SCIENCE OF THE TOTAL ENVIRONMENT 394 (2008) 290–302

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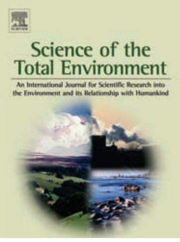

Comparison of PM2.5 source apportionment using positive matrix factorization and molecular marker-based chemical mass balance

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ARTICLE INFO

Article history:
Received 1 October 2007
Received in revised form
3 January 2008
Accepted 15 January 2008
Available online 7 March 2008

Keywords:
CMB-MM
PMF
PM2.5
Source apportionment
Jefferson Street
SEARCH

ABSTRACT

A comprehensive comparison of positive matrix factorization (PMF) and molecular marker-based chemical mass balance (CMB-MM) modeling on PM2.5 source contributions was conducted for particulate matter measurements taken at Jefferson Street, Atlanta, Georgia (JST). The datasets used in each type of receptor modeling were different: CMB-MM used data of primarily organic tracers plus a couple elements measured from 51 24-h PM2.5 samples collected in July 2001 and January 2002. While for PMF, with elements, ions, five gaseous components, and eight temperature-resolved carbon fractions as the input data, both source profiles and contributions were resolved from a total of 932 daily PM2.5 samples covering a 3-year period between January 2000 and December 2002. The model results for the overlapping periods (July 2001 and January 2002) were extracted for comparison. Seven primary sources and three secondary sources were resolved by CMB-MM, while a total of nine primary and secondary factors were resolved by PMF. On average, 107% and 85% of PM2.5 mass were explained by CMB-MM and PMF, respectively, with secondary aerosols handled differently in the above two methods. Four similar sources were resolved by both methods, with good correlation for road dust, but fair for gasoline exhaust and wood combustion. The CMB-MM diesel exhaust has very poor correlation with the PMF resolved diesel exhaust. However, the CMB-MM combined mobile source has improved correlation with the PMF result as compared with the diesel exhaust source. If only the winter data were included, the CMB-MM combined mobile source shows enhanced correlation with the PMF combined source, as compared with the single source of diesel exhaust or gasoline exhaust.

1. Introduction

The complexity in emission sources of urban airborne fine particulate matter (PM2.5) hinders effective air quality control measures and has become a world-wide problem. Understanding of each source contribution to PM2.5 and the extent of accuracy of the apportionment results, is a prerequisite for the formulation of effective control strategies for PM2.5 emissions. Source apportionment can be achieved by using a variety of air quality models. Amongst these, receptor-oriented modeling is one of the conventional techniques and has been in broad use for source apportionment studies in the past decades. The

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doi:10.1016/j.scitotenv.2008.01.030

most commonly used receptor models include element-based or molecular marker-based chemical mass balance (CMB) (i.e., CMB-Regular (Watson and Chow, 2001) and CMB-MM (Schauer and Cass, 2000; Zheng et al., 2002)), positive matrix factorization (PMF) (Paatero and Tapper, 1994), and UNMIX (Henry, 1997).

Applications of PMF using traditional speciation data (i.e., organic carbon (OC), elemental carbon (EC), major ions, and metals) have been reported in the United States (Hopke, 2003; Polissar et al., 1998, 2001) and around the world (Qin and Oduyemi, 2003; Song et al., 2006). It has been reported to use carbon fractions operationally defined by the Desert Research Institute thermal optical reflectance method (Chow et al., 1993) in PMF modeling and the improvement in source identification has been found (Kim et al., 2004a,b). More recently, incorporation of a number of gaseous species as additional constraints has been also suggested (Kim et al., 2005; Zhou et al., 2005). This more advanced PMF approach has shown that the inclusion of temperature-resolved carbon fractions and gaseous components enhanced the resolving power for the factors of gasoline, diesel, and coal combustion/other (Liu et al., 2006).

It is of increasing interest to perform source apportionment research using PMF on the basis of molecular markers (PMF-MM). However, the limitation on sample size (*n*) prevents from obtaining statistically meaningful source apportionment results (*n* is thought to be at least 60–200) until very recently (Jaeckels et al., 2007; Shrivastava et al., 2007). Another challenge in source apportionment modeling of PM2.5 is to verify the model-apportioned results. Direct comparison with the measurement data seems impossible based on current available methods. One alternative is to intercompare the results by applying the same datasets, or different datasets but for the same time period/location, to different modeling methods. As of the recent applications, such intercomparisons mainly focused on results using the same datasets, such as CMB-Regular vs. PMF (Liu et al., submitted for publication), PMF vs. UNMIX (Lewis et al., 2003), and PMF-MM vs. CMB-MM (Jaeckels et al., 2007; Shrivastava et al., 2007). Fewer comparative studies have been reported to use different datasets but for the same time period/location for different model apportionments, which also is believed to be an important distinction (Kim et al., 2004a; Song et al., 2006). However, their studies are preliminary since they just simply compared the averaged results from a limited number of monthly composite samples. As part of the on-going Southeastern Aerosol Research and Characterization (SEARCH) program (Hansen et al., 2003; Zheng et al., 2002), 51 sets of daily observations of organic molecular markers were obtained (Zheng et al., 2007). While statistically 51 is not a huge number considered appropriate to assume a normal distribution, it is still a good trial to gain insight into the correlation between the contributions of similar source categories resolved by different models, such as CMB-MM vs. CMAQ (Park et al., submitted for publication). In this study, a comparison of CMB-MM and PMF determined source contributions to PM2.5 at JST is given. Because of the lack of sufficient molecular marker data for the PMF-MM source apportionment, two different sets of data were applied separately to CMB-MM and PMF: CMB-MM used data of primarily organic tracers plus a couple elements and ions, while PMF used elements, ions, five gaseous components and eight thermal-resolved carbon fractions as the input data.

2. Experimental

2.1. Sampling and chemical analysis

2.1.1. CMB-MM

Twenty four-hour ambient PM2.5 samples for speciation of molecular markers were collected on quartz filters using high-volume (Hi-Vol) samplers located at Jefferson Street, Atlanta, GA (JST) during July 3–August 4, 2001 and January 2–31, 2002, representing the summertime and wintertime, respectively. The summer samples were collected on quartz fiber filters (102 mm in diameter) using a home-made Hi-Vol dichotomous virtual impactor developed at California Institute of Technology; while the winter samples were collected on quartz fiber filters (8×10 in.^{2}) with a Thermo Andersen Hi-Vol sampler (Andersen Instruments, Inc.) (Zheng et al., 2007). These two periods align with the Eastern Supersites Program (ESP) with intensive observations (Solomon, 2001). The average temperatures for the sampling periods were 25.1 ± 1.1 °C (summertime) and 6.8 ± 5.0 °C (wintertime). The JST site, 4.2 km northwest of downtown Atlanta, is located in a light industrial and commercial area, and is one of the urban sites in the SEARCH air monitoring quality network (Hansen et al., 2003). The analysis of molecular markers has been reported in detail elsewhere (Zheng et al., 2002, 2006). Briefly, after spiking deuterated internal standard (IS) mixtures, the quartz filter was extracted successively under mild sonication with hexane and benzene/isopropyl alcohol (2:1, v/v). Extracts were filtered, combined, and concentrated to the initial volume of the IS mixtures spiked. A derivatization step was applied by adding diazomethane to convert organic acids to their methyl ester analogues. Target organic compounds in the extracts were identified and quantified by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard (HP) 6890 GC equipped with a HP mass selective detector (MSD). Robust quality control procedures were introduced in the organic analysis, which included: prebaked glassware at 550 °C, used optima grade or distilled solvents, and performed sensitivity tests on GC/MSD (Zheng et al., 2007). A standard reference material of urban dust (SRM1649a) was used to examine the reproducibility of the analytical method. The recovery range of PAHs is between 70% (fluoranthene) and 144% (benzo(*k*) fluoranthene) of their certified values in SRM1649a. The average uncertainty for organic markers is 16 ± 4% from seven replicate analyses of SRM1649a.

