From the evolution of the ozone and PAN in the forward model, Figure 8, one can see that the initial conditions found for the source at –7 days have a representative city ozone to PAN ratio of about 20. As the air mass trajectory travels towards the point of observation, the ratio increases inversely proportional to the mixing ratio of PAN. At the point of observation, the modeled ratio was 105, while the observed ratio for this trajectory was 109. Because these ratios are within 5% of each other, the assumptions used appear validated for this method for this particular segment studied. Also, the fact that the ozone to PAN ratios are so close to each other can be used as support that for this Asian trajectory, no input of stratospheric ozone is needed to explain the ratios. Therefore, for this trajectory, the ozone to PAN ratio can be explained solely by in-situ photochemistry.

![Figure 8 Ozone to PAN ratio modeled from the initial source to the point of observation.](image)

4. CONCLUSION

The backwards trajectory stepwise modeling approach can be used to estimate the initial NOx and hydrocarbons at the point of emission. These initial conditions can be used to simulate the chemistry along a forward trajectory back to the point of observation. This new method of studying the chemical evolution along air mass trajectory has been proven successful for the case studied. Hydrocarbon and NOx chemistry explain the ozone to PAN ratio for the Asian
trajectory. Therefore, for this urban-aged plume, there is no need to introduce stratospheric ozone into the trajectory.

5. FUTURE WORK
A comparison between models used during TOPSE, such as MOZART and HANK and the one presented here may give interesting information about the dependability of the backward trajectory method to estimate initial source conditions. MOZART stands for the Model for OZone and Related chemical Tracers, and is a 3-D global chemical transport model. HANK is designed to simulate tropospheric chemistry and transport on regional to hemispheric scales. Furthermore, there is the need to test this method by modeling several other trajectories. Once these have been modeled successfully, a comparison between the different source regions might prove useful at quantifying the percent of stratospheric O3 needed during TOPSE in the Arctic.

6. REFERENCES


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