Source characteristics of oxygenated volatile organic compounds and hydrogen cyanide

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[1] Airborne trace gas measurements from Transport and Chemical Evolution over the Pacific (TRACE-P), Pacific Exploratory Mission (PEM)-Tropics B, and Intercontinental Chemical Transport Experiment-North America (INTEX-NA) experiments are analyzed to examine the major source factors contributing to the observed variabilities of oxygenated volatile organic compounds and cyanides. The positive matrix factorization method is applied to coincident measurements of 11 chemicals including CH_3OH, CH_3COCH_3, CH_3CHO, C_2H_2, C_2H_6, i-C_5H_{12}, CO, CH_3Cl, and $CHBr_3$. Measurements of HCN and CH_3CN are available for TRACE-P and INTEX-NA. We identify major source contributions from the terrestrial biosphere, biomass burning, industry/urban regions, and oceans. Spatial and back trajectory characteristics of these factors are examined. On the basis of TRACE-P and PEM-Tropics B data, we find a factor that explains 80–88% of the CH_3OH variability, 20–40% of CH_3COCH_3, 7–35% of CH_3CHO, and 41% of HCN, most likely representing the emissions from terrestrial biosphere. Our analysis suggested that biogenic emissions of HCN may be significant. Cyanogenesis in plants is likely a major emission process for HCN, which was not fully accounted for previously. Larger contributions than previous global estimations to CH_3COCH_3 and CH_3CHO by biomass burning and industry/urban sources likely reflect significant secondary production from volatile organic compound oxidation. No evidence was found for large emissions of CH_3COCH_3 from the ocean. The oceanic CH_3CHO contribution implies large regional variations.

1. Introduction

[2] Oxygenated volatile organic compounds (OVOCs) are a critical component of tropospheric photochemistry [e.g., *Singh et al.*, 2004]. Previous studies found significant emissions of OVOCs from the biosphere, which affect not only trace gas composition and chemistry but also aerosols and subsequently the radiative budget of the atmosphere [e.g., *Fuentes et al.*, 2000; *Guenther et al.*, 2000; *Fall*, 2003]. There have been many efforts to estimate the global budgets of OVOCs [*Guenther et al.*, 1995; *Galbally and Kirstine*, 2002; *Heikes et al.*, 2002; *Jacob et al.*, 2002; *Singh et al.*, 2004]. Despite these efforts, there are still large uncertainties and many unknowns.

[3] Hydrogen cyanide (HCN) is an often used indicator for biomass burning [e.g., *Rinsland et al.*, 1998]. Ocean uptake is considered to be the main sink, leading to a lifetime of a few months [*Li et al.*, 2000]. Additionally, biogenic processes are known to produce HCN and CH_3COCH_3 simultaneously [*Conn*, 1991]. A specific metabolic process is cyanogenesis in plants (for example, food crops, clovers, and eucalyptus leaves), which is part of plant defensive activity to fend off herbivores during the growing season [*Fall*, 2003; *Gleadow and Woodrow*, 2000]. Global estimates of biogenic HCN production are highly uncertain partly because this complicated biochemical process is not well understood over the diverse terrestrial ecosystems.

[4] In order to identify and quantify major source contributions to OVOCs and cyanides, we analyze aircraft measurements made during the Transport and Chemical Evolution over the Pacific (TRACE-P), Pacific Exploratory Mission (PEM)-Tropics B, and Intercontinental Chemical Transport Experiment-North America (INTEX-NA) experiments [*Raper et al.*, 2001; *Singh et al.*, 2002; *Jacob et al.*, 2003]. We apply factor analysis using the positive matrix factorization (PMF) method to analyze these measurements. We show the characteristics of each source factor and calculate their contributions to OVOC and cyanide variability.

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Finally, we compare these results with the global budgets estimated by previous studies.

2. Methodology

[5] We choose a suite of chemicals, including methanol (CH_3OH), acetone (CH_3COCH_3), acetaldehyde (CH_3CHO), ethyne (C_2H_2), ethane (C_2H_6), i-pentane (i-C_5H_{12}), carbon monoxide (CO), methyl chloride (CH_3Cl), and bromoform ($CHBr_3$). The suite of chemicals is chosen to resolve the sources for OVOCs and cyanides; the limited tracer set is not meant to resolve different industrial/urban emission sources. Oxygenated organic chemicals and cyanides are measured by gas chromatography (GC) [*Singh et al.*, 2004] or gas chromatography-mass spectroscopy (GC-MS) [*Apel et al.*, 2003]. Ethyne (C_2H_2), ethane (C_2H_6), i-pentane (i-C_5H_{12}), and halocarbons are captured in canisters and analyzed by GC-MS [*Blake et al.*, 1996]. CO is measured by differential absorption CO measurement (DACOM) with three-tunable-diode-laser spectrometer [*Novelli et al.*, 1994]. Methanol has large terrestrial biogenic emissions [*Fall and Benson*, 1996; *Galbally and Kirstine*, 2002]. Major CH_3COCH_3 sources are from the terrestrial biosphere [*Pouton*, 1990; *Jacob et al.*, 2002; *Singh et al.*, 2004], the biomass burning [*Jost et al.*, 2003], and the ocean [*Jacob et al.*, 2002]. CH_3CHO has known biogenic and oceanic sources [*Harry and Kimmerer*, 1991; *Singh et al.*, 2004] although the uncertainty in the budget is large. CH_3COCH_3 and CH_3CHO also have significant photochemical sources [*Jacob et al.*, 2002; *Singh et al.*, 2004]. All CH_3CHO measurements used in this study were made using the same gas chromatographic instrument. Some cases of inconsistencies of CH_3CHO measurements with concurrent NO_x and PAN measurements were previously found [*Singh et al.*, 2004], indicating the possibility that the CH_3CHO measurements were seriously flawed. However, there is no clear evidence of instrument biases at this point [*Northway et al.*, 2004]. C_2H_2 and CO are good tracers for combustion [*Talbot et al.*, 1997]. C_2H_6 is a good tracer for the usage of fossil fuel [*Staudt et al.*, 2001]. Isopentane is a unique tracer for gasoline evaporation and gasoline-powered motor vehicle emissions and hence the emissions from urban regions in general [*Rubin et al.*, 2006]. It is not included in the PEM-Tropics B analysis because its concentrations in the remote tropical Pacific are generally below the detection limit. CH_3Cl is a tracer for biomass burning and biogenic emissions [*Yoshida et al.*, 2004 and references therein]. $CHBr_3$ is a tracer for oceanic emissions [*Singh et al.*, 2004]. In addition, HCN and CH_3CN, available in TRACE-P and INTEX-NA, are included. They are generally considered biomass-burning tracers [*de Gouw et al.*, 2003; *Li et al.*, 2003; *Singh et al.*, 2003a].

[6] To investigate the major sources contributing to the variability of these tracers, we use the PMF method, which has been applied previously to identify source factors of aerosols and trace gases [e.g., *Paatero*, 1997; *Wang et al.*, 2003; *Liu et al.*, 2005]. The factors are obtained from examining the covariance structure of the data sets [*Paatero*, 1997]. In the analysis, we selected only coincident measurements of the chemicals. Missing data are not used in order to reduce the uncertainty in the analysis.

