

Intercontinental transport of pollution manifested in the variability and seasonal trend of springtime O₃ at northern middle and high latitudes

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[1] 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 O₃ and its seasonal increase at 40°–85°N over North America. Factor analysis using the positive matrix factorization and principal component analysis methods is applied to the data set with 14 chemical tracers (O₃, NO_y, PAN, CO, CH₄, C₂H₂, C₃H₈, CH₃Cl, CH₃Br, C₂Cl₄, CFC-11, HCFC-141B, Halon-1211, and ⁷Be) and one 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 ⁷Be measurements. The identified tracer characteristics for seven factors are generally consistent with the geographical origins derived from their 10 day back trajectories. Stratospherically influenced air accounts for 14 ppbv (35–40%) of the observed O₃ variability for data with O₃ concentrations <100 ppbv at middle and high latitudes. It accounts for about 2.5 ppbv/month (40%) of the seasonal O₃ trend at midlatitudes but for only 0.8 ppbv/month (<20%) at high latitudes, likely reflecting more vigorous midlatitude dynamical systems in spring. At midlatitudes, 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 O₃ variability is significantly influenced by air masses transported from lower latitudes (11 ppbv), which are poor in reactive nitrogen. The O₃ 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 O₃ 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 O₃ variability and its seasonal trend is more important at high latitudes relative to more photochemically active midlatitudes.

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; *KEYWORDS:* TOPSE, springtime tropospheric ozone, stratospheric ozone source

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1. Introduction

[2] 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(¹D), which reacts with H₂O to produce OH radicals. Furthermore, it is an effective greenhouse gas.

[3] An interesting feature of tropospheric O₃ is the observed springtime increase at northern middle and high latitudes. Ozone concentrations at northern middle and high latitudes tend to peak in late spring (April and May) in the lower troposphere and in early/middle 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 three-dimensional (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 O₃ and ⁷Be tends to emphasize the effect of the stratospheric input [e.g., Oltmans and Levy, 1992; Dibb *et al.*, 1994].

[4] 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 (FRETEX'96 and 98) in the Swiss Alps (at an altitude of 3.6 km) [Carpenter *et al.*, 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 O₃ production at midlatitudes are large enough to explain the observed springtime O₃ increase at northern midlatitudes, although in situ O₃ 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 O₃ 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 O₃ chemical production at midlatitudes. Li *et al.* [2002] further suggested that the apparent correlation between surface observations of O₃ and ⁷Be in Bermuda merely reflects the subsidence of O₃ produced in the middle troposphere, not O₃ transported from the stratosphere.

[5] Applying global 3-D chemistry and transport models, a number of recent studies have investigated the effects of intercontinental transport on tropospheric O₃ concentrations from Asia to North America [e.g., Berntsen *et al.*, 1999; Jaffe *et al.*, 1999; Jacob *et al.*, 1999; Bey *et al.*, 2001]. 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].

[6] We analyze here aircraft springtime observations from TOPSE (February–May 2000) [Atlas *et al.*, 2003]. Thirty-eight science flights of the C-130 aircraft were conducted in seven 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 O₃, HO_x (OH + HO₂), and NO_x (NO + NO₂) were measured.

[7] This data set is the largest available that extends over broad latitude and altitude ranges on a seasonal timescale in spring. We will attempt to address in this work the effects on tropospheric O₃ variability and trend by intercontinental transport of O₃ and its precursors from different tropospheric regions and by transport of O₃ 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 O₃ and other species is critical.

2. Methodology

[8] 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 O₃ 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 back trajectory calculations.

[9] 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.

[10] Our results cannot be directly compared to model estimated fractional contributions to tropospheric O₃ 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 nonphysical. We choose the solution that entails the best physical explanation.

[11] 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

$$X = GF + E \quad (1)$$

or

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

where

$$i = 1, \dots, m;$$

$$j = 1, \dots, n;$$

$$k = 1, \dots, p.$$

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,

$$EV_{kj} = \sum_{i=1}^m |g_{ik} f_{kj}| / \left[\sum_{i=1}^m \left(\sum_{k=1}^p |g_{ik} + f_{kj}| + |e_{ij}| \right) \right], \quad (3)$$

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 data set 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].