In addition to molecular markers, data of a number of species including OC, EC, aluminum (Al), silicon (Si), and ions (SO_4^{2-}, NO_3^-, and NH_4^+) that served as inputs in CMB-MM modeling were obtained from other filters for PM2.5 taken simultaneously with a collocated Particulate Composition Monitor (PCM) sampler (Atmospheric Research and Analysis Inc., Durham, NC). Different analytical methods were used for these species, which were thermo-optical reflection (TOR, or IMPROVE) for OC and EC (Chow et al., 1993), energy dispersive X-ray fluorescence (XRF) for Al and Si, ion chromatography (IC) for SO_4^{2-} and NO_3^-, and automated colorimetry (AC) for NH_4^+ (see

Hansen et al., 2003, for details). It should be noted that the OC and EC data were measured with different methods for ambient samples (TOR) and source profiles (thermo-optical transmittance, TOT or NIOSH). To minimize the bias arose from inconsistency in methodology, the TOR OC and EC of ambient samples were converted to TOT OC and EC using two sets of conversion equations to represent for summertime and wintertime (Zheng et al., 2006).

2.1.2. PMF

PM2.5 samples (24-h) for PMF modeling were collected daily using the PCM sampler at the JST site. In addition to particulate samples, daily concentrations of five gaseous components were also obtained by averaging the twenty-four 1-h average values (Hansen et al., 2003). About 932 daily observations from January 2000 to December 2002 were identified as being complete enough to apply PMF. The dataset for each sample included concentrations of 25 species in particulate phase (SO_4^{2-}, NO_3^-, NH_4^+, As, Ba, Br, Cu, Mn, Pb, Se, Ti, Zn, Al, Si, K, Ca, Fe, OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3) and five in gaseous species (CO, SO_2, NO, HNO_3, and NO_y), which served as inputs in the PMF model. The filter-based measurements for particulate species included PM2.5 mass, OC, EC, water-soluble ions, and trace elements; while the continuous or semicontinuous measurements were made for the five gaseous species. The detection approaches of these components also have been described elsewhere (Hansen et al., 2003). The estimated analytical uncertainties and detection limits for OC, EC, gaseous species, trace elements, and ions were also obtained (Hansen et al., 2003).

2.2. CMB-MM and PMF modeling

Receptor modeling for particulate matter in the atmosphere has been discussed in detail by Hopke (2003), and is briefly discussed here. At a given receptor site, a mass balance equation accounting for all conserved chemical species from p independent sources in a given sample can be expressed as follows:

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

where x_{ij} is the concentration of the jth species measured in the ith sample; g_{ik} is the mass contribution from the kth source to the ith sample; f_{kj} is the fractional concentration of the jth species in the kth source; e_{ij} is residual associated with the ambient concentration of the jth species in the ith sample; p is the total number of the contributed sources. The equation in matrix form is:

$$X = GF + E \tag{2}$$

where X is an $n \times m$ data matrix with n measurements and m number of elements; G is an $n \times p$ source contribution matrix with p sources; F is a $p \times m$ source profile matrix; and E is an $n \times m$ matrix of residuals.

CMB-MM is a single-sample receptor model to solve Eq. (1) if emission source profiles (i.e. p and f_{kj}) are known. In this case, the only unknowns are the mass contributions of each source in each sample, g_{ik}. On the other hand, if the source profiles are not known and the number of samples is large enough, Eq. (2) can then be solved by PMF, which is a factor analysis-based technique that identifies structures in the dataset. For the model analysis, CMB-MM results were calculated using CMB7.0 (Watson et al., 1990) while Positive Matrix Factorization (PMF2) (Feb. 1997) vers. 4.2 was performed to solve PMF.

2.2.1. CMB-MM

The source apportionment to fine organic carbon for PM2.5 samples collected at JST during July 3–August 4, 2001 and January 2–31, 2002 was performed using CMB-MM. The candidates of fitting species for CMB-MM include 32 molecular markers along with EC, Al, and Si. The 32 molecular markers are: nine *n*-alkanes (with the number of carbon atom between 25 and 33), seven hopanes and steranes (20S&R-5α(H),14β(H),17β(H)-cholestanes, 20R-5α(H),14α(H),17α(H)-cholestane, 20S&R-5α(H),14β(H),17β(H)-ergostanes, 20S&R-5α(H),14β(H),17β(H)-sitostanes, 22,29,30-tris-norneohopane, 17α(H),21β(H)-29-norhopane, and 17α(H),21 β(H)-hopane), three resin acids (8,15-pimaradien-18-oic acid, pimaric acid, and isopimaric acid), six polycyclic aromatic hydrocarbons (PAHs) (benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*e*)pyrene, indeno(1,2,3-*cd*)fluoranthene, indeno(1,2,3-*cd*)pyrene, and benzo(*ghi*)perylene), two unsaturated fatty acids (hexadecenoic acid and octadecenoic acid), and five other organic compounds (*7H*-benz(de)anthracen-7-one, nonanal, cholesterol, propionylsyringol, and levoglucosan). For fitting species with "missing data" in the ambient data (e.g., due to no measurements or measurements below detection limits), they would not be selected in the input file.

Seven primary source profiles were selected based on the study by Zheng et al. (2002) in the Southeastern US, including emissions from diesel-powered vehicles (Hildemann et al., 1991; Schauer et al., 1999a), combined catalyst and noncatalyst-equipped gasoline powered vehicles (Schauer et al., 2002), wood combustion (Fine et al., 2002), paved road dust (Schauer, 1998), meat cooking (Schauer et al., 1999b), vegetative detritus (Rogge et al., 1993a), and natural gas combustion (Rogge et al., 1993b). Two source profiles, wood combustion and paved road dust, were reconstructed by Zheng et al. (2002) to account for local variability in source profiles. The primary particulate sources contain specific molecular markers, such as levoglucosan and resin acids for wood combustion, hopanes and steranes for motor vehicle emissions, Al and Si for paved road dust, odd-numbered alkanes for vegetative detritus, and cholesterol for meat cooking. It is difficult to distinguish between diesel and gasoline engine exhausts merely based on hopanes and steranes for such components exist in lubricating motor oil used in both types of vehicles. However, if combined with EC, diesel- and gasoline-originated sources can be better separated since the proportion of EC in particles from diesel engines is higher than that from combined catalyst/non-catalyst-equipped gasoline spark-ignition engines (Schauer et al., 1999a, 2002). From CMB-MM, the outputs are concentrations of fine organic carbon contributed from the emission sources resolved. Ions including sulfate, nitrate, and ammonium are from primary or secondary origin. According to the primary OC identified from CMB and the ratios of each ion to OC in source profiles, the amount of ions with primary origin could be calculated. Ions of secondary origin are thus the difference between the measured ambient ionic concentrations and the calculated primary ionic concentrations. Unexplained organic carbon in CMB-MM was converted to organic matter using a factor of 1.7 (Nelson and Sommers, 1996) to include molecules other than carbon such as H, O, N, and S.