[7] The data matrix X of m measurements by n tracers can be decomposed by PMF for p factors as

$$X = GF + E \tag{1}$$

or

$$x_{ij} = \sum_{k=1}^{p} g_{ik}f_{kj} + e_{ij} \tag{2}$$

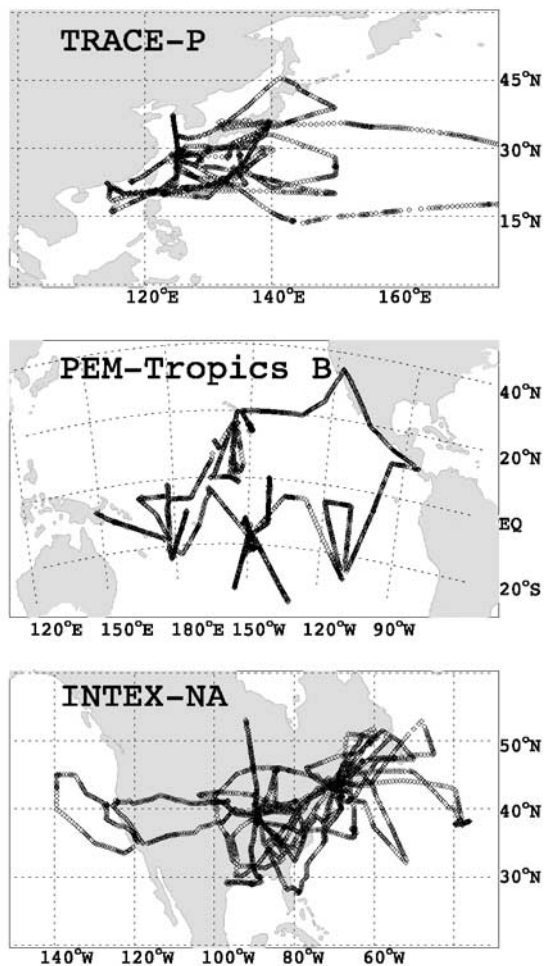$$i = 1, \ldots, m; j = 1, \ldots, n; k = 1, \ldots, p.$$

where the m by p matrix G is the mass contribution (factor score), the p by n matrix F is the gravimetric average contribution (factor loadings), and the m by n matrix E is the error. We also use the explained variation (EV),

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

to define the relative contributions of each factor to chemical species since the mixing ratios of different compounds are not directly comparable. A large EV value of a species in a factor indicates that this particular factor explains a major fraction of the species; that is, the data points associated with this factor represent the air masses that contribute largely to high concentrations of the species over its background level. The analysis approach is the same as that used by *Wang et al.* [2003].

[8] As commonly found in principal component and factor analyses, the minimization of the error matrix does not lead to a unique decomposition of matrix X to matrices G and F. Matrix rotation is one way to explore the constraints of the covariance structure. As in the work of *Wang et al.* [2003], the results presented here are not sensitive to rotation. For factor analysis, a key parameter is the choice of factor number. By evaluating the error matrix E [*Paatero*, 1997; *Paatero et al.*, 2002], a range of factor numbers is determined. We then inspect the PMF results and determine the number of factors (with necessary rotation) that leads to clear separation of tracer signals. Following this procedure, we determined six factors for TRACE-P and five factors for PEM-Tropics B and INTEX-NA, which provide most physically meaningful results.

[9] In the work of *Wang et al.* [2003], PMF analysis was used to identify air mass characteristics. That is the first objective of this work. The second objective is to investigate if the tracer signals in factor contributions can be used to gauge our understanding of emissions of these trace gases. In this case, the nonnegativity in factor contributions calculated using an alternating least squares method in PMF [*Paatero*, 1997] offers a major advantage over less advanced techniques because source contributions by definition can only be positive. In order to attempt the second objective, the inversion of sources using factor analysis makes the assumption that factor profiles represent a linear combination of source contributions. The assumption is obviously false for chemicals with large secondary sources. It is also false if the chemicals have short lifetimes in the tropo-

Figure 1. Location of aircraft measurements during TRACE-P (top), PEM-Tropics B (middle), and INTEX-NA (bottom).

sphere. The influence of transport is difficult to quantify in factor analysis. We note here two specific problems arising from transport. First, the anticorrelation driven by source location difference (for example, the often observed anti-correlation between a ozone transported from the strato-sphere and a CO emitted from the surface), which tends to manifest in principal component analysis, does not pose a problem in PMF analysis. Second, transport processes do not "create" air masses with clean tracer characteristics; mixing during transport reduces source signals instead. As a result, the source characters cannot always be resolved by factor analysis. In this work, we show that the tracer source characteristics can be resolved for TRACE-P and PEM-Tropics B. However, transport/mixing processes during INTEX-NA result in mixed source characteristics. PMF cannot clearly resolve the source contributions in that data set.

[10] Despite all the assumptions, we will attempt to compare source contributions inferred from PMF analysis of the two data sets with current source estimates. The empirical approach is advantageous over three-dimensional model studies when the source types, distributions, and

strengths for the chemicals of interests are not well understood. Furthermore, the PMF results are not affected by uncertainties in three-dimensional model chemistry and transport. Figure 1 shows the measurement regions during the TRACE-P, PEM-Tropics B, and INTEX-NA experiments.
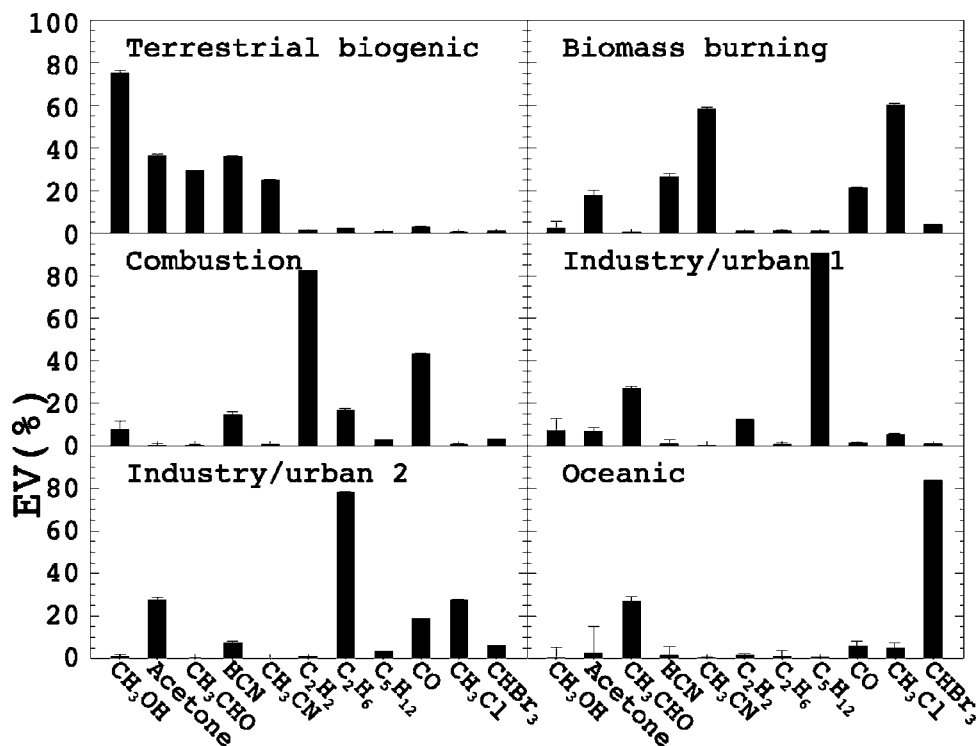
3. Results