[12] 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 O₃) 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 O₃, total reactive nitrogen (NO_y), peroxyacetylnitrate (PAN), CO, CH₄, C₂H₂, C₃H₈, CH₃Cl, CH₃Br, C₂Cl₄, CFC-11 (CCl₃F), HCFC-141B (CH₃CCl₂F), Halon-1211 (CBrClF₂), and ⁷Be. Total reactive nitrogen is a good tracer of air masses that intercepted large tropospheric NO_x emissions or stratospheric air. PAN is a by-product of NO_x oxidation in the presence of >C₂ hydrocarbons. It is a good tracer for tropospheric reactive nitrogen because the lifetime of >C₂ hydrocarbons is too short to be transported into the stratosphere. High concentrations of PAN often indicate occurrences of tropospheric O₃ production in the past and therefore tend to correlate with high O₃ concentrations in pollution plumes. Carbon monoxide and C₂H₂ are good tracers for combustion and C₃H₈ is a good liquefied gas tracer. Methane has many sources, some of which are collocated with industrial pollution sources. Methyl chloride and CH₃Br are thought to have substantial sources from the ocean and biomass burning. Tropical terrestrial biosphere is likely a major CH₃Cl 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 (θ), which is conserved during adiabatic processes. Potential vorticity is another useful dynamic tracer. It needs to be computed on the basis of θ and model simulated horizontal winds; the resulting temporal and spatial resolutions of this variable are much lower than the in situ measurements.

[13] The observed values of each variable are linearly scaled to a dimensionless range of 0–1 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 seven factors, which separate air mass tracer profiles well.

[14] The 10 day kinematic back trajectories used in this work are calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HY-SPLIT) model [Draxler and Hess, 1998]. The meteorological data are taken from the ‘FNL’ 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 back trajectory calculation is somewhat arbitrary; it is long enough to separate local influence from long-range transport [Pochanart *et al.*, 2001].

3. Results and Discussion

[15] The photochemical environment is quite different from middle 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 data set is limited mostly by the availability of ⁷Be data to 137 coincident measurements of all species at midlatitudes (40°–60°N) and 193 coincident measurements at high latitudes (60°–85°N). Including missing ⁷Be data by assigning large uncertainties [Polissar *et al.*, 1998] led to an underweight of the ⁷Be data, resulting in a poor O₃-⁷Be correlation and a large fraction of unexplained ⁷Be variability. As demonstrated by Li *et al.* [2002] and Dibb *et al.* [2003], faithfully capturing the O₃-⁷Be correlation is critical to resolve the contributions by various O₃ sources. Hence no missing ⁷Be data were included. Ozone concentrations in this subset show similar probability distributions (binned by 10 ppbv) as the data set with all measured O₃. The altitude distribution is shifted to higher altitude. The fraction of data above 5 km increases from 50% of all O₃ data to 70%. The seasonal O₃ trend of the subset is in agreement with that of all O₃ measurements above 5 km. Our results are therefore biased toward the middle and upper troposphere. The analysis results are about the same when measurements below 3 km are excluded.

[16] In order to establish the correlation between the stratospheric O₃ and ⁷Be, we have included in our analysis data points with O₃ concentrations >100 ppbv (5% of the data set), which are generally associated with the lower-stratospheric air. To minimize the effects of these lower-stratospheric data, all results shown hereafter are for data with O₃ concentrations <100 ppbv. Relative to the results with all the data included, the effects of the limited O₃ range

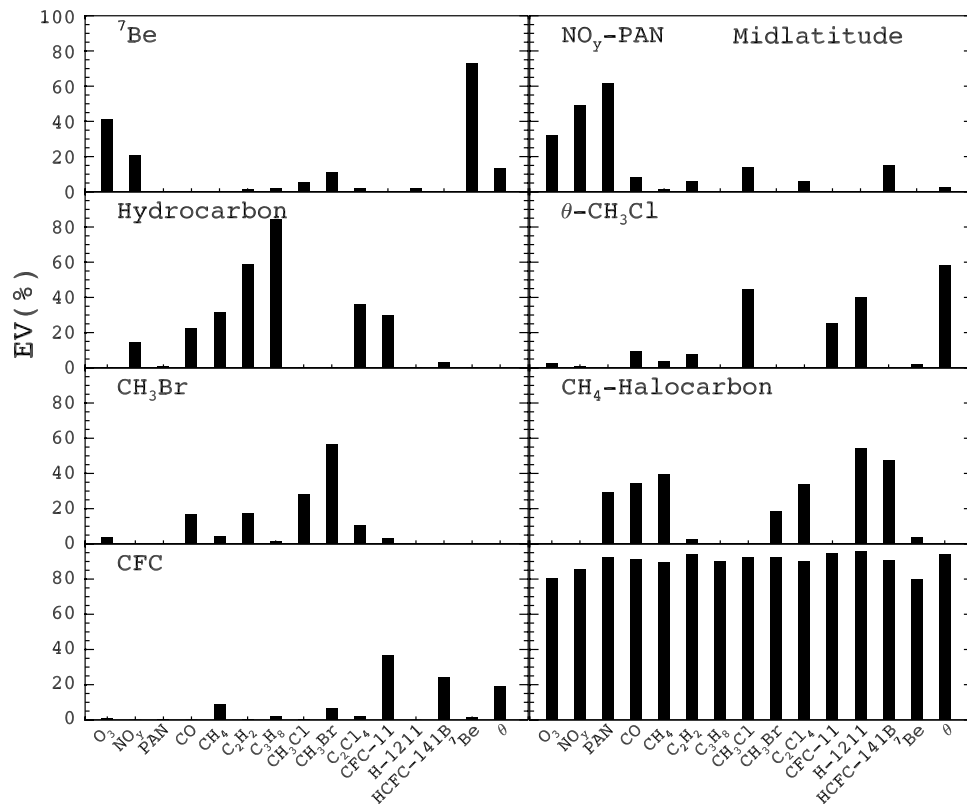


Figure 1. Explained variation (equation (3)) of each tracer in the seven factors at midlatitudes (40° – 60° N). The bottom panel in the right column shows the explained variation (EV) percentages explained by all the factors. The factors are named after the tracers that have strong signals. The results are for data with O_3 concentrations <100 ppbv.

