

# Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite

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**Abstract.** Sources of PM<sub>2.5</sub> at the Fresno Supersite during high PM<sub>2.5</sub> episodes occurring from 15 December 2000–3 February 2001 were estimated with the Chemical Mass Balance (CMB) receptor model. The ability of source profiles with organic markers to distinguish motor vehicle, residential wood combustion (RWC), and cooking emissions was evaluated with simulated data. Organics improved the distinction between gasoline and diesel vehicle emissions and allowed a more precise estimate of the cooking source contribution. Sensitivity tests using average ambient concentrations showed that the gasoline vehicle contribution was not resolved without organics. Organics were not required to estimate hardwood contributions. The most important RWC marker was the water-soluble potassium ion. The estimated cooking contribution did not depend on cholesterol because its concentrations were below the detection limit in most samples. Winter time source contributions were estimated by applying the CMB model to individual and average sample concentrations. RWC was the largest source, contributing 29–31% of measured PM<sub>2.5</sub>. Hardwood and softwood combustion accounted for 16–17% and 12–15%, respectively. Secondary ammonium nitrate and motor vehicle emissions accounted for 31–33% and 9–15%, respectively. The gasoline vehicle contribution (3–10%) was comparable to the diesel vehicle contribution (5–6%). The cooking contribution was 5–19% of PM<sub>2.5</sub>. Fresno source apportionment results were consistent with those estimated in previous studies.

of directly emitted PM<sub>2.5</sub> (582 out of 765 tons/day [t/day]) (California Air Resources Board, 2004). Approximately half of the remaining directly emitted PM<sub>2.5</sub> (13%) originates from on-road and off-road vehicle emissions (97 t/day). Area sources include road/fugitive dust (248 t/day), residential and agriculture burning (123 t/day), construction (42 t/day), and cooking (19 t/day). These contributions vary spatially and temporally (Chow et al., 2006a; Rinehart et al., 2006). For example, residential wood combustion (RWC) is common in populated urban areas during winter.

Previous San Joaquin Valley (SJV) source apportionment studies have shown the importance of fugitive dust, vehicle exhaust, agricultural burning and RWC, and cooking contributions to PM<sub>2.5</sub> and PM<sub>10</sub> (Chow et al., 1992; Magliano et al., 1999; Schauer and Cass, 2000). Primary PM<sub>2.5</sub> and PM<sub>10</sub> contributions from industrial sources were negligible. Chow et al. (1992) and Magliano et al. (1999) used Chemical Mass Balance (CMB) modeling with elements, inorganic ions, organic carbon (OC), and elemental carbon (EC). Neither of these studies distinguished diesel- from gasoline-powered motor vehicle contributions or vegetative burning from cooking contributions. Both applications included a “pure” OC profile to explain ambient OC concentrations. Magliano et al. (1999) suggested that the pure OC source represented unidentified activities that might also include secondary organic aerosol (SOA).

Organic compounds measured by different methods have been used to help distinguish among source contributions to the PM carbon fraction (Schauer et al., 1996; Watson et al., 1998a; Zheng et al., 2002, 2006; Manchester-Neesvig et al., 2003; Hannigan et al., 2005; Labban et al., 2006). Schauer et al. (2000) applied the CMB model to three multi-day episodes during winter 1995/1996 and reported contributions from diesel and gasoline exhaust, hardwood and softwood combustion, cooking, and natural gas combustion at four SJV locations, including the Fresno Supersite (Watson et al., 2000), where PM<sub>2.5</sub> carbon levels are high during

## 1 Introduction

According to the California emission inventory, area-wide sources account for about 76% of the statewide emissions

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winter (Chow and Watson, 2002; Chow et al., 2006a, b; Park et al., 2006).

Results are reported here from CMB source apportionment of samples at the Fresno Supersite during high  $\text{PM}_{2.5}$  episodes in winter 2000/2001 as part of the California Regional  $\text{PM}_{10}/\text{PM}_{2.5}$  Air Quality Study (CRPAQS; Watson and Chow, 2002; Chow et al., 2005a; Rinehart et al., 2006). These data are used with source profile measurements to quantify and evaluate the uncertainty of source contributions during this period using the effective variance solution (Watson et al., 1984) to the CMB equations. Tests with simulated data and with and without the inclusion of marker compounds were undertaken to determine the feasibility and stability of the source contribution estimates.