3.1. TRACE-P

[11] The TRACE-P experiment was conducted to investigate the Asian outflow to the Pacific during springtime (March–April 2001) [*Jacob et al.*, 2003]. There are 386 coincident measurements of the species of interest over the region of $15°–45°N$ and $114°E–124°W$. Fifty percent of the selected data is distributed below 3 km. Figure 2 shows the EV profiles of six factors, while Figure 3 shows the absolute variability explained by each factor.

[12] We label each factor based on its key chemical signatures. The "terrestrial biogenic" factor is characterized with large signals in CH_3OH (80%, 862 pptv) and CH_3COCH_3 (40%, 215 pptv). The terrestrial biosphere is the largest known source for CH_3OH [e.g., *Heikes et al.*, 2002] and a substantial source for CH_3COCH_3 [e.g., *Jacob et al.*, 2002]. HCN is thought to originate mainly from biomass burning. However, the terrestrial biogenic factor also explains a large fraction of the HCN variability (41%, 72 pptv). Cyanogenesis is likely to be a major biogenic process emitting HCN and its by-product, CH_3COCH_3 (40%, 215 pptv), from a variety of plants [*Pouton*, 1990; *Vetter*, 2000; *Fall*, 2003]. The biogenic factor explains 30% of CH_3CN (27 pptv). However, this fraction is not as significant considering its large measurement uncertainty of 35 pptv (Table 1). The biogenic CH_3CHO variability (35%, 79 pptv) is much greater than its measurement uncertainty (Table 1), providing support for its biogenic production [*Harry and Kimmerer*, 1991; *de Gouw et al.*, 1999; *Schade and Goldstein.*, 2001; *Karl et al.*, 2002]. We note that the tracer separation from combustion signatures such as CO and CH_3Cl and the follow-up analysis of the factor correlation with the ratio of C_2H_6 and C_3H_8, both of which are emitted by biomass burning, indicate that this factor is not affected by biomass burning. Direct emission measurements of HCN from midlatitude forests in Southeast Asia are necessary to confirm our finding and to estimate the source magnitude.

[13] The "biomass burning" factor is loaded with largest signals of CH_3CN (69%, 63 pptv) and CH_3Cl (61%, 40pptv), two chemicals with large biomass-burning sources [e.g., *Singh et al.*, 2003a; *Yoshida et al.*, 2004]. HCN, known to have a large biomass-burning source [e.g., *Li et al.*, 2000], also has a large signal (30%, 53 pptv). The signals of CH_3COCH_3 (19%, 104 pptv) and CO (23%, 22 ppbv) are also significant in this factor.

[14] Two key combustion tracers, C_2H_2 (82%, 392 pptv) and CO (46%, 44 ppbv), appear in the "combustion" factor. Both gases are emitted from biomass burning and motor vehicle combustion. The similarity in the correlations of these two tracers results in one factor that represents a mixture of two sources. The source ambiguity, however, does not affect the gases of interest in this study.

[15] The industry and urban pollution contributions are split into two factors. The first factor has significant signals of CH_3CHO (32%, 73 pptv), C_2H_2 (12%, 58 pptv), and

Figure 2. Explained variations of chemical compounds in the six factors for TRACE-P. The factors are named based on the chemical characteristics.
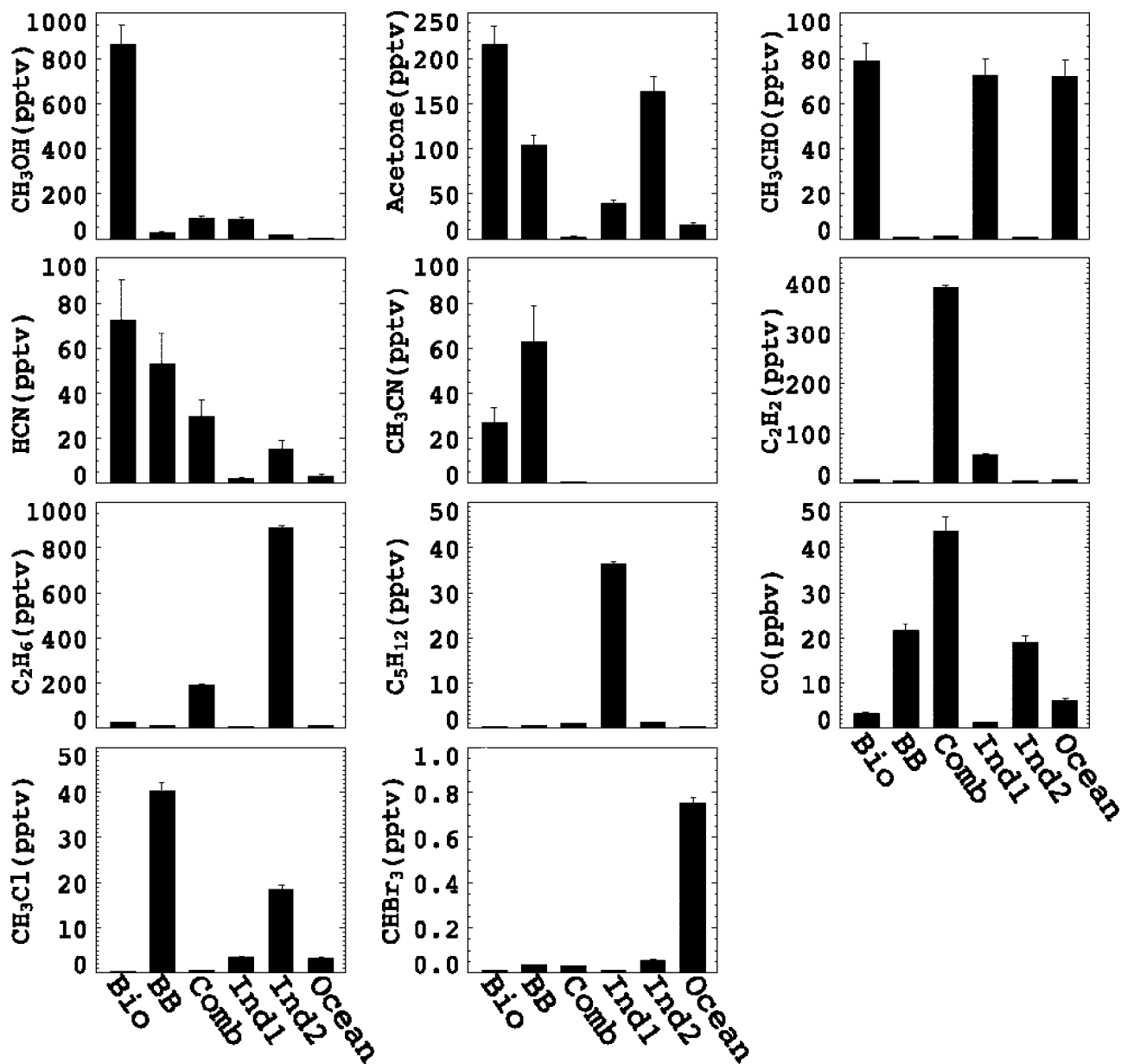
i-C_5H_{12} (91%, 37 pptv) (industry/urban 1), while the second factor shows notable variabilities of C_2H_6 (78%, 888 pptv), CH_3COCH_3 (30%, 163 pptv), and CO (20%, 19 ppbv) (industry/urban 2). The first factor is more characteristic of urban emissions, while the second factor is more of industrial emissions since i-C_5H_{12} is uniquely associated with gasoline evaporation and gasoline-powered motor vehicle emissions. The CH_3CHO variability explained by the industry/urban 1 factor is much higher than the primary biomass burning (5%) or industrial (<1%) CH_3CHO source estimated by *Singh et al.* [2004], which likely reflects secondary production of CH_3CHO from VOC oxidation. The variability of CH_3Cl (28%, 18 pptv) in the industry/urban 2 factor is much higher than the global industrial source fraction of 4% [*McCulloch et al.*, 1999], likely reflecting the influence by biofuel combustion in relatively fresh industrial plumes sampled during TRACE-P. The most prominent component in the "oceanic" factor is $CHBr_3$ (84%, 0.75 pptv). This factor also explains 32% of CH_3CHO (72 pptv), supporting the notion of substantial CH_3CHO oceanic emissions [*Singh et al.*, 2003b].