are only apparent for O_3 and ^7Be and the estimated stratospheric contribution to O_3 variability is reduced. The EV percentages of O_3 in the factors (equation (3)) change by $<5\%$. The largest changes are seen in the explained variations of O_3 and ^7Be in the ^7Be factor, which decrease by 6 ppbv and 100–150 fCi/SCM, respectively.

3.1. Midlatitudes

[17] The EV profiles of the seven factors and the total EV explained by the analysis for data with O_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.

[18] Among the seven factors, only ^7Be and NO_y -PAN factors account for $>5\%$ of the observed variability of O_3 . The tracer profile of the ^7Be factor is consistent with a stratospheric origin. Potential temperature and HNO_3 concentrations in the stratosphere are much higher than those in the troposphere. The latter is reflected in the signal of NO_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_3Cl , we believe that the signal of CH_3Cl in the ^7Be factor likely reflects a general latitudinal increase of

CH_3Cl toward tropics and the isentropic mixing of tropical and stratospheric air. The variability of CH_3Cl and CH_3Br explained by this factor is relatively small at 4 pptv and 0.15 pptv, respectively.

[19] We estimate that stratospherically influenced air accounts for about 40% (14 ppbv) of the observed O_3 variation (Figures 1 and 2). An uncertainty in our analysis comes from the significant ^7Be source in the upper troposphere [e.g., Liu *et al.*, 2001; Allen *et al.*, 2003]. However, ^7Be concentrations are much lower in the upper troposphere than the stratosphere due to the large difference of air residence time. Allen *et al.* [2003] showed that the variability due to ^7Be 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 ^7Be source does not necessarily imply that it will bias our results to favor the effect of stratospheric O_3 . On the contrary, it could lead to an underestimate of the effect of stratospheric O_3 if the enhancement in ^7Be is not accompanied by comparable enhancement in O_3 concentrations. During TOPSE, the $\Delta O_3/\Delta ^7\text{Be}$ ratio from a least squares fit for data above 6 km is about half of that for those below 6 km; the least squares fitted $\Delta O_3/\Delta ^7\text{Be}$ ratio for the whole data set is about the same as that for data above 6 km.

[20] The Bermuda O_3 - ^7Be 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