## 2 Methods

### 2.1 Ambient measurements

Sampling and analysis details are reported elsewhere (Chow, 1995; Chow et al., 2005a, b) and summarized here. The Fresno Supersite is located at 3425 First Street, Fresno, CA, approximately five km from the downtown district. Air quality monitors are operated on the roof of a two-story building. Samples were collected with Desert Research Institute (DRI; Reno, NV) sequential filter samplers (SFS) preceded by  $\text{PM}_{2.5}$  size-selective inlets (Sensidyne Bendix 240 cyclones) and aluminum oxide tubular nitric acid ( $\text{HNO}_3$ ) denuders (Chow et al., 2005b). Teflon-membrane (Pall Sciences, R2PJ047, Ann Arbor, MI) filters were analyzed for  $\text{PM}_{2.5}$  mass by gravimetry and for elements by x-ray fluorescence (Watson et al., 1999). Quartz-fiber (Pall Sciences, QAT2500-VP, Ann Arbor, MI) filters were analyzed for chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) by ion chromatography (Chow and Watson, 1999), ammonium ( $\text{NH}_4^+$ ) by automated colorimetry, and water-soluble sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) by atomic absorption spectrometry. OC and EC were analyzed by the IMPROVE thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001, 2004a, 2005c). OC1-OC4 fractions evolve at 120, 250, 450, and 550°C, respectively, in a 100% helium (He) atmosphere. The OP fraction is pyrolyzed OC. OC is the sum of OC1-OC4 plus OP. The EC1-EC3 fractions evolve at 550, 700, and 800°C, respectively, in a 98% He/2% oxygen ( $\text{O}_2$ ) atmosphere. EC is the sum of EC1-EC3 minus OP.

$\text{PM}_{2.5}$  samples for semi-volatile organic compounds (SVOCs) were acquired with DRI sequential fine particle/semi-volatile organic samplers on Teflon-impregnated glass-fiber filters (TIGF) to collect particles followed by PUF/XAD/PUF (polyurethane foam, polystyrene-divinylbenzene XAD-4 resin) cartridges (Zielinska et al., 1998, 2003). Two- to four-ring polycyclic aromatic hydrocarbons (PAHs), methoxy-phenol derivatives, alkanes, and organic acids are present in both the gas and

particle phases while hopanes, steranes, and high molecular weight organic acids and alkanes are present mainly in the particle phase (Zielinska et al., 2004a). For SVOC analysis (Zielinska and Fujita, 2003; Zielinska et al., 2003; Rinehart, 2005; Rinehart et al., 2006), deuterated internal standards were added to each filter-sorbent pair. TIGF/XAD and PUF samples were extracted in dichloromethane and 10% diethyl ether in hexane, respectively, followed by acetone extraction using an Accelerated Solvent Extractor (ASE-300, Dionex, Sunnyvale, CA). The solvent volumes were generally 150 ml. The solvent extracts from the PUF plugs and filter-XAD pairs for individual samples were combined and concentrated by rotary evaporation at 20°C under gentle vacuum to ~1 ml. The samples were then split into two equivalent fractions. The final sample volume of both halves was reduced under a gentle stream of nitrogen and adjusted to 0.1 ml with acetonitrile.

The non-derivatized SVOC fraction was analyzed by electron impact (EI) gas chromatography/mass spectrometry (GC/MS) for PAHs, hopanes, steranes, and high molecular weight alkanes on a Varian CP 3800 GC with a CP-Sil 8 Chrompack (Varian, Inc., Palo Alto, CA) column connected to a Varian Saturn 2000 Ion Trap. Polar compounds in the second fraction (organic acids, cholesterol, sitosterol, levoglucosan, and methoxy-phenols) were converted to their trimethylsilyl derivatives using a mixture of N,O-bis (trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane, and pyridine. The calibration solutions were freshly prepared and derivatized just prior to the analysis of each sample set and all samples were analyzed by GC/MS within 18 h to avoid degradation. Samples were analyzed by chemical ionization GC/MS with isobutane as a reagent gas using a Varian CP 3800 GC with a CP-Sil 8 Chrompack (Varian, Inc.) column connected to a Varian Saturn 2000 Ion Trap (Zielinska et al., 2003; Rinehart, 2005, Rinehart et al., 2006).

