Intercontinental transport of pollution manifested in the variability and seasonal trend of springtime $O_3$ at northern mid and high latitudes

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Abstract. Observations (0-8 km) from the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment are analyzed to examine air masses contributing to the observed variability of springtime O$_3$ and its seasonal increase at 40-85° N over North America. Factor analysis using the PMF and PCA methods is applied to the dataset with 14 chemical tracers (O$_3$, NO$_y$, PAN, CO, CH$_4$, C$_2$H$_2$, C$_3$H$_8$, CH$_3$Cl, CH$_3$Br, C$_2$Cl$_4$, CFC-11, HCFC-141B, Halon-1211, and $^7$Be) and 1 dynamic tracer (potential temperature). Our analysis results are biased by the measurements at 5-8 km (70% of the data) due to the availability of $^7$Be measurements. The identified tracer characteristics for 7 factors are generally consistent with the geographical origins derived from their 10-day backtrajectories. Stratospherically influenced air accounts for 14 ppbv (35-40%) of the observed O$_3$ variability for data with O$_3$ concentrations < 100 ppbv at mid and high latitudes. It accounts for about 2.5 ppbv/month (40%) of the seasonal O$_3$ trend at mid latitudes but only 0.8 ppbv/month (<20%) at high latitudes, likely reflecting more vigorous mid-latitude dynamical systems in spring. At mid latitudes, reactive nitrogen rich air masses transported through Asia are much more significant (11 ppbv in variability and 3.5 ppbv/month in trend) than other tropospheric contributors. At high latitudes, the O$_3$ variability is significantly influenced by air masses transported from lower latitudes (11 ppbv), which are poor in reactive nitrogen. The O$_3$ trend, in contrast, is largely defined by air masses rich in reactive nitrogen transported through Asia and Europe across the Pacific or the Arctic (3 ppbv/month). The influence from the stratospheric source is more apparent at 6-8 km while the effect of O$_3$ production and transport within the troposphere is more apparent at lower altitudes. The overall effect of tropospheric photochemical production, through long-range transport, on the observed O$_3$
variability and its seasonal trend is more important at high latitudes relative to more photochemically active mid latitudes.
1. Introduction

Ozone in the troposphere is either produced photochemically within the troposphere or transported from the stratosphere. Its concentrations have important environmental ramifications. At high concentrations near the surface, it is hazardous to humans and plants. It is important for maintaining the oxidation capacity of the atmosphere through its photolysis to O($^1$D), which reacts with H$_2$O to produce OH radicals. Furthermore, it is an effective greenhouse gas.

An interesting feature of tropospheric O$_3$ is the observed springtime increase at northern mid and high latitudes. Ozone concentrations at northern mid and high latitudes tend to peak in late spring (April and May) in the lower troposphere and in early/mid summer (May-July) in the middle troposphere [e.g., Logan, 1985]. Levy et al. [1985] was able to simulate the springtime increase in a global 3-D model, which did not incorporate tropospheric chemistry. Penkett and Brice [1986] and Liu et al. [1987] suggested that the increase is driven by photochemical production in the troposphere. However, subsequent analysis work based on the observed correlation between O$_3$ and $^7$Be tends to emphasize the effect of the stratospheric input [e.g., Oltmans and Levy, 1992; Dibb et al., 1994].

More recent analyses using photochemical models tend to emphasize the effect of tropospheric photochemical production. Photochemical box model calculations based on the measurements during the Free Tropospheric Experiment (FREETEX’96 and 98) in the Swiss Alps (at an altitude of 3.6 km) [Carpenter, 2000; Zanis et al., 2000] and aircraft observations during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment [e.g., Cantrell et al., 2003; Wang et al., 2003] showed that tropospheric O$_3$ production at mid latitudes are large enough to explain the observed
springtime O\textsubscript{3} increase at northern mid latitudes, although in situ O\textsubscript{3} production is ineffective at high latitudes [Wang et al., 2003]. Using global 3-D chemistry and transport models, Wang et al. [1998] showed that both factors contributed to the simulated springtime O\textsubscript{3} maximum at low altitudes (0-2 km) with one peaking in early spring and the other peaking in early summer, while Yienger et al. [1999] emphasized the effect of net O\textsubscript{3} chemical production at mid latitudes. Li et al. [2002] further suggested that the apparent correlation between surface observations of O\textsubscript{3} and $^7$Be in Bermuda merely reflects the subsidence of O\textsubscript{3} produced in the middle troposphere not transported from the stratosphere.