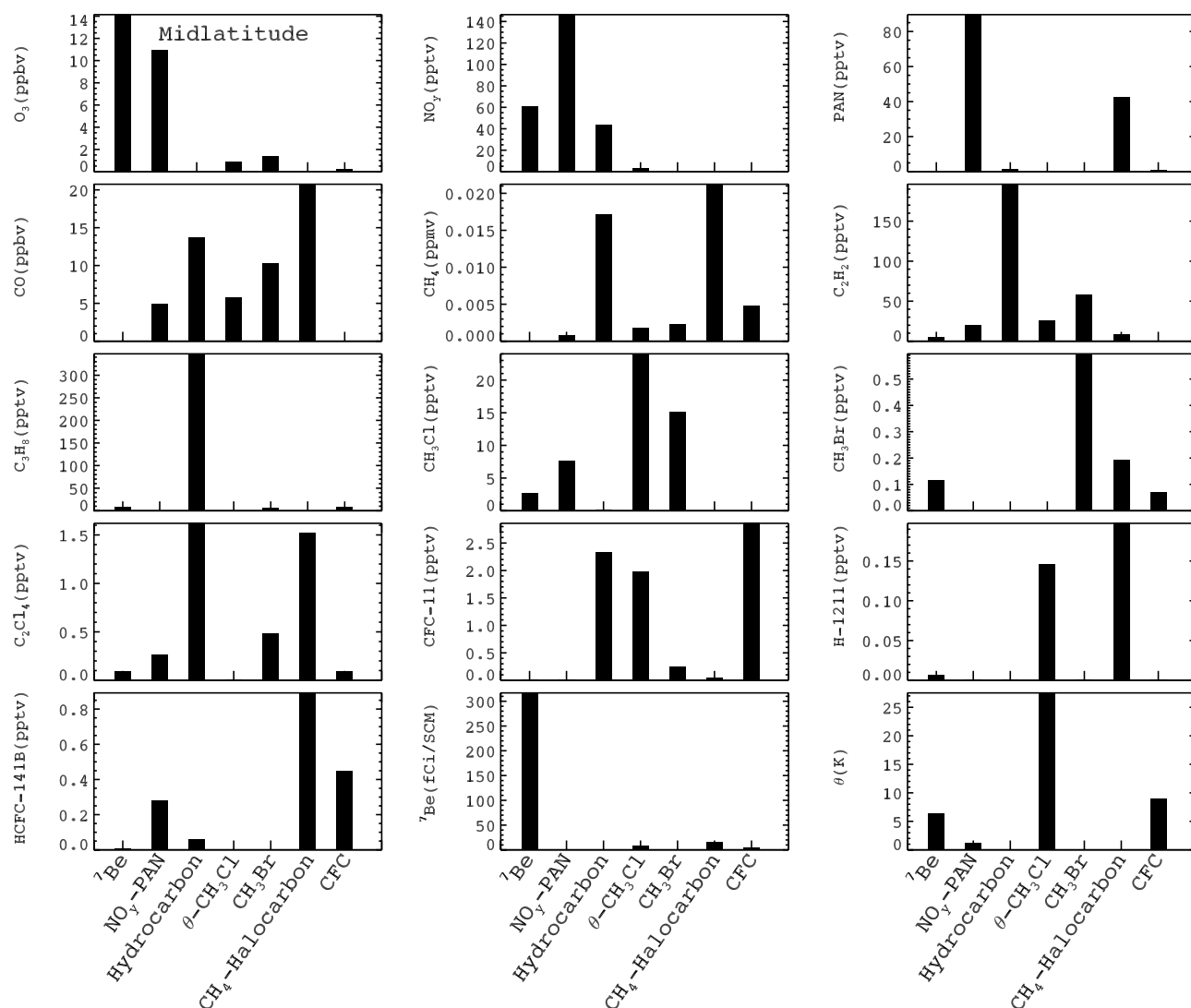


Figure 2. The tracer variation ($[\text{tracer}] - [\text{tracer}]_{\min}$) explained by each factor. The results are for data with O_3 concentrations < 100 ppbv.

during March–May 1996 in Bermuda (32°N). The season is similar but the latitude and sampling altitude are different. During TOPSE, ^7Be concentrations up to 4000 fCi/SCM were observed while the Bermuda site measurements are < 250 fCi/SCM. A least squares fit of TOPSE midlatitude observations yields a slope of 0.04 ppbv/(fCi/SCM). The correlation coefficient is 0.8, indicating that the variance of ^7Be explains about 65% of the O_3 variance. The variability ratio of O_3 to ^7Be in the ^7Be factor shows a similar value, 0.045 ppbv/(fCi/SCM) (Figure 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 - ^7Be 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 $\Delta\text{O}_3/\Delta^7\text{Be}$ ratio obtained from the PMF analysis to the maximum variability of ^7Be 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 $\Delta\text{O}_3/\Delta^7\text{Be}$ 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].

[21] 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 ^7Be factor. There are only two main factors for PAN variability (Figure 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

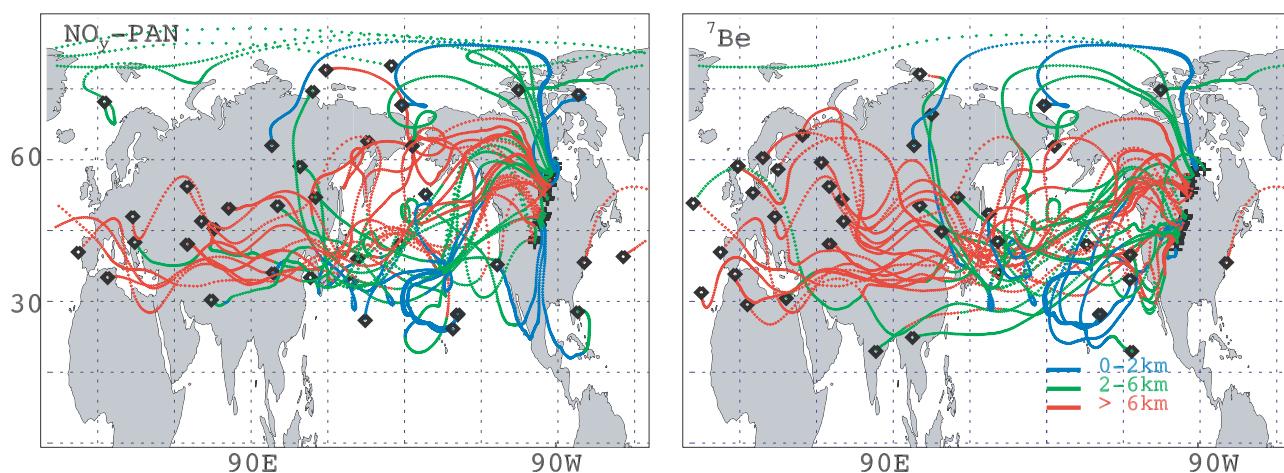


Figure 3. Ten day back trajectories of data points that rank in the top 30% by factor score (equation (2)) for the NO_y -PAN and ^7Be factors at midlatitudes. The crosses show the locations of measurements. The back trajectory location every hour is represented by a dot, and the end point is marked by a diamond. The results are for data with O_3 concentrations < 100 ppbv.