[16] Previous studies suggested large sources of CH_3Cl from the terrestrial biosphere [*Yoshida et al.*, 2004 and references therein]. However, the CH_3Cl variability explained by the terrestrial biogenic factor is negligible. The fairly small variability of the biogenic CH_3Cl likely reflects its dispersed terrestrial sources in the tropics [*Yoshida et al.*, 2004] and mixing during long-range transport. Considering the small contribution to CH_3Cl by its largest known source from the tropical terrestrial ecosystems to this factor, the much larger HCN signal here in turn likely indicates that measured enhancements originate

from the forests at midlatitudes, not in the tropics. Figure 4 shows the 5-day kinematic back trajectories of biogenic and biomass-burning factors calculated with the European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological fields [*Fuelberg et al.*, 2003]. The biomass-burning factor is associated with transport from tropical regions, while the terrestrial biogenic factor is related to transport from dispersed continental locations.

[17] To further investigate the characteristics of the biomass-burning factor, we examine how the factor correlates with latitude, altitude, and C_2H_6/C_3H_8 ratio (Figure 5). Higher C_2H_6/C_3H_8 ratios indicate more aged air masses [*Wang and Zeng*, 2004]. The correlation is strongest with C_2H_6/C_3H_8 ratio ($r = 0.73$), indicating aged biomass-burning air masses. The positive correlation with altitude ($r = 0.59$) and the (small) negative correlation with latitude ($r = -0.31$) indicate transport of aged biomass-burning air masses from tropical regions at high altitude after initial plume rise driven by combustion heating, consistent with back trajectories (Figure 4).

[18] The large positive correlations of the biomass-burning factor with altitude and C_2H_6/C_3H_8 ratio are unique (Table 2). The same approaches are used to characterize the other factors. The terrestrial biogenic factor has no apparent correlation with latitude or altitude, implying a geographically dispersed distant source. The lack of correlation with C_2H_6/C_3H_8 ratio reflects in part that the biogenic sources are not collocated with alkane sources. The two industry/urban factors show clear anticorrelations with altitude and C_2H_6/C_3H_8 ratio, representing relatively fresh plumes from low-altitude sources. Between them, the industry/urban 2 factor with more chemical signatures of

Figure 3. The variabilities in mixing ratio explained by each factor for TRACE-P. "Bio" denotes terrestrial biogenic; "BB" denotes biomass burning; "Comb" denotes combustion; and "Ind" denotes industry/urban. The vertical bars show the uncertainties of the PMF analysis.

industrial than urban emissions has stronger anticorrelations with altitude and C_2H_6/C_3H_8 ratio. It also has clear latitude dependence. These characteristics are consistent with more industrial activities in the northeast of China and more disperse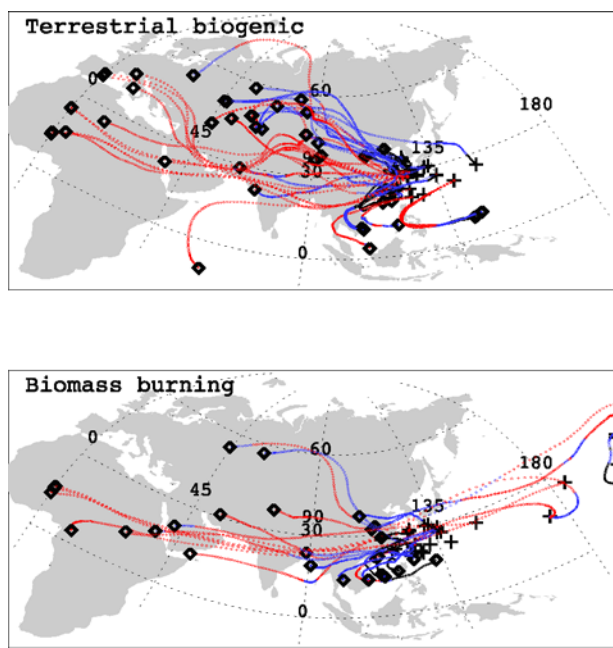d urban distributions in the region. The oceanic factor has anticorrelations with altitude and C_2H_6/C_3H_8 ratio, consistent with the characteristics of fresh surface emissions. The anticorrelation with C_2H_6/C_3H_8 ratio reflects in part a positive correlation of the hydrocarbon ratio with altitude.

Table 1. Relative and Average Absolute Measurement Uncertainties[a]

	CH_3OH	CH_3COCH_3	CH_3CHO	HCN	CH_3CN	C_2H_2	C_2H_6	C_5H_{12}	CO	CH_3Cl	$CHBr_3$
Relative Uncertainty (%)	10	10	10	∼25	∼25	1	1	1	7	2	5
TRACE-P[b]	110	90	30	50	35	5	15	2	7	12	0.03
PEM-Tropics B[b]	90	40	10	–	–	3	3	–	4	12	0.03

[a]The uncertainties are based on the reported accuracies and precisions of the measurements.
[b]Unit is pptv except for CO (ppbv).