2.2.2. *PMF*

Error estimation for the input data in PMF modeling is required to be chosen carefully to reflect the quality and reliability of each data point. By adjusting the corresponding error estimates, the weight of missing and below-detection-limit data in the solution can be decreased. There were missing and below-detection-limit values for different chemical species in four samples in the present study. Missing data were replaced by the geometric means of corresponding elements and four times of geometric mean as the corresponding error estimates (Polissar et al., 1998). Half of the detection limit was used for the values below the detection limit and 5/6 of the detection limit was used for the corresponding error estimate (Polissar et al., 1998). Considering the high uncertainty of gaseous species in measurements, we decreased the weight of gaseous species in model fit by assigning the uncertainty as 4 times their measured concentrations (Kim et al., 2005).

The mass concentration of PM2.5 for each sample was regressed against the factor scores obtained from PMF using multiple linear regression (MLR) (Xie et al., 1999). Uncertainties introduced by the measurement matrix, which is an unexplained portion of the measured variations not captured by PMF, were also taken into account by regressing the factor scores only to the explained portion of the mass concentrations. The regression coefficients were used to convert the factor profiles and contributions to physically reasonable unit of $\mu g\ m^{-3}$. PMF results for the overlapping periods as in CMB-MM (July 2001 and January 2002) were extracted for comparison.

3. Results and discussion

3.1. *Source apportionment by CMB-MM*

Detailed PM2.5 mass contributions for the seven primary sources resolved by CMB-MM as well as ion concentrations of secondary sulfate, nitrate, and ammonium have been reported elsewhere (Zheng et al., 2007). Briefly, contributions from the primary sources identified plus secondary aerosol formation accounted for 94% and 120% on average of the measured PM2.5 mass at JST in July 2001 and January 2002, respectively. Dominant sources contributed to total identified PM2.5 varied by season, with secondary sulfate (40%), other OM (25%), and secondary ammonium (17%) dominating in July 2001, and wood combustion (18%), other OM (18%), gasoline exhaust (16%), secondary sulfate (13%), secondary nitrate (11%), and secondary ammonium (9%) dominating in January 2002.

3.2. *Source apportionment by PMF*

Nine source factors were resolved by PMF from the 3-year dataset (January 2000 through December 2002) at the JST site (Liu et al., 2006). Based on their compositions, these factors are linked to actual emission source categories including diesel exhaust, gasoline exhaust, wood combustion, road dust, coal combustion, sulfate factor, nitrate factor, industry 1 (cement), and industry 2 (Zn). Among these nine source profiles, the sulfate factor is dominated by high concentrations of sulfate and ammonium while the nitrate factor has higher nitrate and the associated ammonium. The wood combustion factor contains high concentrations of EC, OC and K. For the diesel and gasoline exhaust factors, EC and OC are dominant, with the presence of some soil dust-related elements, likely due to road dust. The motor vehicle exhaust factors are also characterized by enriched gaseous species such as CO, NO, and NO_y. Coal combustion has high concentrations of sulfate, EC, OC, and Se, while road dust has high concentrations of Al, Ca, Fe, K, Si and Ti. Contributions from the nine PMF resolved sources accounted for 77% and 93% on average of measured PM2.5 mass concentrations in July 2001 and January 2002, respectively. Sulfate, diesel exhaust, and wood combustion were major contributors to PM2.5 in July 2001 accounting for 10–41% of measured PM2.5 mass. However, in January 2002, wood combustion, nitrate, sulfate, gasoline exhaust, and diesel exhaust (in descending order) dominated, accounting for 10–32% of measured PM2.5 mass.

3.3. *Comparison of source apportionment results*

3.3.1. *Effect of including gaseous components and thermal-resolved carbonaceous fractions on PMF simulated results*

The inclusion of gaseous species and thermal-resolved carbonaceous fractions as additional constraints for PMF model fit has been suggested (Kim et al., 2005; Liu et al., 2006). As a result, the resolution power of PMF is thought to be enhanced and the split of diesel exhaust and gasoline exhaust can be achieved (Liu et al., 2006). The source apportionment results from two PMF approaches using different input species were compared in a study by Liu et al. (2006). Here we present a summary of the results comparison (Table 1). When the gas phase and carbon fractions were included as input species in PMF (assigned as PMF-1 in Table 1), among the eight resolved sources, mass contributions from three sources of wood combustion, road dust, and nitrate increased while that from four sources of sulfate, coal combustion, industry factor 1 (cement), and industry factor 2 (Zn) decreased, regardless of the seasonal change (Table 1). Contributions from motor vehicle exhaust, however, showed an increase in the summer month while a decrease in the winter month. The inclusion of carbonaceous fractions and gas phase components in PMF (PMF-1) aids differentiating diesel and gasoline exhausts, which could not be achieved in the earlier PMF source apportionment practice using bulk OC and EC (PMF-2); however, it should be noted that the unapportioned PM mass is larger using PMF-1 than using PMF-2 in both seasons, accounting for 2–3% more of the total mass. The major contributors to the increase in unapportioned PM2.5 may be sulfate (2.33 $\mu g\ m^{-3}$ or 20% less) in summer and motor vehicle exhaust (0.53 $\mu g\ m^{-3}$ or 16% less) and sulfate (0.47 $\mu g\ m^{-3}$ or 18% less) in winter. On the contrary, consistently higher mass concentrations from wood combustion were estimated by PMF-1 than by PMF-2 in either summer (1.13 $\mu g\ m^{-3}$ or 110% more) or winter (1.07 $\mu g\ m^{-3}$ or 34% more).

Table 1 – Comparison of source contributions to PM2.5 ($\mu g\ m^{-3}$) in two different PMF methods

Resolved source	July 2001				January 2002			
	PMF-1[a]	PMF-2[b]	Difference[c]	% Difference	PMF-1	PMF-2	Difference	% Difference
Sulfate	9.12±4.81	11.45±5.71	−2.33	−20	2.12±0.71	2.59±0.83	−0.47	−18
Nitrate	0.65±022	0.56±0.20	0.09	15	2.30±1.26	2.02±1.05	0.28	14
Diesel exhaust	2.56±1.14	–	–	–	1.28±0.71	–	–	–
Gasoline exhaust	0.28±0.26	–	–	–	1.54±1.21	–	–	–
Motor vehicle exhaust[d]	2.84±1.20	2.05±1.27	0.79	38	2.82±1.26	3.35±2.10	−0.53	−16
Wood combustion	2.15±1.63	1.02±0.76	1.13	110	4.23±2.82	3.16±1.61	1.07	34
Road dust	1.12±1.24	0.70±0.89	0.42	61	0.26±0.30	0.16±0.18	0.10	62
Coal combustion	0.33±0.29	0.64±0.52	−0.31	−49	0.23±0.22	0.43±0.35	−0.20	−46
Industry factor 1 (cement)	0.73±0.67	0.99±0.76	−0.26	−27	0.22±0.19	0.44±0.28	−0.22	−50
Industry factor 2 (Zn)	0.09±0.07	0.28±0.21	−0.19	−69	0.18±0.10	0.49±0.27	−0.31	−63
Unapportioned	5.07±3.47	4.38±3.16	0.69	16	0.92±3.35	0.64±1.20	0.28	43

[a] PMF-1, PMF with five gaseous components and eight thermal-resolved carbon fractions (OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3 based on TOR carbon analysis protocol (Chow et al., 1993, 2001).

[b] PMF-2, PMF with only two carbon fractions and no gaseous species.

[c] The difference is calculated by subtracting the average contributions for PMF-2 from that for PMF-1.

[d] Motor vehicle exhaust is defined as the sum of diesel exhaust and gasoline exhaust.