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_y , shows that the variance of PAN explains about 30% of that of NO_y .

[22] Figure 3 shows the 10 day back trajectories for data points with high factor scores for the ^7Be and NO_y -PAN factors. Both are associated with the westerlies at northern midlatitudes in spring. The trajectories related to the ^7Be factor tend to extend farther west into Europe whereas those related to the NO_y -PAN factor tend to cluster over the western Pacific. The back trajectory altitude of the ^7Be factor resides mostly above 6 km, while those related to NO_y -PAN factor reside more likely at 2–6 km. Very few back trajectories initiated at 0–2 km or south of 30°N . Midlatitude emissions of O_3 precursors from East Asia, after being lifted out of the boundary layer, could have contributed significantly to the O_3 enhancement in the NO_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.

[23] The observed tropospheric O_3 increase at midlatitudes can now be attributed to different factors. We conduct the least squares fits for the variability of observed O_3 and that explained by each factor (Figure 4). We analyze the linear seasonal trend because it reasonably represents the increase of monthly median O_3 variation and facilitates the evaluation of the contribution from different factors. The observed seasonal O_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_y -PAN factor is largest at 3.5 ppbv/month and that from the ^7Be 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

[24] At high latitudes, the ^7Be factor is still the largest contributor to the observed O_3 variability at about 35% (Figure 5). The $\Delta\text{O}_3/\Delta^7\text{Be}$ ratio in this factor is

0.03 ppbv/(fCi/SCM) (Figure 6), lower than at midlatitudes. The lower ratio is entirely due to higher variability in ^7Be at high latitudes, which is consistent with higher ^7Be sources near the poles. The θ 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 θ and many halocarbons, respectively. The NO_y -PAN factor, in contrast, accounts for only about 5% of the observed O_3 variability.

[25] The 10 day back trajectories for data points with high factor scores in the ^7Be and θ factors at high latitudes are quite different (Figure 7). A large fraction of data contributing to the ^7Be factor circulated within the polar region

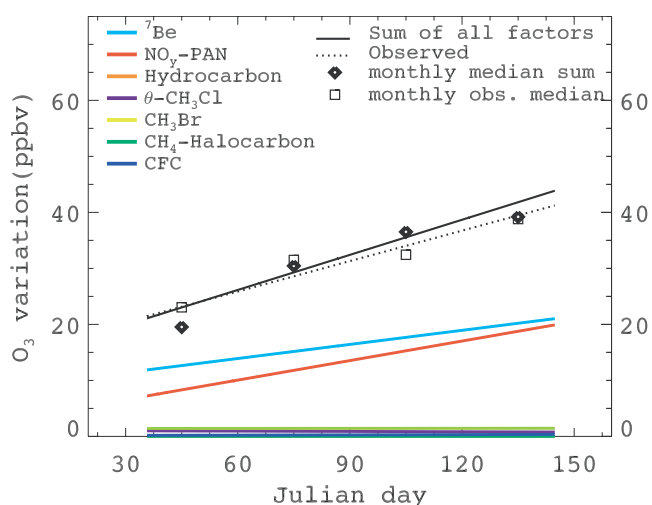


Figure 4. Least squares fits of O_3 variation ($[\text{O}_3] - [\text{O}_3]_{\min}$) as a function of Julian day for the observed and positive matrix factorization-fitted O_3 and that explained by each factor at midlatitudes. The monthly medians for the O_3 variations from the observations and the sum of all factors are also shown. The minimum O_3 concentration in the data set is 27 ppbv. The results are for data with O_3 concentrations < 100 ppbv.