Figure 4. Five-day back trajectories of data points that rank in the top 10% by factor score for the terrestrial biogenic (top) and biomass-burning (bottom) factors in TRACE-P. The crosses show the locations of measurements. The back trajectory locations are represented by dots with colors indicating heights [black (<2 km), blue (2−6 km), and red (>6 km)], and the end point is marked by a diamond.
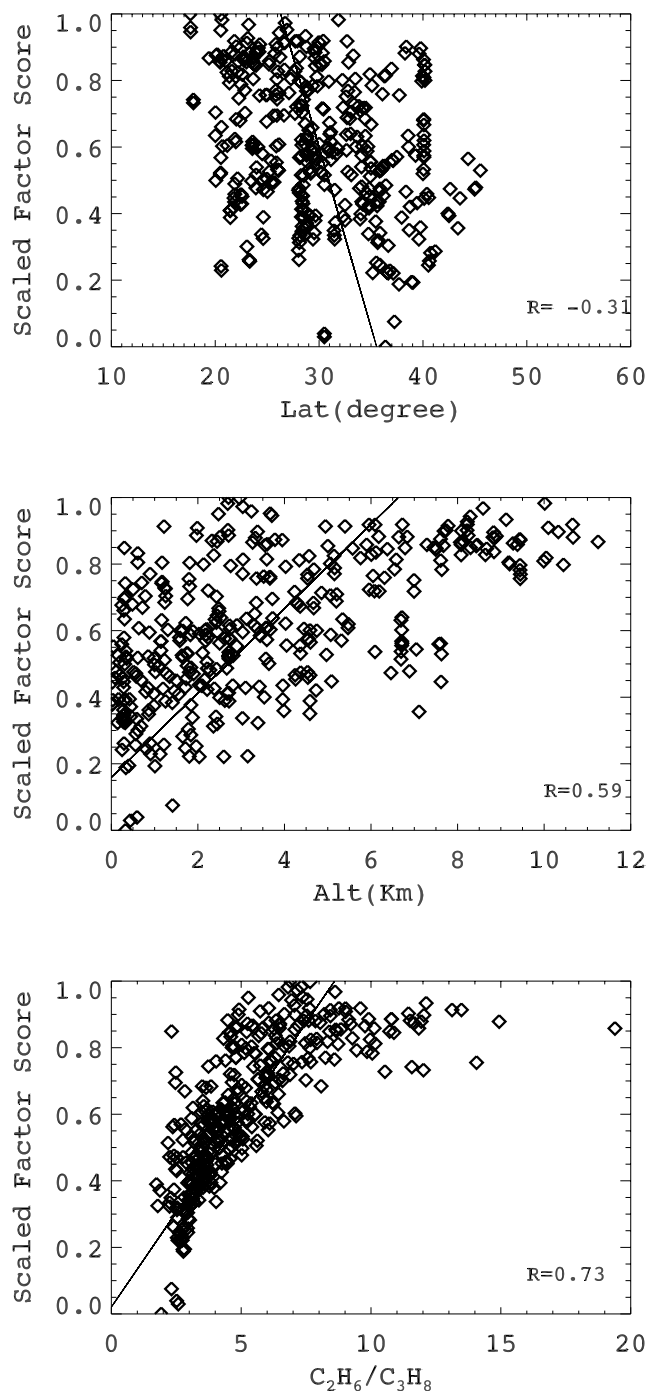
3.2. PEM-Tropics B

[19] The PEM-Tropics B campaign was conducted during the wet season over the tropical Pacific (March−April 1999) [*Raper et al.*, 2001]. Some 581 coincident measurements of eight chemicals over the region of 36°S−35°N and 107°W−162°E are analyzed. Sixty-three percent of the selected data is distributed above 5 km. We find no evident bias in the spatial distributions of the selected data set compared to the entire data set.

[20] Five factors are resolved by PMF (section 2). Figure 6 shows the EV profiles, while Figure 7 shows the absolute chemical variability. Compared to TRACE-P (Figures 2 and 3), the tracer variability during PEM-Tropics B is much lower, leading to more ambiguity in interpretation of the analysis results because observed variabilities were at times smaller than measurement uncertainties (Table 1). As one could expect, the tracer variabilities of industry/urban-related factors in PEM-Tropics B are much smaller than those in TRACE-P, which reflects the sampling of photochemically aged air masses during PEM-Tropics B.

[21] As in the previous, we label each factor based on its key chemical signatures. The "terrestrial biogenic" factor is characterized by the large variability of CH_3OH (88%, 653 pptv). The signal of CH_3COCH_3 is below the measurement uncertainty. The "biomass-burning" factor has large signals of CH_3COCH_3 (55%, 98 pptv), CH_3CHO (64%, 30 pptv), CO (52%, 11 ppbv), and CH_3Cl (82%, 44 pptv). The "combustion/industry" factors reflect a mix of biomass burning, automobile combustion, industry, and urban sources. There are substantial signals of C_2H_2 (84%, 28 pptv)

and C_2H_6 (9%, 21 pptv) in the combustion/industry 1 factor, and there are large signals of C_2H_6 (76%, 188 pptv) and CO (34%, 8 ppbv) in the combustion/industry 2 factor. The CH_3Cl fraction (13%, 7 pptv) in the latter factor is below the measurement uncertainty. The "oceanic" factor explains 94% of $CHBr_3$ variability (0.55 pptv) and does not show significant variability in the other chemicals.

[22] We analyze the correlations between factors and latitude, altitude, and C_2H_6/C_3H_8 ratio to help identify the

Figure 5. Factor score correlation with latitude (upper), altitude (middle), and C_2H_6/C_3H_8 ratio (bottom) for the biomass-burning factor in TRACE-P.

Table 2. Correlations (R) Between Factor Scores and Latitudes, Altitudes, and C_2H_6/C_3H_8 Ratio for TRACE-P

Factors	Latitude	Altitude	C_2H_6/C_3H_8 Ratio
Terrestrial Biogenic	0.06	0.01	0.08
Biomass Burning	−0.31	0.59	0.73
Combustion	0.1	−0.21	−0.37
Industry/Urban 1	0.04	−0.27	−0.39
Industry/Urban 2	0.29	−0.53	−0.78
Oceanic	0.1	−0.57	−0.55

source characteristics (Table 3). As for TRACE-P, the terrestrial biogenic factor shows no clear correlations reflecting geographically dispersed sources. The biomass-burning factor is anticorrelated with latitude, implying a southern hemispheric origin particularly from Africa and Australia (Figure 8). As in TRACE-P, it is positively correlated with C_2H_6/C_3H_8 ratio, indicating long-range transport of aged pollutants after initial rise due to combustion heating. The combustion/industry 1 and combustion/industry 2 factors show clear positive correlations with latitude and negative correlations with C_2H_6/C_3H_8 ratio, implying that most long-range transport of industrial/urban/combustion emissions originated from the Northern Hemisphere [*Wang et al.*, 2001]. As in TRACE-P, the oceanic factor shows anticorrelation with altitude.