It is still unclear why the inclusion of gas phase and carbonaceous fractions leads to higher proportions of undetermined mass (Liu et al., 2006). While a possible reason may be the additional constraints, which reduce the chance of incorrect apportionment of the unresolved PM2.5 mass to the resolved sources. In order to examine this hypothesis, we compared the proportional data of three important components of OC, EC, and SO_4^{2-} in the major source profiles resolved by CMB-MM, PMF-1, and PMF-2 from the previous studies (Liu et al., 2006; Zheng et al., 2007), and the results are summarized in Table 2. Similar source profiles developed for CMB analysis of the traditional species (CMB-Regular) in the Big Bend Regional Aerosol Visibility and Obvervational (BRAVO) study (Chow et al., 2004) were also included for comparison purpose. As can be seen, for the SO_4^{2-} factor, with the split between diesel and gasoline exhausts, the proportion of SO_4^{2-} in each of the PMF resolved PM2.5 profiles of diesel exhaust, gasoline exhaust, and coal combustion increased, while that in wood combustion decreased. Therefore, ambient SO_4^{2-} mass would be apportioned to six sources in PMF-1 instead of five in PMF-2, which might result in the reduction in contributions of SO_4^{2-} to PM2.5 when PMF-1 was employed. For the wood combustion

Table 2 – Percentage of OC, EC, and SO_4^{2-} to PM2.5 mass (%) in some important source profiles resolved by CMB-MM and/or PMF in the present study

Component	Model	Motor vehicle exhaust	Diesel exhaust	Gasoline exhaust	Wood combustion	Road dust[a]	Coal combustion	Industry 1 (cement)	Cooking	SO_4^{2-} factor
OC	PMF-1[b]	–	25.7	58.8	64.5	37.3	22.1	52.1	–	3
	PMF-2[c]	68.1	–	–	76.6	37.6	41.5	4.5	–	5.7
	CMB-MM	–	30.4	47.9	74.9	13.1	–	–	56.6	–
	CMB-Regular[d]	58.7	–	–	64.5	13.3	27.2	12.8	86.7	–
EC	PMF-1	–	25.7	29.4	32.8	2.8	17	NV[e]	–	NV
	PMF-2	28.3	–	–	4.8	3.3	14.2	18.2	–	0.1
	CMB-MM	–	40.5	1.2	8.2	0.9	–	–	UDL[f]	–
	CMB-Regular	37.2	–	–	15.8	2.4	1.4	3	10.2	–
SO_4^{2-}	PMF-1	–	8.9	6.6	0.1	16.4	40.9	20.2	–	70.9
	PMF-2	1.8	–	–	11.5	26.2	29.7	17.6	–	65.5
	CMB-MM	–	1.0	0.4	0.4	1.2	–	–	UDL	–
	CMB-Regular	2.2	–	–	2.4	0.5	28.7	31.4	0.4	–
$OC+EC+SO_4^{2-}$	PMF-1	–	60.3	94.8	97.4	56.5	80	72.3	–	73.9
	PMF-2	98.2	–	–	92.9	67.1	85.4	40.3	–	71.3
	CMB-MM	–	61.2	49.5	83.5	15.2	–	–	56.6	–
	CMB-Regular	98.1	–	–	82.7	16.2	57.3	47.2	97.3	–

Similar source profiles developed for CMB modeling with traditional species (Chow et al., 2004) are included for comparison.

[a] Road dust, paved road dust profiles were selected for CMB-MM (Zheng et al., 2002) and CMB-Regular (Chow et al., 2004).

[b] PMF-1, PMF using eight carbon fractions and five gaseous species (Liu et al., 2006).

[c] PMF-2, PMF using bulk OC and EC (Liu et al., 2005).

[d] CMB-Regular, CMB with traditional species (Chow et al., 2004). All selected source types except for road dust are averaged composite source profiles as listed in Table 3 of the paper.

[e] NV: negative value.

[f] UDL: under detection limit.

source, in spite of the relatively minor changes in OC proportion (64.5% in the PMF-1 resolved profile and 76.6% in the PMF-2 resolved profile), the EC fraction increased dramatically from 4.8% in the PMF-2 resolved profile to 32.8% in the PMF-1 resolved profile. It is reasonable to infer that the increase in contributions from wood combustion for both seasons is mainly due to the increase in EC proportion in the source profile. Significant changes can also be seen in OC proportions for coal combustion and industry 1 (cement), and in EC proportions for industry 1 (cement) (Table 2). In terms of the diesel and gasoline exhaust sources, the summed proportion of EC in the PMF-1 resolved profile doubles that in the PMF-2 resolved profile of motor vehicle exhaust; however, the summed proportion of OC in the PMF-1 resolved profile increases by around 25% as compared with that in the PMF-2 resolved profile. Seasonal variability in contributions from motor vehicle exhaust is merely found for PMF-2 (3.35 $\mu g\ m^{-3}$ in winter while 2.05 $\mu g\ m^{-3}$ in summer) but not for PMF-1.

3.3.2. *Comparison of source contributions by CMB-MM and PMF*

The foundation for the intercomparison of CMB-MM and PMF is that a number of emission sources resolved by both methods are similar and can be compared. In this study, the source categories/factors shared by both CMB-MM and PMF include diesel exhaust, gasoline exhaust, wood combustion, road dust, sulfate, and nitrate. It should be noted that the sulfate and nitrate sources from the CMB-MM model are the measured values after subtracting the summed mass of sulfate and nitrate directly emitted from the selected primary sources (calculation was made based on their proportions to PM mass in each source profile). The comparison of these ion sources from PMF with that from CMB-MM is really just a comparison of the PMF result with the measured data. Therefore, the method comparison in this study will be focused on the sources of diesel exhaust, gasoline exhaust, wood combustion, and road dust. In addition, secondary organic aerosol (SOA) estimated from PMF and CMB-MM will be compared and discussed, as it is a very important component in the total OC (or organic matter, OM).

3.3.2.1. *Diesel exhaust.* Contributions from diesel exhaust resolved by PMF in general were higher than by CMB-MM for both seasons, especially for summer (by a factor of 2.6 on average) (Figs. 1 and 2). Daily variability of diesel exhaust was different, as reflected by the poor correlations (squared correlation coefficient (R^2) <0.02) (panel (a) of Fig. 3). The source profile of diesel exhaust used in CMB-MM is characterized by EC, Al, Si, and a number of *n*-alkanes, hopanes and steranes, while the PMF resolved source profile of diesel exhaust is characterized by the eight fractions of EC and OC determined by the IMPROVE method. In addition, the gaseous species are also characteristic of diesel exhaust. EC is the key species in both methods. The OC/EC ratio in the diesel exhaust profile used in CMB-MM is 0.75 (Schauer et al., 1999a), similar to that resolved by PMF (0.88) (Kim et al., 2003) and to that measured in diesel exhaust for PM10 (0.72) (Cadle et al., 1999). For the diesel exhaust profile resolved by PMF, the OC/EC ratio is 1.0, slightly higher than these values. However, this different scale is not large enough to explain the huge difference between the CMB-MM and PMF results. We observed that there was a significant amount of SO_4^{2-} (8.9% of the total mass) in the PMF resolved profile, which is much higher than that (1% of the total mass) in the CMB-MM profile (Table 2). Sulfate is considered as a secondary product converted from its precursor SO_2 after emitted to the atmosphere. Instead, the CMB-MM model only predicts primary PM contributions from diesel exhaust. It is then inferable that the much higher diesel exhaust simulated by PMF than by CMB-MM in July may be due in part to that PMF estimates both primary and secondary PM2.5 that associated with diesel exhaust while CMB-MM estimates only primary particulate matter released by diesel engines. It is believed that photochemical reactions are much more active in summer than in winter, resulting in correspondingly higher levels of PM2.5 from PMF resolved diesel exhaust in the summertime.