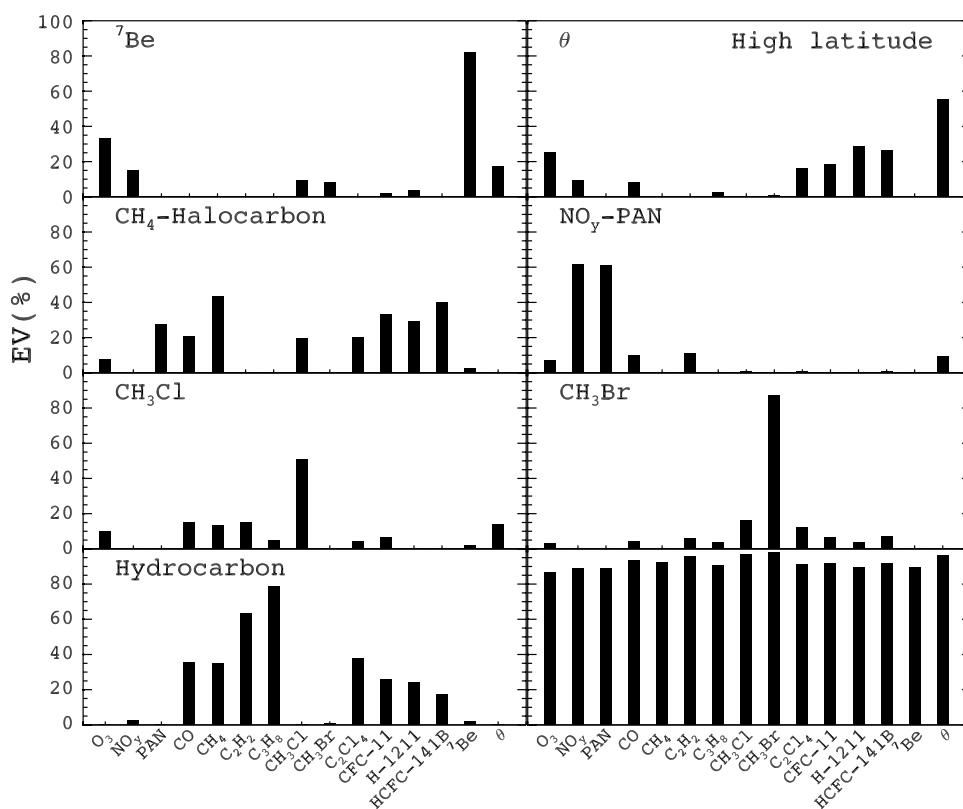


Figure 5. Same as Figure 1 but for high latitudes (60° – 85° N).

north of 60° N. These back trajectories reside generally above 6 km. In contrast, most of the data for the θ factor came from regions south of 60° N carried by the strong westerlies and were transported northward in the western United States. The related back trajectories 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.

[26] These two factors also account for much of the explained variability in θ . The gradient of θ is much stronger from the stratosphere into the troposphere as compared to that from middle to high latitudes in the troposphere [e.g., Holton *et al.*, 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 θ - CH_3Cl factor that explains most of the variability of θ at midlatitudes (Figure 1) is related to transport from the subtropics into midlatitudes (not shown) and that it is associated with transport of CH_3Cl into the region. The larger contribution of latitudinal transport to the observed variability of θ across a much smaller gradient compared to transport from the stratosphere reflects much stronger latitudinal mixing in the northern hemisphere.

[27] Although the 7Be and θ 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 (Figure 8). The observed seasonal trend for tropospheric O_3 at high latitudes is 5.5 ppbv/month; the trend explained by all seven factors is 4.6 ppbv/month. The 7Be and θ 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 (Figures 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 .

[28] The 10 day back trajectories for data points with high factor scores in the NO_y -PAN factor (Figure 7) show two primary pathways of transport via either midlatitude 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 midlatitudes (Figure 3), the transport into the high latitudes tends to occur more below 6 km and is more likely to be affected by surface emissions.

[29] 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 seven 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_2H_2 and C_3H_8 (Figure 5). The strong CH_4 signal in the CH_4 -halocarbon factor likely reflects