Applying global 3-D chemistry and transport models, a number of recent studies have investigated the effects of intercontinental transport on tropospheric O\textsubscript{3} concentrations from Asia to North America [e.g., Bey et al., 2001; Berntsen et al., 1999; Jacob et al., 1999; Jaffe et al., 1999]. The effect of trans-Pacific transport is particularly large in spring [e.g., Wang et al., 1998; Jacob et al., 1999; Mauzerall et al., 2000; Wild and Akimoto, 2001; Tanimoto et al., 2002].

We analyze here aircraft springtime observations from TOPSE (February-May, 2000) [Atlas et al., 1993]. Thirty eight science flights of the C-130 aircraft were conducted in 7 deployments (1-2 weeks apart), covering a latitude range of 40-85° N (Colorado to north of Thule, Greenland) and an altitude range from the surface up to 8 km. A comprehensive suite of chemical species related to the tropospheric chemistry of O\textsubscript{3}, HO\textsubscript{x} (OH+HO\textsubscript{2}), and NO\textsubscript{x} (NO+NO\textsubscript{2}) were measured.

This dataset is the largest available that extends over broad latitude and altitude ranges on a seasonal time scale in spring. We will attempt to address in this work the
effects on tropospheric O$_3$ variability and trend by intercontinental transport of O$_3$ and its precursors from different tropospheric regions and by transport of O$_3$ from the stratosphere on the basis of TOPSE observations. We will apply a multivariate analysis technique in this work. As illustrated by Li et al. [2002] and Browell et al. [2003], considering multiple correlations among O$_3$ and other species is critical.

2. Methodology

In this work, we analyze the covariant factors of 14 relatively long-lived chemical tracers and potential temperature. Our hypothesis is that air masses with varying contributions to the observed O$_3$ variability and trend can be differentiated on the basis of the covariance of their chemical compositions and that their geographical origins can be evaluated using backtrajectory calculations.

To examine the tracer profiles of various air masses, we applied two analytical methods, Principal Component Analysis (PCA) and the Positive Matrix Factorization (PMF) method. Covariance among the tracers is analyzed in these methods to define key components or factors that explain the variability of the data set. The PCA method [Press et al., 1992] with varimax rotation [Kaiser, 1958] yields comparable results as those by PMF. We find, however, that the PMF results are clearer for physical interpretations and for the separation of air masses than those by PCA because the latter lumps positively correlated tracers with negatively correlated tracers. Furthermore, the PMF results are more robust with respect to rotation. Only PMF results are discussed hereafter.

Our results cannot be directly compared to model estimated fractional contributions to tropospheric O$_3$ from different sources. Any correlation-based methods including the ones used here can only be used to examine the variability in the
observations. However, the results from variability analysis as those to be presented here are valuable because (1) they are based on the observations and are not affected by model imperfections and (2) the resulting concentration variability is often a key parameter with regard to potential environmental impact of a given factor. In order to fully reconcile our data analysis with those from the 3-D chemistry and transport models, we will need to conduct detailed simulations with the same species and equivalent spatial and temporal resolutions as in the observations. That is beyond the scope of this work. It is also useful to note that the validity of the linear covariance assumption of PMF, PCA, and other similar analysis techniques is tested on whether the resulting factors or principal components can be physically explained. These mathematical techniques evaluate only the “likelihood” of a given setup of factors or principal components; the results may be non-physical. We choose the solution that entails the best physical explanation.

The profiles of covariant elements (factors) are identified through matrix decomposition in the PMF method [Paatero, 1997]. The data matrix $X$ of $m$ measurements by $n$ tracers can be decomposed for $p$ factors as,

$$X = GF + E$$  \hspace{1cm} (1)

Or

$$x_{ij} = \sum_{k=1}^{p} g_{ik}f_{kj} + e_{ij}$$  \hspace{1cm} (2)

where the $m$ by $p$ matrix $G$ is the factor score, the $p$ by $n$ matrix $F$ is the tracer profile, and the $m$ by $n$ matrix $E$ is the error. In our analysis we use explained variation

$$(EV_{kj} = \frac{\sum_{i=1}^{m}|g_{ik}f_{kj}|}{\left(\sum_{i=1}^{m}\sum_{k=1}^{p}|g_{ik}f_{kj}| + |e_{ij}|\right)}$$

to define the contributions from each factor [Lee
et al., 1999]. Necessary matrix rotation is determined [Paatero et al., 2002]; we find that for this dataset the PMF results are not as sensitive to rotation as those with PCA. The PMF method has been used previously to identify sources of aerosols and trace gases [Polissar et al., 1998; Paterson et al., 1999; Ramadan et al., 2000].