3.3.2.2. *Gasoline exhaust.* Unlike diesel exhaust, PM2.5 from gasoline exhaust estimated by CMB-MM was higher than by PMF. In addition, both methods estimated much higher contributions in January 2002 than in July 2001, indicating a seasonal impact on this source (Figs. 1 and 2). Recent studies have shown that gasoline spark-ignition vehicles emit more particulates under poor combustion conditions (Schauer et al., 1999a, 2003). Cold starts at low temperature (e.g., in winter) are one of these combustion conditions. The difference in emissions of EC and high molecular weight PAHs such as benzo[*ghi*]perylene (BgP) and coronene can be 10 times greater from poor combustion conditions as compared to that from more complete ones (Schauer et al., 1999a). However, Schauer et al. (2003) also reported that the emissions of hopanes under cold-start conditions may be comparable to those under hot-start or steady-state driving conditions. Similar results have been found by Fine et al. (2004) in an investigation on ultrafine organic particulate in Los Angeles basin. The higher contributions from gasoline exhaust but not from diesel exhaust in winter may be because of the different constraints in CMB-MM source apportionments. For gasoline exhaust, there are more molecular markers including hopanes, steranes, and PAHs as constraints than diesel exhaust, while the latter puts more weight on EC.

Gasoline exhaust contributions estimated by CMB-MM and PMF agreed fairly well when all of the summer and winter data were included (R^2=0.49, n=0.39). Poor correlations were found when only summer (R^2=0.04, n=20) or winter (R^2=0.20, n=19) data were included. Compared to the CMB-MM gasoline exhaust profile, the PMF resolved profile has much higher EC proportion (29.4% vs. 1% of the total mass). The profile of PMF resolved gasoline exhaust is very similar to that of diesel exhaust, though with lower EC and different relative contributions of OC, SO_4^{2-}, NH_4, and gaseous species, which have multiple origins. For CMB-MM, the gasoline exhaust profile has significantly different relative contributions of EC, hopanes and steranes, and PAHs compared to the diesel exhaust profile. More importantly, hopanes and steranes are characteristics of motor vehicle emissions, which are unlikely to be influenced by other origins. Again, significant amount of sulfate ion also was found in the PMF resolved gasoline exhaust profile (6.6% of the total mass) (Table 2), suggesting that PM2.5 from gasoline exhaust estimated by PMF may be a mix of primary and secondary origins.

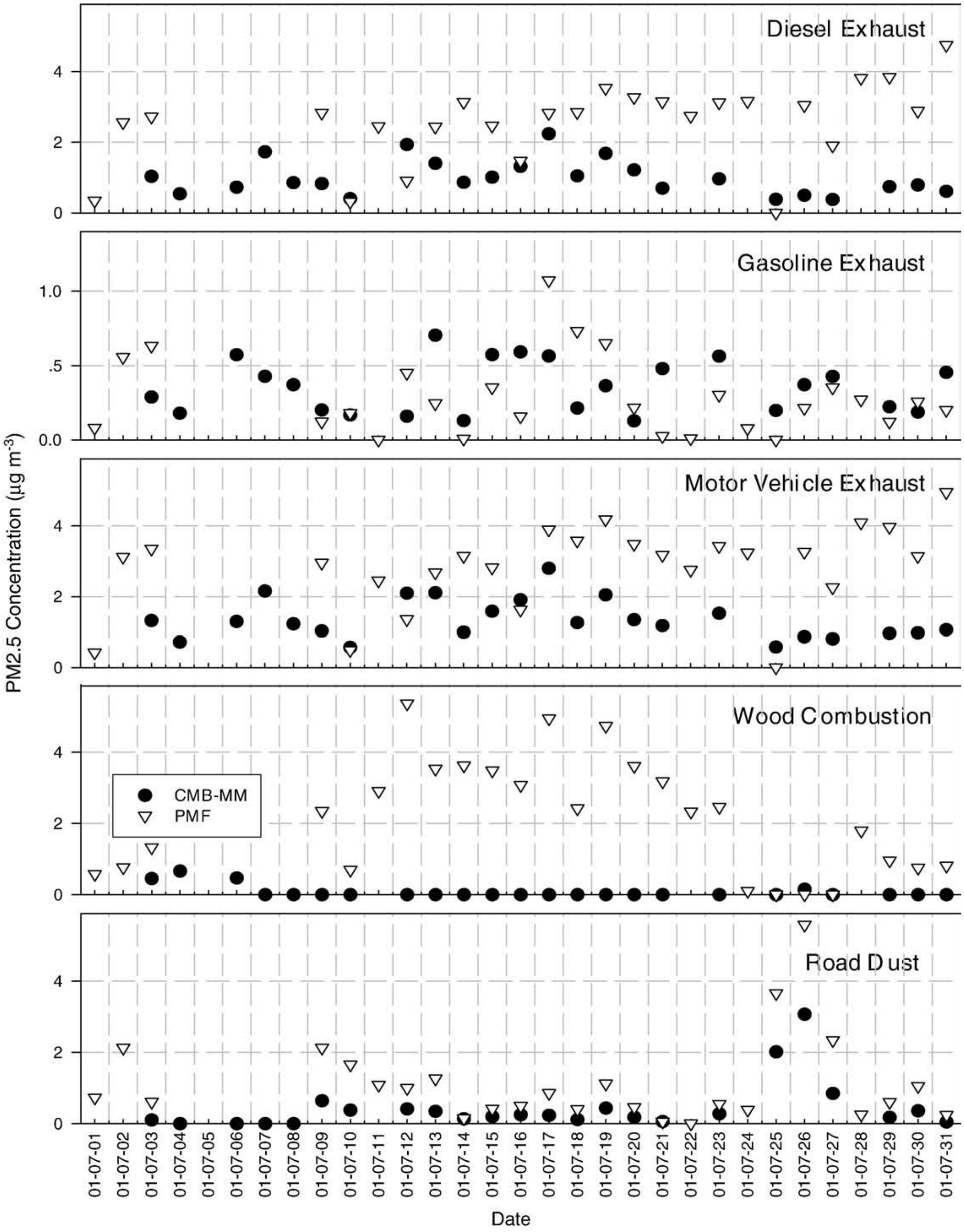

Fig. 1 – Comparison of CMB-MM and PMF-1 for daily variations in contributions from eight sources to PM2.5 at JST in July 2001. PMF-1, PMF using eight carbon fractions and five gaseous species.

The eight-carbon-faction PMF (PMF-1) with an important advantage over the regular PMF (PMF-2) is the capability of spliting diesel and gasoline exhausts. In order to clarify how well the two methods correlate to each other, one step is to combine the diesel and gasoline exhaust sources resolved by PMF-1 before compared with the unresolved mobile source by PMF-2 (Liu et al., 2006). This also is applicable to the comparison of CMB and PMF. In this study, the CMB-MM mobile source results were compared with that of PMF-1 and PMF-2, respectively, after combining the diesel and gasoline exhaust sources (panel (c) of Fig. 3 and panel (a) of Fig. 4). The CMB-MM combined mobile source has improved correlation with the PMF-1 combined mobile source ($R^2=0.12$, $n=39$), as compared with the diesel exhaust source ($R^2=0.003$, $n=39$); while the correlation between the combined sources is poorer than that between the gasoline exhaust source ($R^2=0.49$, $n=39$). However, when only the winter data are included, the CMB-MM combined mobile source shows enhanced correlation with the PMF-1 combined source ($R^2=0.30$,