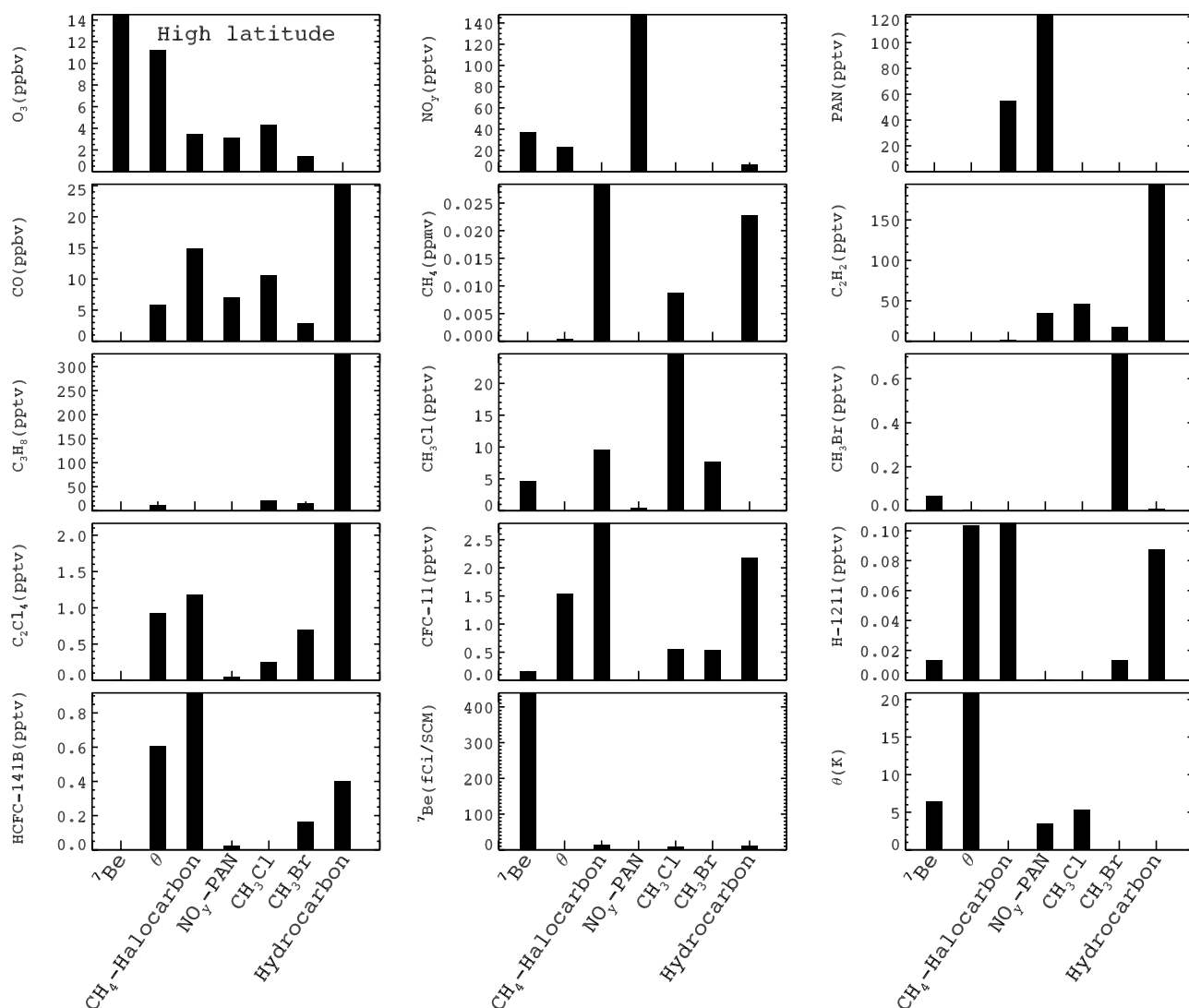


Figure 6. Same as Figure 2 but for high latitudes.

natural gas leaks from Russia, which has a large reservoir and active production of natural gas [van Meurs, 1997].

[30] The CH_4 -halocarbon and θ factors have large halocarbon signatures (Figures 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 θ 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.

[31] 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.* [2003] could estimate the stratospheric contribution to O_3 concentrations. Dibb *et al.* [2003], by analyzing the O_3 - ^7Be correlation, found that high-latitude O_3 from the stratosphere does not contribute to the seasonal O_3 increase; we draw a similar conclusion in our

analysis. They estimated that >85% of high-latitude O_3 is related to the stratospheric source by further interpreting the “residual O_3 ” from the intercept values of O_3 - ^7Be 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_3 trend is due to tropospheric photochemistry on the basis of O_3 correlations with observed aerosol concentrations and model computed potential vorticity. Our result at high latitudes agrees well with their estimate. At midlatitudes, we estimate a much higher stratospheric contribution (about 40%) to the observed O_3 trend. It is unclear if their estimate would be closer to ours if only observations at midlatitudes (rather than the whole data set) are considered in their analysis.

4. Conclusions

[32] 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_3 and its seasonal trend observed during spring 2000 at middle and high latitudes. A suite of 14 chemical