Samples were collected from 15 through 18 December 2000, from 26 through 28 December 2000, from 4 through 7 January 2001, and from 31 January through 3 February 2001 based on forecasts of high  $\text{PM}_{2.5}$  conditions. Forecasting was done by San Joaquin Valley Air Pollution Control District meteorologists using a regression-based prognostic model that predicts 5-day  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations based on variables including atmospheric stability, wind speed, upper-air temperature, and continuous  $\text{NO}_3^-$  and carbon measurements. The study management team reviewed the model predictions daily over an afternoon conference call, and initiated intensive operating periods when the expected  $\text{PM}_{2.5}$  concentrations exceeded the national  $\text{PM}_{2.5}$  standard of  $65 \mu\text{g}/\text{m}^3$ . Samples were taken throughout the day to bound periods of differing source contributions (Watson and Chow, 2002; Chow et al., 2006a; Watson et al., 2006a, b): 1) 00:00–05:00 PST (Pacific Standard Time, GMT–8) for an aged nighttime mixture, 2) 05:00–10:00 PST for the morning rush-hour, 3) 10:00–16:00 PST for mixing

down of aged/secondary aerosol; and 4) 16:00–24:00 PST for evening traffic, cooking, and home heating.

## 2.2 Chemical Mass Balance model

The CMB receptor model (Hidy and Friedlander, 1971) describes  $C_{it}$ , the ambient concentration of the  $i$ -th chemical species measured at time  $t$ , as the linear sum of contributions from  $J$  sources:

$$C_{it} = \sum_{j=1}^J F_{ij} S_{jt} + E_{it} \quad (1)$$

where  $F_{ij}$  is the fractional abundance (source profile) of the  $i$ -th species in the  $j$ -th source type,  $S_{jt}$  is the mass contribution of the  $j$ -th source at time  $t$ , and  $E_{it}$  represents the difference between the measured and estimated ambient concentration. Ideally,  $E_{it}$  reflects random measurement uncertainty. There are numerous solutions to the CMB equations, including Positive Matrix Factorization (PMF) and UNMIX (Watson et al., 2002a; Watson and Chow, 2004), which have also been applied to  $PM_{2.5}$  data in central California (Chen et al., 2007). The effective variance weighted least squares minimization solution (Watson et al., 1984) is most commonly used for obtaining source contribution estimates ( $S_{jt}$ ), as implemented with CMB8 software (Watson et al., 1997, 1998b). As applied here, samples with  $S_{jt} < 0$  are eliminated and the solution is iterated until all remaining  $S_{jt}$  are positive for each sample. Wang and Hopke (1989) showed that this approach provides more precise estimates than does an unconstrained solution for sources whose profiles are collinear.

CMB results are evaluated with performance measures such as  $r$ -square (R SQR) and chi-square (CHI SQR) and the percentage of measured mass (PCMASS) accounted for by the sum of the  $S_{jt}$  (Watson and Chow, 2005). Although acceptable values for these metrics are necessary, they are not sufficient to guarantee  $S_{jt}$  that represent reality. The most important potential biases in the CMB model are related to improper specification of the contributing sources and unrealistic source profiles.

## 2.3 Source profiles

The  $PM_{2.5}$  source profiles in Table 1 were derived from emission studies of vehicle exhaust, wood burning, and cooking specific to fuels and operating conditions in California. Owing to differences in methods used to measure thermal carbon fractions (Watson et al., 2005), it is necessary to use profiles that were obtained using the same method applied to the receptor samples. It is also important that the organic compounds measured in the source profiles match those measured at the receptor. These profiles have been integrated into a documented data base with other recent profiles that is available from the authors (Chow et al., 2005a) and are being incorporated into the U.S. EPA's SPECIATE data base (U.S. EPA, 2007).