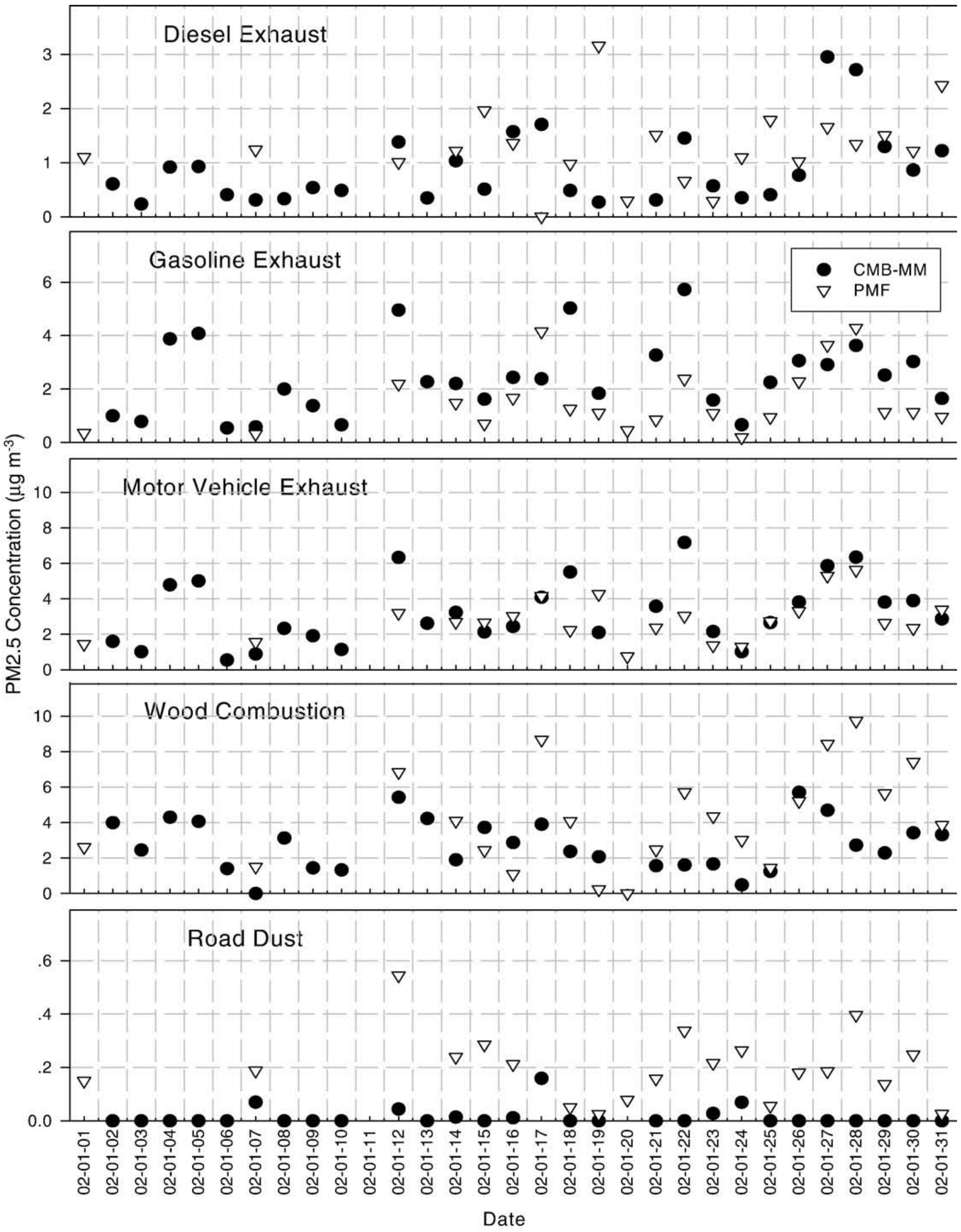

Fig. 2 – Comparison of CMB-MM and PMF-1 for daily variations in contributions from eight sources to PM2.5 at JST in January 2002.

n=19), as compared with the single source of diesel exhaust (R^2=0.02, n=19) or gasoline exhaust (R^2=20, n=19). A recent source apportionment study using the molecular marker-based PMF model (PMF-MM) also has reported that the PMF-MM mobile source factor has poor correlation with both the CMB diesel and gasoline exhausts but has reasonable correlation with a combination of diesel, gasoline, and smoker sources (Jaeckels et al., 2007). It is quite surprised that the CMB-MM combined mobile source has quite good correlation with the PMF-2 combined mobile source (R^2=0.60, n=39) (panel (a) of Fig. 4). It can be seen that the proportion of sulfate is quite low in the PMF-2 motor vehicle exhaust (1.8% of the total mass) (Table 2), indicating that the PMF-2 motor vehicle exhaust contains less secondary PM2.5 as compared with the PMF-1 motor vehicle exhaust. Jaeckels et al. (2007) have suggested that the CMB-MM source apportionment estimate of a combined motor vehicle source is reasonable, after comparing the PMF-MM result with the measured concentrations of the molecular