Among the available measurements during TOPSE, we chose 14 chemical tracers and one dynamic tracer. They are among the longer-lived tracers in the TOPSE measurements. The tracers (other than \( \text{O}_3 \)) must also have unique source or concentration distributions, so they could be used to identify the origins of air masses. The chemical tracers chosen for the analysis are \( \text{O}_3 \), total reactive nitrogen (\( \text{NO}_x \)), peroxyacetylnitrinate (PAN), CO, CH\(_4\), C\(_2\)H\(_2\), C\(_3\)H\(_8\), CH\(_3\)Cl, CH\(_3\)Br, C\(_2\)Cl\(_4\), CFC-11 (CCl\(_3\)F), HCFC-141B (CH\(_3\)CCl\(_2\)F), Halon-1211 (CBrCl\(_2\)F), and \(^7\)Be. Total reactive nitrogen is a good tracer of air masses that intercepted large tropospheric NO\(_x\) emissions or stratospheric air. PAN is a byproduct of NO\(_x\) oxidation and is a good tracer for tropospheric reactive nitrogen. High concentrations of PAN often indicate occurrences of tropospheric \( \text{O}_3 \) production in the past and therefore tend to correlate with high \( \text{O}_3 \) concentrations in pollution plumes. Carbon monoxide and C\(_2\)H\(_2\) are good tracers for combustion and C\(_3\)H\(_8\) is a good liquefied gas tracer. Methane has many sources, some of which are collocated with industrial pollution sources. Methyl chloride and CH\(_3\)Br are thought to have substantial sources from the ocean and biomass burning. Tropical terrestrial biosphere is likely a major CH\(_3\)Cl source region [Yokouchi et al., 2000; Lee-Taylor et al., 2001]. Tetrachloroethene is mainly a tracer for industrial activities. The production of CFC-11 and Halon-1211 was phased out in the developed countries at the end of 1995 and will be phased out in developing countries by 2010. HCFC-141b is a replacement for CFCs. Beryllium-7 is
produced by cosmic rays and is generally used as a tracer for stratospheric air [e.g., Dibb et al., 2003]. The other tracer we use in the analysis is potential temperature ($\theta$), which is conserved during adiabatic processes. Potential vorticity is another useful dynamic tracer. It needs to be computed on the basis of $\theta$ and model simulated horizontal winds; the resulting temporal and spatial resolutions of this variable are much lower than the in situ measurements.

The observed values of each variable are linearly scaled to a dimensionless range of 0 to 1 and a small constant error estimate is assigned for equal weighting. In our analysis, no tracer should be weighted more than the other because they represent different processes. Our goal is not to define the best correlation between two specific tracers but rather to define the best tracer characteristics of air masses on the basis of the variability of all the tracers. Only data above the detection limits are used. By evaluating the error matrix $E$ [Paatero, 1997; Lee et al., 1999; Paatero et al., 2002], we found that a range of 6-10 factors are appropriate for our data sets. We chose to use 7 factors, which separate air mass tracer profiles well.

The 10-day kinematic backtrajectories used in this work are calculated using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Hess, 1998]. The meteorological data are taken from the ‘FN’ archive produced in the NOAA Air Resources Laboratory. The 6-hour archive is computed using a global data assimilation system [Kanamitsu, 1989]. This type of trajectory calculation is generally accurate for identifying large geographical features of air mass origins [Stohl, 1998]. The choice of 10 days for the backtrajectory calculation is somewhat arbitrary; it is long enough to separate local influence from long-range transport [Pocharnart et al., 2001].
3. Results and discussion