3.3. INTEX-NA

[23] The INTEX-NA experiment was conducted to investigate the formation and transport of tracers and aerosols and inflow and outflow of pollutants over North America during the summer (July–August 2004) [*Singh et al.*, 2002]. Two characteristics separate INTEX-NA from TRACE-P and PEM-Tropics B. First, mixing processes are much more active over the continent in summer than over the western Pacific in spring (TRACE-P) or the tropical Pacific (PEM-Tropics B). Second, North American urban and industrial sources are more dispersed than over East Asia, where major industrial and urban emissions are densely located near coastal regions. As a result, we find that source separation is much more ambiguous in INTEX-NA data set than the other two. In the selected data set, 35% of the data is measured below 2 km; 50% is measured above 5 km. We find five factors in the PMF analysis. Figure 9 shows the EV profiles. The factors are named after the tracer that has the largest EV. The C_2H_2 factor is a combustion factor with a large CH_3OH signal (>25%), representing either a large industrial-related CH_3OH source over North America or a mixture of combustion and biogenic emissions because we cannot define a clear biogenic factor. The CH_3Cl factor with large signals of biomass burning (CH_3Cl, CO, HCN, and CH_3CN) and biogenic tracers (CH_3OH, CH_3COCH_3, and HCN) likely represents a mixture of the two. The CH_3Br, C_2H_6, and i-C_5H_{12} factors are dominated by a single species. Photochemical oxidation and mixing during INTEX-NA (summer) are considerably faster than TRACE-P (spring). Assuming similar emissions, we would expect lower concentrations in INTEX-NA than TRACE-P. Inspection of vertical profiles of trace gases we selected (not shown) indicates that it is true for most species, including CO, C_2H_2, and CH_3Cl which are enhanced during INTEX-
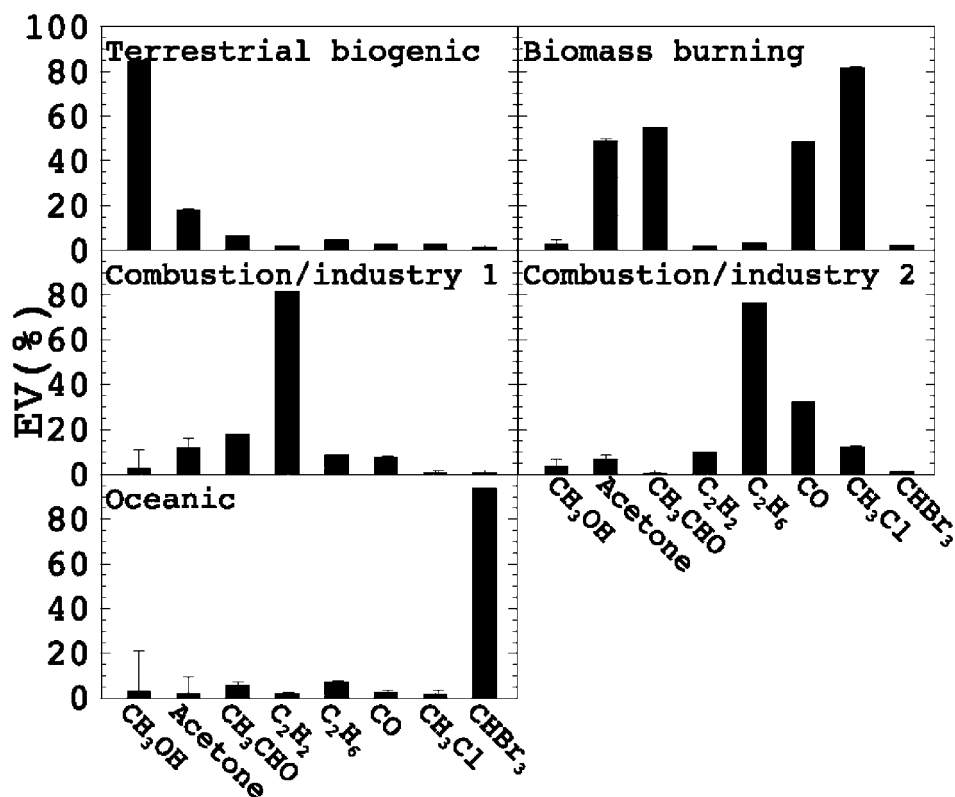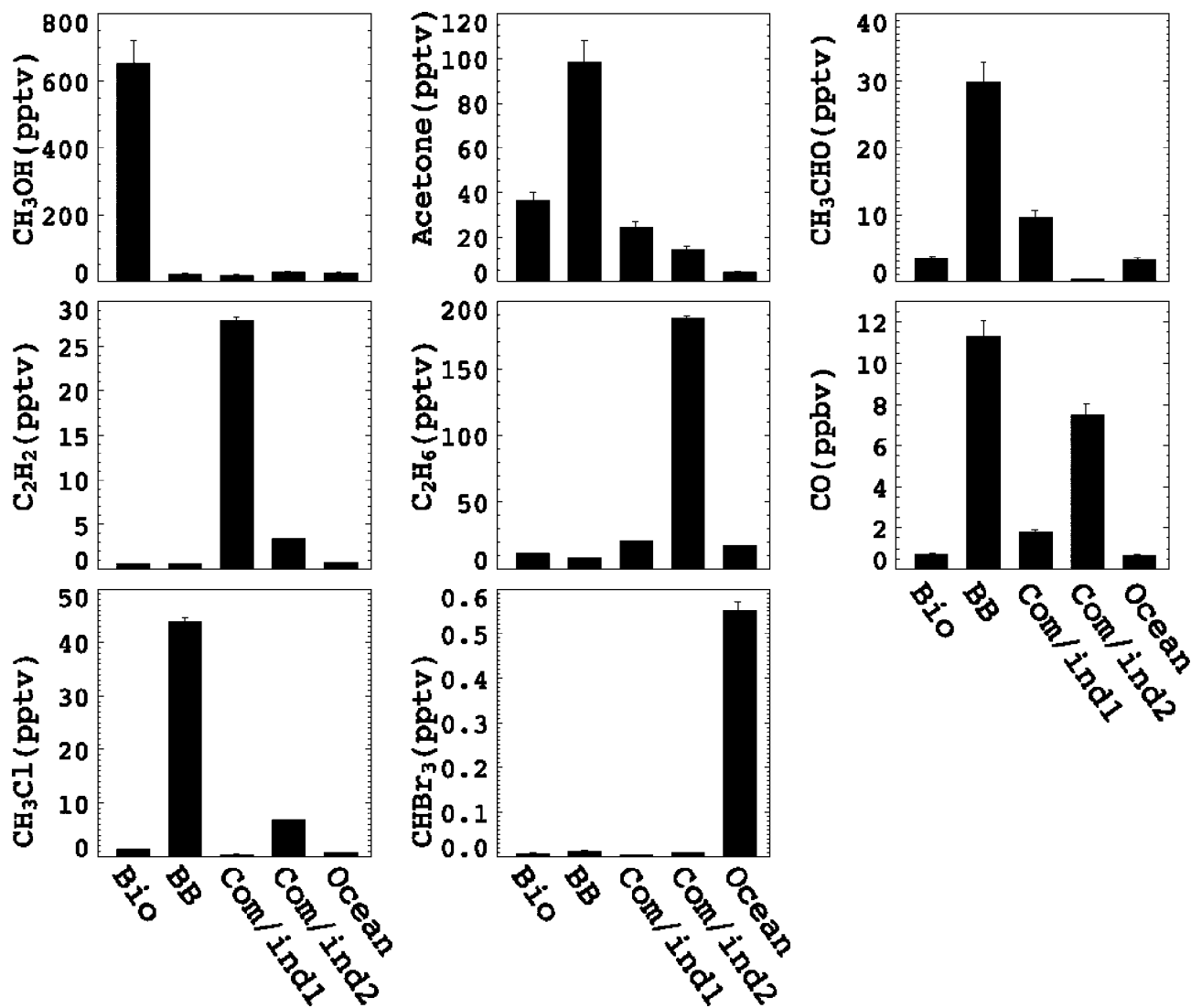

Figure 6. Same as Figure 2 but for PEM-Tropics B.