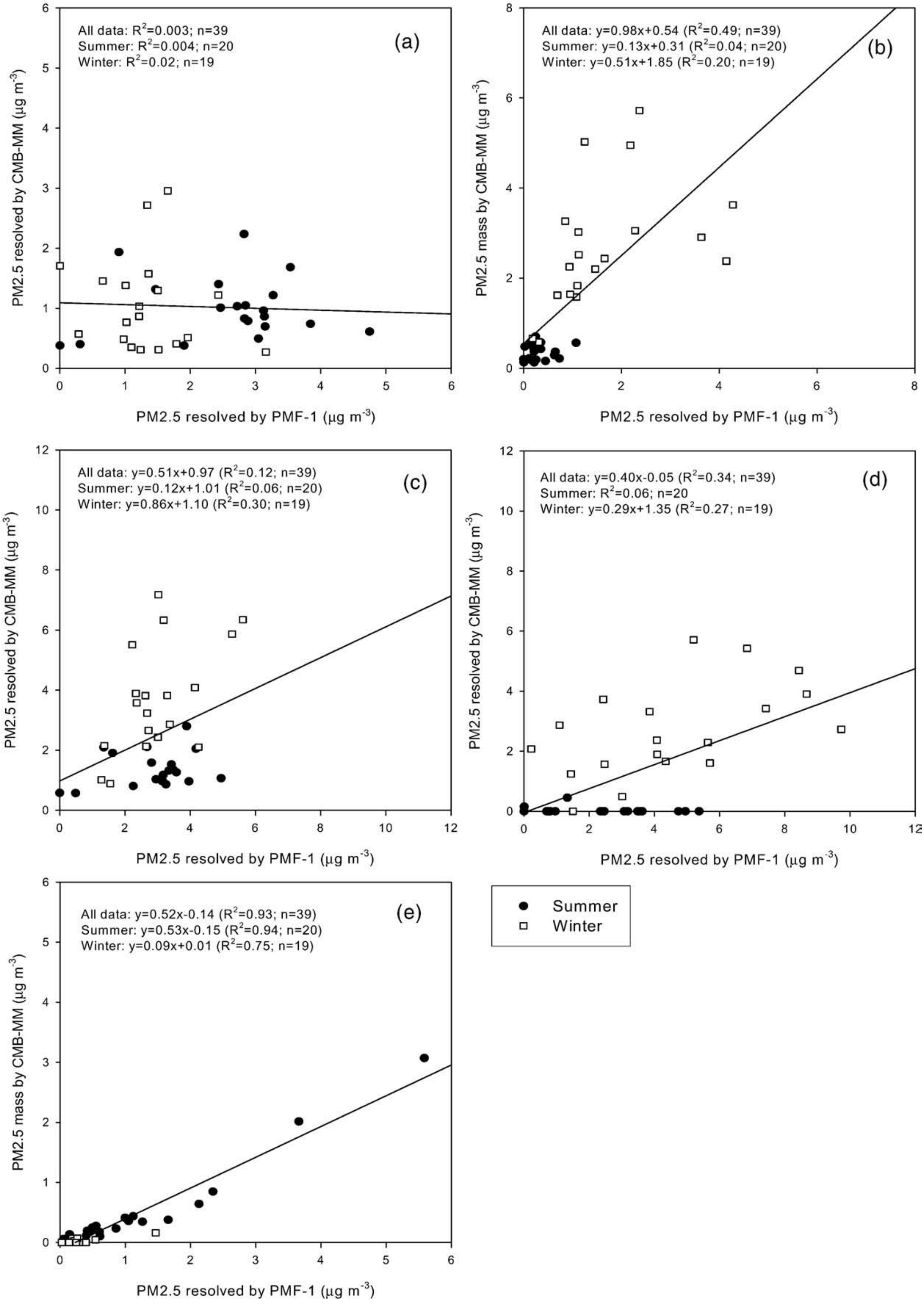

Fig. 3 – Comparison of the PM2.5 source contributions estimated by CMB-MM and PMF-1: (a) diesel exhaust, (b) gasoline exhaust, (c) motor vehicle exhaust (diesel+gasoline), (d) wood combustion, (e) road dust. The linear regression lines are based on all data.

marker of mobile source. To this end, the inclusion of the eight carbon fractions and five gas species in PMF-1 may not be able to reasonably apportion primary motor vehicle exhaust from ambient PM2.5 data as CMB-MM does.

3.3.2.3. *Wood combustion.* The daily distribution pattern for PM2.5 from wood combustion differed significantly between CMB-MM and PMF especially in the summer season (Fig. 1). In July, only four out of 24 samples had wood combustion-originated PM2.5 detected at a very low level (less than 0.66 μg m^{-3}), resulting in an extremely low average impact. In contrast, PMF-estimated mass concentrations from wood combustion fluctuated between undetectable and 5.37 μg m^{-3}, averaged 2.1 μg m^{-3}, a factor of 20 higher than by CMB-MM. It is noticed from Fig. 1 that the level of wood combustion exhaust started to go up on July 9th (no sample was taken between July 4th and 8th for PMF analysis), and stayed at a relatively high level (between 2.3 and 5.4 μg m^{-3}) until the end of July (July 24th and onward). On the contrary, estimated contributions of wood combustion by both methods were in better agreement for the winter data ($R^2=0.27$, $n=19$) (panel (d) of Fig. 3), with lower estimates by CMB-MM than by PMF.

The large difference for July samples may be linked to the difference in source profiles. For CMB-MM, wood combustion profile is characterized by enriched EC and OC as well as a number of molecular markers such as levoglucosan and resin acids. In this study, levoglucosan served as a key element for apportioning wood combustion. The quantification of levoglucosan is constrained by the detection limit. The wood combustion source can only be resolved when levoglucosan is detectable (the detection limit for levoglucosan by MM analysis is 5.3 ng m^{-3}). The lowest detectable concentration of levoglucosan was 14.2 ng m^{-3} from the sample taken on July 26th, leading to an apportioned PM2.5 contribution of 0.15 μg m^{-3} from wood combustion exhaust. For most of the July 2001 samples, levoglucosan was undetectable, which resulted in no contribution from wood combustion. For PMF, the resolved wood combustion profile is characterized by high OC, EC, and K (Watson and Chow, 2001), of which the sources can be multiple. Especially for some early July samples, they may be influenced by the July 4th fireworks, which is also a source for high K (Kim et al., 2003; Polissar et al., 2001). This might partially contribute to the high levels of wood combustion exhaust resolved by PMF in some July samples in the present study. The CMB-MM wood combustion results were also compared with the PMF-2 results (panel (b) of Fig. 4). Similarly, the CMB-MM wood combustion source has better correlation with the PMF-2 wood combustion source ($R^2=0.51$, $n=39$) than with the PMF-1 one ($R^2=0.34$, $n=39$). Based on the comparison between CMB-MM and PMF-2, it shows that PMF-1 tends to have a high bias and the CMB-MM estimated wood combustion contribution might be closer to the real situation.

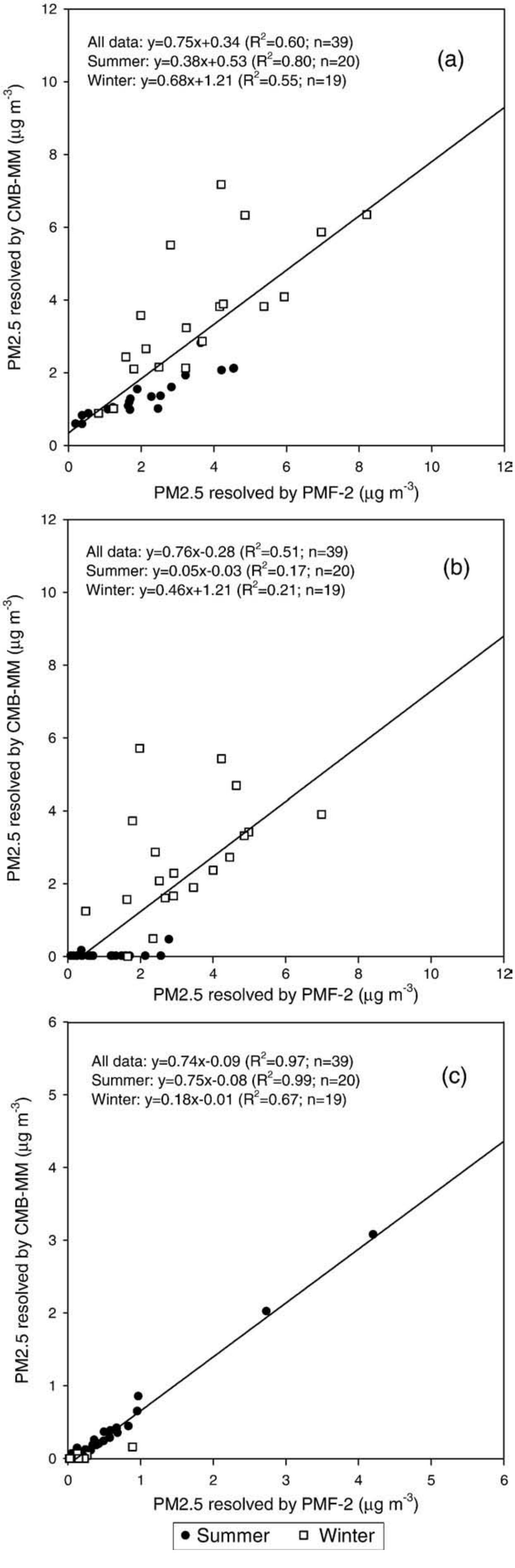

Fig. 4 – Comparison of the PM2.5 source contributions estimated by CMB-MM and PMF-2 (PMF using bulk OC and EC): (a) motor vehicle exhaust (diesel + gasoline), (b) wood combustion, (c) road dust. The linear regression lines are based on all data.