The photochemical environment is quite different from mid to high latitudes due in part to varying solar isolation [Wang et al., 2003]. Consequently, our analysis is conducted separately for these two regions. The size of our dataset is limited mostly by the availability of $^7$Be data to 137 coincident measurements of all species at mid latitudes (40-60° N) and 193 coincident measurements at high latitudes (60-85° N). Including missing $^7$Be data by assigning large uncertainties [Polissar et al., 1998] led to an underweight of the $^7$Be data, resulting in a poor O$_3$-$^7$Be correlation and a large fraction of unexplained $^7$Be variability. As demonstrated by Li et al. [2002] and Dibb et al. [2003], faithfully capturing the O$_3$-$^7$Be correlation is critical to resolve the contributions by various O$_3$ sources. Hence no missing $^7$Be data were included. Ozone concentrations in this subset show similar probability distributions (binned by 10 ppbv) as the dataset with all measured O$_3$. The altitude distribution is shifted to higher altitude. The fraction of data above 5 km increases from 50% of all O$_3$ data to 70%. The seasonal O$_3$ trend of the subset is in agreement with that of all O$_3$ measurements above 5 km. Our results are therefore biased towards the middle and upper troposphere. The analysis results are about the same when measurements below 3 km are excluded.

In order to establish the correlation between the stratospheric O$_3$ and $^7$Be, we have included in our analysis data points with O$_3$ concentrations $> 100$ ppbv (5% of the dataset), which are generally associated with the lower stratospheric air. To minimize the effects of these lower stratospheric data, our results are shown for data with O$_3$ concentrations $< 100$ ppbv. Relative to the results with all the data included, the effects of limited O$_3$ range are only apparent for O$_3$ and $^7$Be and the estimated stratospheric contribution to O$_3$ variability is reduced. The EV percentages of O$_3$ in the factors
(defined in section 2) change by < 5%. The largest changes are seen in the explained variations of O\textsubscript{3} and \textsuperscript{7}Be in the \textsuperscript{7}Be factor, which decrease by 6 ppbv and 100-150 fCi/SCM, respectively.

### 3.1 Mid latitudes

The EV profiles of the 7 factors and the total EV explained by the analysis for data with O\textsubscript{3} concentrations < 100 ppbv are shown in Figure 1. The factors are named after their major components. Our analysis captures 80-95% of the observed variation of each tracer. The absolute tracer variation explained by each factor is shown in Figure 2. Five factors are mostly related to the sources and transport of CO, hydrocarbons, and halocarbons. The seasonal decrease of CO and hydrocarbons [e.g., Blake et al., 2003] is captured by the hydrocarbon factor.

Among the 7 factors, only \textsuperscript{7}Be and NO\textsubscript{y}-PAN factors account for >5% of the observed variability of O\textsubscript{3}. The tracer profile of the \textsuperscript{7}Be factor is consistent with a stratospheric origin. Potential temperature and HNO\textsubscript{3} concentrations in the stratosphere are much higher than those in the troposphere. The latter is reflected in the signal of NO\textsubscript{y}, which encompasses all reactive nitrogen species. The factor shows no signal of PAN, which is produced in the troposphere. On the basis of our preliminary global 3-D simulations of CH\textsubscript{3}Cl, we believe that the signal of CH\textsubscript{3}Cl in the \textsuperscript{7}Be factor likely reflects a general latitudinal gradient increasing towards tropics and the isentropic mixing of tropical and stratospheric air. The variability of CH\textsubscript{3}Cl and CH\textsubscript{2}Br explained by this factor is relatively small at 4 pptv and 0.15 pptv, respectively.

We estimate that stratospherically influenced air accounts for about 40% (14 ppbv) of the observed O\textsubscript{3} variation (Figs. 1 and 2). An uncertainty in our analysis comes from
the significant $^7$Be source in the upper troposphere [e.g., Liu et al., 2001; Allen et al., 2003]. However, $^7$Be concentrations are much lower in the upper tropospheric than the stratosphere due to the large difference of air residence time. Allen et al. [2003] showed that the variability due to $^7$Be produced in the stratosphere is much larger than that produced in the troposphere. It is a good tracer for the stratospheric air in the context of the observed variability during TOPSE [D. Allen, personal communication, 2002]. Furthermore, an upper tropospheric $^7$Be source does not necessarily imply that it will bias our results to favor the effect of stratospheric O$_3$. On the contrary, it would lead to an underestimate of the effect of stratospheric O$_3$ if the enhancement in $^7$Be is not accompanied by comparable enhancement in O$_3$ concentrations. It is in fact the case for TOPSE; the $\Delta$O$_3$/ $\Delta^7$Be ratio from a least-squares fit for data above 6 km is about half of that for those below 6 km. The resulting bias for our analysis is small because the least-squares fitted $\Delta$O$_3$/ $\Delta^7$Be ratio for the whole dataset is about the same as that for data above 6 km.