Figure 7. Same as Figure 3 but for PEM-Tropics B. "Com/ind1" and "Com/ind2" denote combustion/industry 1 and 2, respectively.

NA due to fire emissions. However, concentrations of CH_3OH, acetone, and HCN are much higher in INTEX-NA than TRACE-P. We postulate that these enhancements are due at least in part to larger biogenic emissions in summer. However, the analysis method used in this study cannot be applied to evaluate our hypothesis.

4. Comparisons to Global Estimations

[24] Despite the limitations of PMF methods (section 2), it is still instructive to compare our results with previous global budget estimations. Additional precautions must also be heeded to prevent oversimplifications. First, our results are drawn from only two aircraft missions (TRACE-P and PEM-Tropics B). Second, the factor contributions do not necessarily translate into source strengths. Third, it is generally hard to distinguish primary sources from secondary chemical production in the factor analysis. However, the following assessment points to the directions of needed research when large discrepancies are found

between previous emission estimations and our results. Table 4 summarizes the contributions of various factors to OVOCs and HCN for TRACE-P and PEM-Tropics B; previous global estimates are also listed for comparison purposes.

[25] The factor showing 80–88% variability of CH_3OH from this study represents the terrestrial biogenic factor, and it is consistent with the estimated global biogenic fractions of 62–81% [*Heikes et al.*, 2002; *Singh et al.*, 2004; *Jacob et al.*, 2005]. For CH_3COCH_3, the biogenic

Table 3. Correlations (R) Between Factor Scores and Latitudes, Altitudes, and C_2H_6/C_3H_8 Ratio for PEM-Tropics B

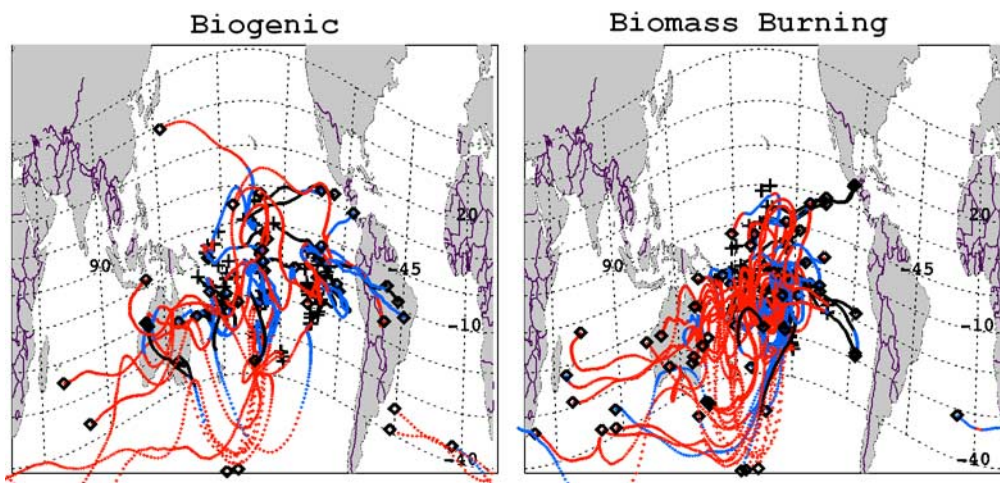| Factors	Latitude	Altitude	C_2H_6/C_3H_8 Ratio
Terrestrial Biogenic	0.01	−0.09	−0.14
Biomass Burning	−0.51	0.16	0.45
Combustion/Industry 1	0.6	−0.1	−0.54
Combustion/Industry 2	0.68	−0.07	−0.57
Oceanic	0.13	−0.42	−0.17

Figure 8. Same as Figure 4 but 10-day back trajectories for PEM-Tropics B based on *Fuelberg et al.* [2001].

fractions of this study (20–40%) are also comparable with the global estimates (27–53%) [*Jacob et al.*, 2002; *Singh et al.*, 2004].

[26] Biogenic HCN sources were usually ignored in previous studies [*Cicerone and Zellner*, 1983; *Lobert et al.*, 1990; *Li et al.*, 2000; *Andreae and Merlet*, 2001]. *Li et al.* [2003] estimated the global biogenic HCN fractions by ~18% in order to balance estimated global loss rates from ocean uptake. Large terrestrial biogenic HCN variability (41%) is found during TRACE-P in this study, considerably higher than the global biogenic fraction estimate.

The cyanogenic process in plants is known to emit both CH_3COCH_3 and HCN. It appears to be a key contributor to HCN emissions [*Fall*, 2003] from geographically dispersed source regions. Contribution of biomass burning to HCN (~30%) in TRACE-P is much smaller than the global estimates (>80%). The industry/urban/ocean factor contributions are uncertain since they are less than the measurement uncertainty of HCN (~25%).

[27] The CH_3COCH_3 variabilities explained by industry/urban and biomass-burning factors (8–30 and 19–55%, respectively) are much higher than the estimated primary
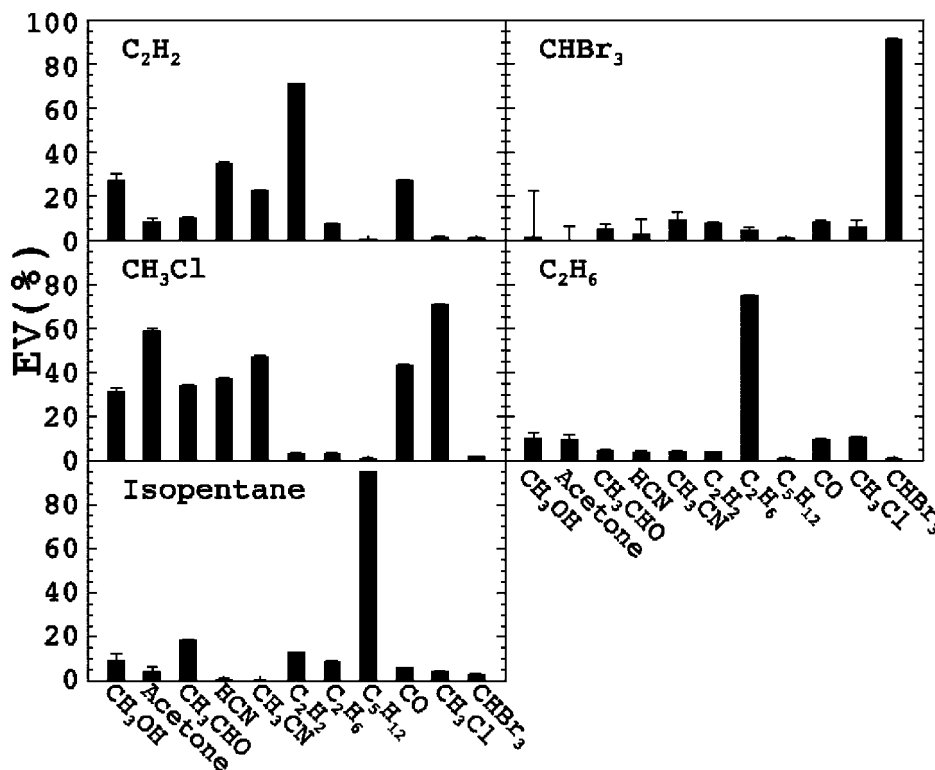

Figure 9. Same as Figure 2 but for INTEX-NA.