3.3.2.4. Road dust. Contributions from road dust resolved by PMF were much higher than by CMB-MM, with 1.1 and 0.4 μg m^{-3} on average for PMF and CMB-MM, respectively. Both CMB-MM and PMF-estimated road dust contributions were much lower in January 2002 than in July 2001 (Figs. 1 and 2). The road dust source could not be resolved for many January 2002 samples by CMB-MM, which may be due to very low concentrations of Al and Si concentrations in the ambient samples. PMF-1 results show higher levels of the so called "road dust" than CMB-MM. It is probably because that "road dust" in PMF includes all types of airborne dust from unpaved roads, construction sites, and wind-blown soil dust (Kim et al., 2003), while CMB-MM apportions base only on Al and Si in a set profile of paved road dust, which may not be always representative of all road dust. Although PMF estimates higher road dust contribution than CMB-MM, the daily variability of road dust concentrations by CMB-MM and PMF gave similar trends (R^2=0.93, n=39) (Fig. 3), which may be due to the similarity of key tracers (Al and Si) in road dust source profile used in CMB-MM and resolved by PMF-1. It should be stressed that a regression analysis with a few high days in winter shows that road dust is not really a good metric of agreement (R^2=0.67, n=19) (Fig. 2 and panel (c) in Fig. 4). It may be due to the very low concentrations of Al and Si, which resulted in the road dust contributions not resolved by CMB-MM for many winter samples. However, since both PMF and CMB-MM resolved road dust concentrations in winter are low (<0.5 μg m^{-3}), the data did not affect much the good correlation between PMF and CMB-MM results when the summer and winter data were combined (R^2=0.93, n=39). Higher correlations of road dust estimates were also found between CMB-MM and PMF-2 (R^2=0.97, n=39) (panel (c) of Fig. 4). From Table 2, it can be seen that sulfate fraction is in high proportion in the PMF-2 road dust profile (26.2% of the total mass) than in the PMF-1 road dust profile (16.4% of the total mass), resulting in higher mass contributions from the PMF-1 road dust source than from the PMF-2 road dust source.

3.3.2.5. SOA estimates. It is of great interest in estimating SOA with different approaches, such as CMB-MM (Zheng et al., 2002), PMF-MM (Shrivastava et al., 2007), PMF analysis of traditional species data (PMF-regular) (Pekney et al., 2006), EC-tracer method (Polidori et al., 2006), and factor analysis of aerosol mass spectrometer (AMS) data (Zhang et al., 2005). CMB-MM is an indirect method for SOA estimation defined as the difference between the measured ambient OC and the OC apportioned by CMB-MM to primary sources. PMF-regular also is an indirect method to estimate SOA by considering the OC portion in secondary sulfate as SOA (Pekney et al., 2006). In this study, the OC from both of the PMF resolved secondary sulfate and nitrate factors were calculated based on their proportions to the PM mass, and then combined to estimate the SOA. As shown in Fig. 5, the CMB-MM estimated SOA has good correlation with both of the PMF-1 estimated SOA (R^2=0.43, slope=7.42, n=39) and the PMF-2 estimated SOA (R^2=0.50, slope=3.18, n=39). As can be seen from the slope, CMB-MM estimates much higher SOA than PMF-1 and PMF-2, by a factor of 7.42 and 3.18, respectively. Pekney et al. (2006) also reported that only half as much OC to SOA from the sulfate factor by PMF-2 as the PMF-MM analysis by Shrivastava et al. (2007). The difference in SOA estimates by CMB-MM and PMF-1/PMF-2 may be due to: (1) the unresolved primary OC that would attribute to the CMB-MM SOA (high bias) and (2) the SOA from the resolved primary sources that have not been included in the PMF-1/PMF-2 SOA (low bias), as indicated by the significant sulfate portions in some PMF resolved source profiles shown in Table 2.

4. Conclusions

A comprehensive comparison of CMB-MM and PMF in the current study shows that the PM2.5 mass contributions from road dust, gasoline exhaust, and wood combustion are in fair to good agreement between the CMB-MM and PMF results. The CMB-MM diesel exhaust has poor correlation with the PMF

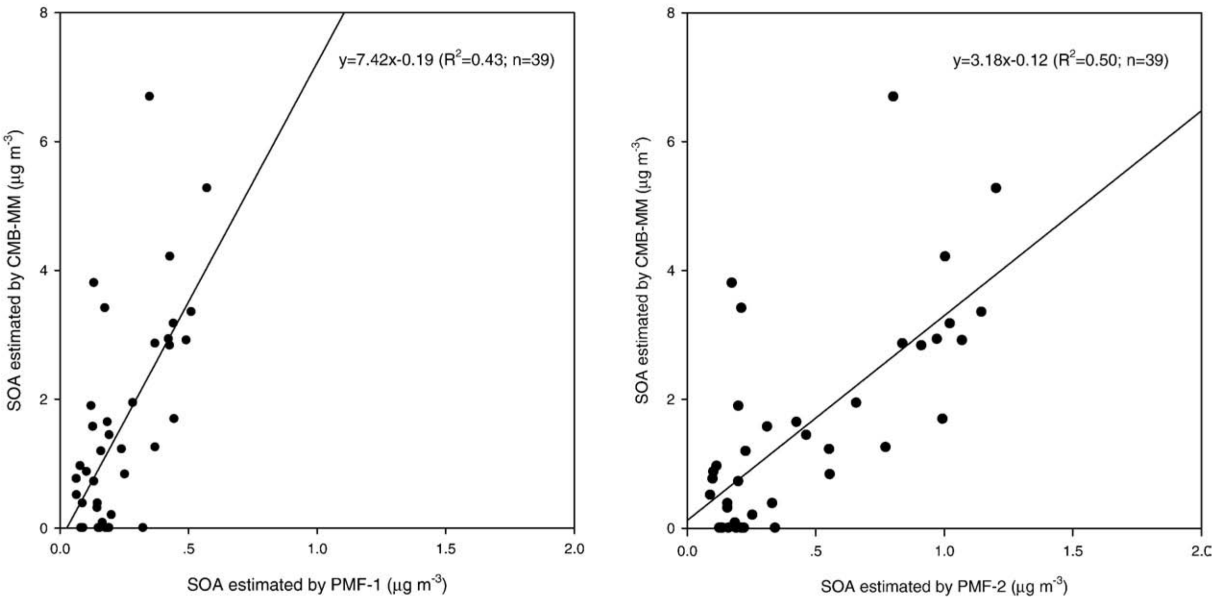

Fig. 5 – Comparison of PM2.5 mass concentrations from secondary organic aerosol estimated by CMB-MM and PMF.

diesel exhaust. The discrepancy in source apportionment results between CMB-MM and PMF may be due to the different source compositions or tracers in their source profiles. Basically, if there were more overlap in the compounds used in each type of analysis, better agreement may be expected. However, this may also mask errors in the results. There are still fundamental differences between PMF and CMB-MM, as evidenced shown by Jaeckels et al. (2007). Our study also shows that the CMB-MM results are in better agreement with the PMF analysis of traditional speciation data than with the eight-carbon-fraction PMF analysis.

CMB-MM is a powerful tool to apportion sources characterized by unique molecular markers such as wood combustion and meat cooking. It performed fairly well for motor vehicle exhaust. The split between diesel and gasoline exhaust might be improved if thermal-resolved carbonaceous fractions were able to be incorporated into molecular marker-based source profile in the source tests. For PMF, the inclusion of gaseous species as well as carbonaceous fractions gives more constraints to model fits and helps to split diesel exhaust and gasoline exhaust estimates, though it may not be as powerful for apportioning primary motor vehicle exhaust from the ambient PM2.5 data as CMB-MM.

Acknowledgements

The authors are grateful to Fu Wang and Josh Maudlin for their assistance in organic speciation analysis, and Bo Yan, Bo Wang and Xiang Ding for valuable comments on CMB modeling. This work was supported by the Southern Company and the US EPA under grants RD83096001, RD82897602 and RD83107601.

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