The Bermuda O$_3$-$^7$Be correlation analysis by Li et al. [2002] appears to show results that differ from our work for TOPSE. The data they used were collected near the surface during March-May, 1996 in Bermuda (32° N). The season is similar but the latitude and sampling altitude are different. During TOPSE, $^7$Be concentrations up to 4000 fCi/SCM were observed while the Bermuda site measurements are < 250 fCi/SCM. A least-squares fit of TOPSE mid-latitude observations yields a slope of 0.04 ppbv/fCi/SCM. The correlation coefficient is 0.8, indicating that the variance of $^7$Be explains about 65% of the O$_3$ variance. The variability ratio of O$_3$ to $^7$Be in the $^7$Be factor shows a similar value, 0.045 ppbv/fCi/SCM (Fig. 2). In comparison, Li et al. [2002]
showed a much larger slope of 0.45 ppbv/fCi/SCM; the correlation coefficient is very low, at only 0.36. The much higher $O_3$-$^7$Be slope at Bermuda indicates that transport from the stratosphere is not the major source of $O_3$ variability at Bermuda. If we simply scale the $\Delta O_3/\Delta ^7$Be obtained from the PMF analysis to the maximum variability of $^7$Be at Bermuda (about 160 fCi/SCM), we would estimate a maximum stratospheric contribution of 7 ppbv to the observed $O_3$ variability at Bermuda during March-May, 1996. Furthermore, if we assume that only 0.045 out of 0.45 ppbv/fCi/SCM in the observed $\Delta O_3/\Delta ^7$Be ratio can be expected from the stratospheric contribution based on our PMF analysis, the tropospheric contribution to the observed $O_3$ variability is about 90% at Bermuda. This result is consistent with that by Li et al. [2002].

The $NO_y$-PAN factor reflects $O_3$ production within the troposphere. During the oxidation of CO and hydrocarbons, freshly emitted $NO_x$ can be converted to $HNO_3$ and PAN, and $O_3$ is produced. The observed $O_3$ variation accounted for by this factor is about 30%, less than that by the $^7$Be factor. There are only two main factors for PAN variability (Fig. 2). Beside the $NO_y$-PAN factor, the other one is the $CH_4$-halocarbon factor. The latter is the most dominant factor for CO and $CH_4$ variability. It also contributes largely to the variability of the industrial tracer $C_2Cl_4$, suggesting that this factor is associated with air masses affected by industrial emissions. There is not a significant PAN signal in the hydrocarbon factor, which has large CO, $CH_4$, and $C_2Cl_4$ signals because the seasonal trend of this factor is opposite to that of PAN. The lack of $NO_y$ signal in the $CH_4$-halocarbon factor, despite its large PAN signal, may reflect the different seasonal trends of $NO_y$ and PAN during TOPSE [Wang et al., 2003]. The sum of $NO_y$ components including PAN and $HNO_3$ is generally higher than the observed $NO_y$ and the former has a
stronger seasonal trend; the reason for this discrepancy is unclear [Wang et al., 2003]. A least-squares fit of PAN and NO\textsubscript{y} shows that the variance of PAN explains about 30% of that of NO\textsubscript{y}.

Figure 3 shows the 10-day backtrajectories for data points with high factor scores for the \(^{7}\text{Be}\) and NO\textsubscript{y}-PAN factors. Both are associated with the westerlies at northern mid latitudes in spring. The trajectories related to the \(^{7}\text{Be}\) factor tend to extend further west into Europe whereas those related to the NO\textsubscript{y}-PAN factor tend to cluster over the western Pacific. The backtrajectory altitude of the \(^{7}\text{Be}\) factor resides mostly above 6 km, while those related to NO\textsubscript{y}-PAN factor reside more likely at 2-6 km. Very few backtrajectories initiated at 0-2 km or south of 30° N. Mid-latitude emissions of O\textsubscript{3} precursors from East Asia, after being lifted out of the boundary layer, could have contributed significantly to the O\textsubscript{3} enhancement in the NO\textsubscript{y}-PAN factor. Pollutions from the Middle East and southern Europe, lifted by convection to high altitudes (> 6 km), could also contribute to the enhancement.