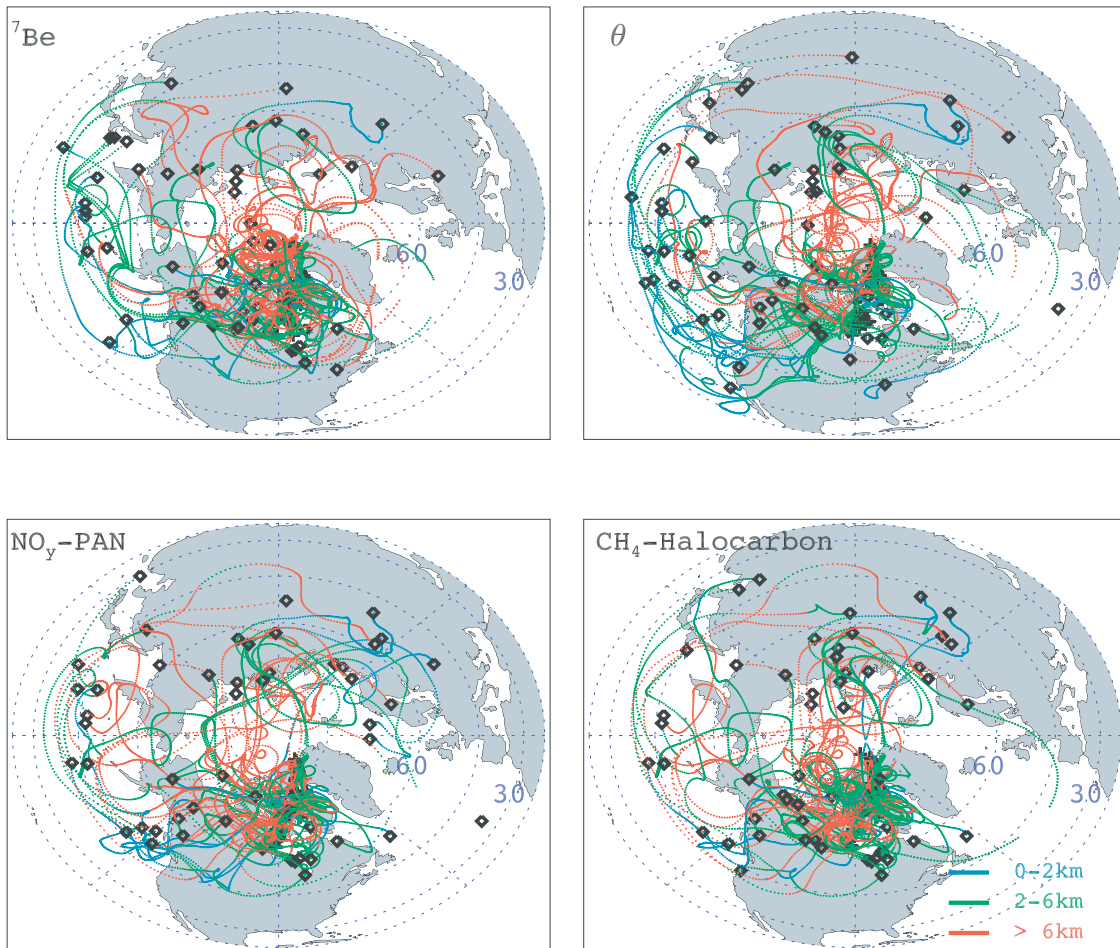


Figure 7. Same as Figure 3 but for the ${}^7\text{Be}$, θ , $\text{NO}_y\text{-PAN}$, and $\text{CH}_4\text{-halocarbon}$ factors at high latitudes.

tracers and one 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 ${}^7\text{Be}$ measurements. As a result, our results are biased toward the middle and upper troposphere. We find no bias in the probability distribution of O_3 concentrations (binned by 10 ppbv) in the subset, but a larger fraction of measurements, 70% vs. 50% for the whole data set, 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.

[33] We find that the PMF results are clearer for physical interpretation than those of PCA. Computed 10 day back trajectories contributing to each factor are examined to define the geographical origins of the air masses. The chemical characteristics from factor analysis and the associated back trajectories provide complementary 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 middle and high latitudes.

[34] The intercontinental nature of pollution transport in spring is clearly evident in our results. At midlatitudes, the

timescale of transport of pollutants from Eurasia to North America is only 1–2 weeks by midlatitude 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

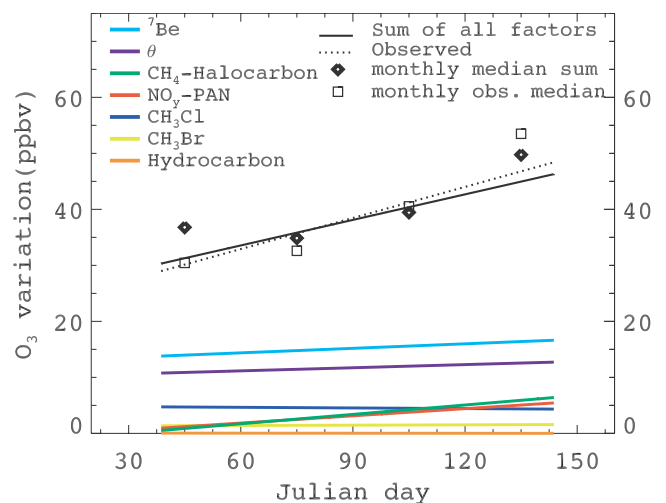


Figure 8. Same as Figure 4 but for high latitudes. The minimum O_3 concentration in the data set is 26 ppbv.

factor leading to the observed O₃ variability and seasonal trend during TOPSE. We estimate that this source, related to the PAN-NO_y factor, explains an O₃ enhancement of 11 ppbv and a seasonal trend of 3.5 ppbv/month.

[35] At high latitudes, the effect of intercontinental transport becomes even more prominent in part because spring-time photochemistry in the region is relatively slow. It is manifested in the transport of O₃ and its precursors. The dominant tropospheric factor affecting the observed O₃ 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-NO_y 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.

[36] 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 middle and high latitudes. There is a large latitudinal difference in its contribution to the seasonal trend. It is 2.5 ppbv/month (40%) at midlatitudes but only 0.8 ppbv/month (<20%) at high latitudes. The difference probably reflects increasing activity of the more vigorous dynamical systems at midlatitudes in spring.

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