Table 4. Comparison Factor Contributions With Global Estimates[a] of OVOCs (%)

	CH$_3$OH		CH$_3$COCH$_3$		CH$_3$CHO		HCN	
	Global Estimates	PMF	Global Estimates	PMF	Global Estimates	PMF	Global Estimates	PMF
Biogenic	60−80	80−88	27−53	20−40	17.5	7−35	0−18	41
BB	5−9	3−16	4−10	19−55	5	1−68	80−98	30
Industry/Urban	2−4	3−5	1−4	8−30	0.5	1−28	0−2	10
Ocean	0	0.5−3	0−28	2−4	62.5	6−36	0	2
Others[b]	15−33	−	30−50	−	15	−	−	17

[a]Global estimates are compiled from the studies of *Heikes et al.* [2002], *Li et al.* [2003], *Singh et al.* [2004], and *Jacob et al.* [2002, 2005].
[b]Unexplained fraction for PMF.

sources (1−4 and 4−10%, respectively). The total difference between PMF factor contributions and previously estimated primary sources, however, is comparable to the 30−50% contribution from VOC oxidation [*Jacob et al.*, 2002; *Singh et al.*, 2004], indicating secondary productions in those factors. There is no clear evidence for significant oceanic CH$_3$COCH$_3$ emissions, which is consistent with the recent measurements by *Marandino et al.* [2005].

[28] The terrestrial biogenic CH$_3$CHO variability is quite different between TRACE-P and PEM-Tropics B (35 and 7%, respectively), likely reflecting relatively fast photochemical loss of CH$_3$CHO or its precursors during long-range transport to the remote PEM-Tropics B region. We note that there are lingering questions on the quality of CH$_3$CHO measurements used in this study (section 2). The corresponding global fraction estimated by *Singh et al.* [2004] is 18%. We find large contributions from industry/urban 1 (28%) for TRACE-P and from biomass burning (68%) for PEM-Tropics B. Given the relatively short lifetime of CH$_3$CHO (∼1 day), our results indicate that secondary production from VOCs, likely produced in combustion processes, is a major source of observed CH$_3$CHO. The oceanic CH$_3$CHO variability is significant during TRACE-P (36%) but not PEM-Tropics B, indicating the possibility of regional variations in oceanic CH$_3$CHO emissions. In comparison, the estimated global oceanic contribution is much larger at 63% [*Singh et al.*, 2004].

5. Conclusions

[29] We apply an advanced factor analysis method, PMF, to analyze the source contributions to OVOCs and cyanides measured in three aircraft experiments. In order to identify contributions by emissions from terrestrial biosphere, biomass burning, industry/urban regions, and ocean, we select a suite of trace chemicals including CH$_3$OH, CH$_3$COCH$_3$, CH$_3$CHO, C$_2$H$_2$, C$_2$H$_6$, i-C$_5$H$_{12}$, CO, CH$_3$Cl, and CHBr$_3$. While feasible for TRACE-P and PEM-Tropics B measurements, PMF analysis cannot clearly separate source contributions in INTEX-NA measurements. More active transport/mixing processes during summer over North America and broad collocations of different types of sources in the region are likely the reasons.

[30] We resolve six factors for TRACE-P and five factors for PEM-Tropics B. In TRACE-P, the factor representing terrestrial biogenic sources explains a large fraction of HCN variability (41%, 72 pptv). Back trajectory analysis and a lack of correlation of this factor with altitude, latitude, or C$_2$H$_6$/C$_3$H$_8$ ratio imply widely dispersed continental sources. The significant variabilities of HCN and CH$_3$COCH$_3$ in this factor likely reflect emissions from cyanogenesis in diverse plants.

[31] The biomass-burning factor shows the characteristics of long-range transport and aged biomass-burning air masses at high altitude with a subtropical/tropical origin. The combustion factor reflects a mixture of biomass-burning, industrial, and urban sources. The factor indicates relatively fresh surface emissions. There are two industry/urban factors. One is affected more by urban emissions, while the other is affected more by industrial emissions. As a result, the second factor has a stronger dependence on latitude likely due to the high density of industries over the northeast of China. Both factors are associated with surface sources and transport. The oceanic factor has likely a surface origin with a substantial CH$_3$CHO variability (36%, 72 pptv), implying a significant oceanic contribution to CH$_3$CHO.

[32] Compared to TRACE-P, the factor contributions in PEM-Tropics B are smaller because of transport over longer distance to the region. The terrestrial biogenic factor shows similar chemical signatures and characteristics to TRACE-P without the cyanides. The biomass-burning factor represents long-range transport of aged masses at high altitude over the Southern Hemisphere. The two combustion/industry factors show long-range transport of industrial/urban/combustion emissions from the Northern Hemisphere. The oceanic factor in PEM-Tropics B does not have a significant CH$_3$CHO signal.

[33] We compare the source contributions from two aircraft field experiments to previous global estimations; large discrepancies identified point to the directions of needed research. First, the terrestrial biogenic contribution of HCN in TRACE-P is substantially higher than previous global emission estimates. Cyanogenesis in plants from widely dispersed regions is likely to be a major source of HCN. Second, the biogenic contribution to CH$_3$COCH$_3$ variability is comparable with the global emission estimates. However, there are much larger CH$_3$COCH$_3$ industry/urban and biomass-burning contributions in this study than the previous global emission estimates, reflecting the importance of secondary productions. We do not find large oceanic contributions to CH$_3$COCH$_3$. Last, the large contributions to CH$_3$CHO variability from industry/urban 1 for TRACE-P and from biomass burning for PEM-Tropics B imply that secondary production from combustion/industrial VOCs is likely an important source. The oceanic CH$_3$CHO contri-

bution shows considerable regional dependence, and it is lower than the previous global emission estimates. On the basis of this analysis, three specific areas emerge for future research: the global sources of CH_3COCH_3 and HCN from the cyanogenic process in plants, the VOC precursors to sustain CH_3COCH_3 and CH_3CHO concentrations in industry/urban and biomass-burning plumes, and the magnitudes and regional variability of oceanic CH_3CHO emissions.

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