The observed tropospheric O\textsubscript{3} increase at mid latitudes can now be attributed to different factors. We conduct the least-squares fits for the variability of observed O\textsubscript{3} and that explained by each factor (Fig. 4). We analyze the linear seasonal trend because it reasonably represents the increase of monthly median O\textsubscript{3} variation and facilitates the evaluation of the contribution from different factors. The observed seasonal O\textsubscript{3} increase is 5.4 ppbv/month while that from the contribution of all factors is 6.3 ppbv/month. The seasonal increase contributed by the NO\textsubscript{y}-PAN factor is largest at 3.5 ppbv/month and that from the \(^{7}\text{Be}\) factor is at 2.5 ppbv/month. Contributions from the other factors are
negligible. Photochemistry within the troposphere therefore appears to be more important to the seasonal O$_3$ increase than transport from the stratosphere.

### 3.2 High latitudes

At high latitudes, the $^7$Be factor is still the largest contributor to the observed O$_3$ variability at about 35% (Fig. 5). The $\Delta$O$_3$/$\Delta^7$Be ratio in this factor is 0.03 fCi/SCM/ppbv (Fig. 6), lower than at mid latitudes. The lower ratio is entirely due to higher variability in $^7$Be at high latitudes, which is consistent with higher $^7$Be sources near the poles. The $\theta$ factor is the other one that has a large contribution (25%) of the observed O$_3$ variability. It also explains 60% and 20-30% of the variability in $\theta$ and many halocarbons, respectively. The NO$_y$-PAN factor, in contrast, accounts for only about 5% of the observed O$_3$ variability.

The 10-day backtrajectories for data points with high factor scores in the $^7$Be and $\theta$ factors at high latitudes are quite different (Fig. 7). A large fraction of data contributing to the $^7$Be factor circulated within the polar region north of 60° N. These backtrajectories reside generally above 6 km. In contrast, most of the data for the $\theta$ factor came from regions south of 60° N carried by the strong westerlies and were transported northward in the western United States. The related backtrajectories more likely reside below 6 km. Higher O$_3$ concentrations appear to be transported in the middle troposphere from the lower latitudes into high latitudes. Despite low in situ chemical production of O$_3$ [Wang et al., 2003], photochemical production of O$_3$ within the troposphere, through long-range transport from lower latitudes where photochemistry is active, still contributes significantly to the observed O$_3$ variability at high latitudes.
These two factors also account for much of the explained variability in $\theta$. The gradient of $\theta$ is much stronger from the stratosphere into the troposphere as compared to that from mid to high latitudes in the troposphere [e.g., Holton, 1995]; the former is reflected in the vertical stability in the stratosphere and the latter is limited by tropospheric baroclinic adjustment processes. Similarly we find that the $\theta$-CH$_3$Cl factor that explains most of the variability of $\theta$ at mid latitudes (Fig. 1) is related to transport from the subtropics into mid latitudes (not shown) and that it is associated with transport of CH$_3$Cl into the region. The larger contribution of latitudinal transport to the observed variability of $\theta$ across a much smaller gradient compared to transport from the stratosphere reflects much stronger latitudinal mixing in the northern hemisphere.

Although the $^7$Be and $\theta$ factors account for about 60% of the observed O$_3$ variability at high latitudes, their contribution to the seasonal trend of tropospheric O$_3$ is much smaller (Fig. 8). The observed seasonal trend for tropospheric O$_3$ at high latitudes is 5.5 ppbv/month; the trend explained by all 7 factors is 4.6 ppbv/month. The $^7$Be and $\theta$ factors account for 0.8 and 0.6 ppbv/month, respectively. The bulk of the seasonal O$_3$ increase is attributed to the NO$_y$-PAN and CH$_4$-halocarbon factors, accounting for 1.3 ppbv/month and 1.7 ppbv/month, respectively. These two factors also explain about 90% of the variability in observed PAN concentrations (Figs. 5 and 6). PAN is of tropospheric origin. These two factors therefore signify the effects of tropospheric production on the seasonal increase of tropospheric O$_3$.

The 10-day backtrajectories for data points with high factors scores in the NO$_y$-PAN factor (Fig. 7) show two primary pathways of transport via either mid-latitude westerlies over the Pacific or across the polar region. East Asia and northern Europe are
the likely source regions for the transported reactive nitrogen. Comparing to the transport of reactive nitrogen at mid latitudes (Fig. 3), the transport into the high latitudes tends to occur more below 6 km and is more likely to be affected by surface emissions.

Air masses contributing to the CH$_4$-halocarbon factor tend to be more stagnant than those to the NO$_y$-PAN factor with a large fraction of air circulating over Canada in the last 10 days. The tracer profile of the CH$_4$-halocarbon factor also reflects the origins of air masses. Among the 7 factors, two account for about 80% of the observed CH$_4$ variability. One is the CH$_4$-halocarbon factor. The other factor, which accounts for about 35% of the observed CH$_4$ variability, is associated with the seasonal decrease of hydrocarbons as defined largely by C$_2$H$_2$ and C$_3$H$_8$ (Fig. 5). The strong CH$_4$ signal likely reflects natural gas leaks from Russia, which has a large reservoir and active production of natural gas [van Meurs & Associates, 1997].

The CH$_4$-halocarbon and $\theta$ factors have strong halocarbon signatures (Figs. 5 and 6). These two factors and the hydrocarbon factor explain most of the observed variability in these species. Production of CFC-11 and Halon-1211 has been banned in developed countries. The halocarbon signals in the cross-Pacific transport as illustrated by the $\theta$ factor likely reflect the release of these halocarbons from China. The halocarbon signals in the CH$_4$-halocarbon factor appear to suggest continuing release of halocarbons (including CFC-11 and Halon-1211) from Russia.

Our results on the stratospheric contribution to the O$_3$ variability and seasonal trend are generally consistent with those derived from the global 3-D simulation by Allen et al. [2003]. The two results cannot be compared directly because we can only examine the variability and trend using our methodology while Allen et al. could estimate the
stratospheric contribution to O\textsubscript{3} concentrations. Dibb et al. [2003], by analyzing the O\textsubscript{3}-\textsuperscript{7}Be correlation, found that high-latitude O\textsubscript{3} from the stratosphere does not contribute to the seasonal O\textsubscript{3} increase; we draw a similar conclusion in our analysis. They estimated that >85\% of high-latitude O\textsubscript{3} is related to the stratospheric source by further interpreting the “residual O\textsubscript{3}” from the intercept values of O\textsubscript{3}-\textsuperscript{7}Be least-squares fitting. This estimate is larger than our estimates, although we have attempted to resolve only the variability. Browell et al. [2003] suggests that > 80\% of the O\textsubscript{3} trend is due to tropospheric photochemistry on the basis of O\textsubscript{3} correlations with observed aerosol concentrations and model computed potential vorticity. Our result at high latitudes agrees well with their estimate. At mid latitudes, we estimate a much higher stratospheric contribution (about 40\%) to the observed O\textsubscript{3} trend. It is unclear if their estimate would be closer to ours if only observations at middle latitude (rather than the whole dataset) are considered in their analysis.

4. Conclusions

PMF and PCA analysis techniques are applied to analyze the TOPSE observations to investigate the various factors contributing to the observed variability of tropospheric O\textsubscript{3} and its seasonal trend observed during spring 2000 at mid and high latitudes. A suite of 14 chemical tracers and 1 dynamic tracer were used to define the chemical characteristics of the air masses. The coincident data of 15 tracers we used in the analysis are a small subset of all TOPSE measurements due largely to the availability of \textsuperscript{7}Be measurements. As a result, our results are biased towards the middle and upper troposphere. We find no bias in the probability distribution of O\textsubscript{3} concentrations (binned by 10 ppbv) in the subset, but a larger fraction of measurements, 70\% vs. 50\% for the
whole dataset, was taken at 5-8 km. The seasonal O$_3$ trend in the subset is in agreement with all O$_3$ data above 5 km.

We find that the PMF results are clearer for physical interpretation than those of PCA. Computed 10-day backtrajectories contributing to each factor are examined to define the geographical characteristics of the air masses. The chemical characteristics from factor analysis and the associated backtrajectories provide complimentary information that is in general consistent with our current understanding of the source distributions of chemical and dynamical tracers. While it cannot offer the depth of information that can be extracted from 3-D model simulations, the analysis provides important observation-based constraints on the controlling factors for springtime O$_3$ variability and its seasonal trend at northern mid and high latitudes.

The intercontinental nature of pollution transport in spring is clearly evident in our results. At mid latitudes, the timescale of transport of pollutants from Eurasia to North America is only 1-2 weeks by mid-latitude westerlies. Coupled with a favorable photochemical environment, O$_3$ production by reactive nitrogen emitted from Eurasia (with possible contributions from North America) is a major factor leading to the observed O$_3$ variability and seasonal trend during TOPSE. We estimate that this source, related to the PAN-NO$_y$ factor, explains an O$_3$ enhancement of 11 ppbv and a seasonal trend of 3.5 ppbv/month.

At high latitudes, the effect of intercontinental transport becomes even more prominent in part because springtime photochemistry in the region is relatively slow. It is manifested in the transport of O$_3$ and its precursors. The dominant tropospheric factor affecting the observed O$_3$ variability is related to the transport of potential temperature (θ
factor) from lower latitudes, where the high availability of photons and anthropogenic emissions result in a general “background” O₃ enhancement compared to high latitudes. We estimate that it contributes to an O₃ enhancement of about 11 ppbv but only 0.6 ppbv/month in the seasonal trend. In contrast, the PAN-NOₓ and CH₄-halocarbon factors, which explain all the variability of PAN (120 and 60 pptv, respectively), contribute respectively 1.3 and 1.7 ppbv/month to the seasonal trend even though their contribution to the O₃ variability is about 4 ppbv each. Therefore, transport of O₃ from lower latitudes, which is poor in reactive nitrogen, tends to dominate O₃ variability while transport of reactive nitrogen rich air masses tends to dominate the seasonal trend. Cross-Pacific transport is important in all cases; cross-Arctic transport is also important for reactive nitrogen rich air masses. In addition, the halocarbon signals in the CH₄-halocarbon factor appear to indicate continuing release of halocarbons (including CFC-11 and Halon-1211) from Russia.

Transport from the stratosphere, diagnosed through the ⁷Be factor, is also important. It is manifested mostly above 6 km while transport of tropospheric O₃ and its precursors is more likely to be important at 2-6 km, indicating that the stratospheric influence decreases with altitude. We estimate that it contributes to an O₃ enhancement of about 14 ppbv (35-40%) for data with O₃ concentrations < 100 ppbv at mid and high latitudes. There is a large latitudinal difference in its contribution to the seasonal trend, at 2.5 ppbv/month (40%) at mid latitudes but only 0.8 ppbv/month (<20%) at high latitudes. The difference probably reflects increasing activity of the more vigorous dynamical systems at mid latitudes in spring.
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References


**Figure captions**

**Fig. 1.** Explained variation (defined in section 2) of each tracer in the 7 factors at mid latitudes (40-60° N). The last panel in the right column shows the EV percentages explained by all the factors. The factors are named after the tracers that have strong signals. The results are for data with O₃ concentrations < 100 ppbv.

**Fig. 2.** The tracer variation ([tracer]-[tracer]ₘᵢₙ) explained by each factor. The results are for data with O₃ concentrations < 100 ppbv.

**Fig. 3.** 10-day backtrajectories of data points that rank top 30% by the factor score (Eq. 2) for the NOₓ-PAN and ⁷Be factors at mid latitudes. The pluses show the locations of measurements. The backtrajectory location every hour is represented by a dot and the end point is marked by a diamond. The results are for data with O₃ concentrations < 100 ppbv.

**Fig. 4.** Least-squares fits of O₃ variation ([O₃]-[O₃]ₘᵢₙ) as a function of Julian day for the observed and PMF fitted O₃, and that explained by each factor at mid latitudes. The monthly medians for the O₃ variations from the observations and the sum of all factors are also shown. The minimum O₃ concentration in the dataset is 27 ppbv. The results are for data with O₃ concentrations < 100 ppbv.

**Fig. 5.** Same as Fig. 1 but for high latitudes (60-85 ° N).

**Fig. 6.** Same as Fig. 2 but for high latitudes.

**Fig. 7.** Same as Fig. 3 but for the ⁷Be, θ, NOₓ-PAN, and CH₄-halocarbon factors at high latitudes.

**Fig. 8.** Same as Fig. 4 but for high latitudes. The minimum O₃ concentration in the dataset is 26 ppbv.
Figure 1
Figure 2
Figure 4
Figure 5
Figure 6
Figure 8