Composite diesel (DIES) and gasoline (GAS) exhaust profiles were derived from many dynamometer tests on a wide range of vehicles during the summer of 2001 (Fujita et al., 2006, 2007<sup>1</sup>). The sum of species in the diesel exhaust profile was larger than the measured mass, probably because the Teflon filters on which mass was determined were overloaded or because of VOC absorption by the quartz-fiber filter (Turpin et al., 1994). Therefore, the diesel exhaust profile (DIES) was normalized to the sum of species. The most useful components for separating diesel- from gasoline-exhaust contributions are three PAHs (i.e., indeno[123-cd]pyrene, benzo(ghi)perylene, and coronene) and EC (Miguel et al., 1998; Zielinska et al., 2004a, b; Fujita et al., 2007<sup>1</sup>). High temperature EC (EC2, evolved at 700°C in an oxidative environment; Watson et al., 1994) was abundant in the diesel engine tests.

Hardwood (BURN-H) and softwood (BURN-S) profiles from RWC were determined from oak, eucalyptus, and almond (hardwood) and tamarack (softwood) burns under controlled conditions (McDonald et al., 2000; Fitz et al., 2003). The emission inventory suggested that there was more hardwood than softwood combustion in Fresno during 1995 (Magliano et al., 1999).  $PM_{2.5}$   $K^+$  and polar organic compounds including levoglucosan, syringols, and guaiacols are markers for wood burning emissions (Rinehart, 2005; Rinehart et al., 2006).

Meat cooking (McDonald et al., 2003; Chow et al., 2004b) is represented by composite meat cooking profiles for charbroiled chicken (CHCHICK), chicken over propane (PRCHICK), and charbroiled hamburger (CHHAMB); an average meat cooking profile (COOK) was derived from these three. A smoked chicken profile (SMCHICK) was not included because it was enriched in levoglucosan from wood smoke. The primary markers for cooking are thought to be polar compounds such as cholesterol, palmitic acid, palmitoleic acid, stearic acid, and oleic acid (Fraser et al., 2003; Rinehart, 2005; Rinehart et al., 2006). However, these fatty acids can be emitted by sources other than meat cooking as they are abundant in seed oils used for cooking processes. Fatty acids are also present in vegetative burning, personal care products, plastic additives, household and industrial cleaners, and other domestic products. Cholesterol, a marker compound for meat cooking (Rogge et al., 1991), is also a constituent of biogenic detritus (Simoneit, 1989).

Geological source profiles were determined from SJV suspended dust samples (Ashbaugh et al., 2003; Chow et al., 2003) representing a wide range of urban and non-urban soils. Composite source profiles were created for: paved road dust (PVRD), unpaved road dust (UPVRD), agricultural soil

<sup>1</sup>Fujita, E. M., Campbell, D. E., Arnott, W. P., Zielinska, B., and Chow, J. C.: Evaluations of source apportionment methods for determining contributions of gasoline and diesel exhaust to ambient carbonaceous aerosols, *J. Air Waste Manage. Assoc.*, in review, 2007.





**Table 2.** Average absolute error (AAE %) between the CMB estimated and true source contribution estimates from simulated data.

Case	Organics	Ambient Uncert.	Source Uncert.	AAE (%) by Source code <sup>a</sup>										
				PVRD	GAS	DIES	MOBILE <sup>b</sup>	BURN-H	BURN-S	BURN <sup>c</sup>	COOK	MARINE	AMSUL	AMNIT
1	N	10%	30%	26	84	19	15	13	34	10	45	107	24	18
2	Y	10%	30%	22	10	8	7	10	29	8	14	103	23	18
3	N	Actual	Actual	72	178	29	33	17	108	20	70	268	18	8
4	Y	Actual	Actual	67	52	21	19	13	98	16	20	272	16	8
5	Y	Actual	Actual	76	50	21	16	20	–	20	21	282	16	8
6	Y	Actual	Actual	58	50	19	17	8	–	8	20	210	16	7

<sup>a</sup> See Table 1 for source codes

<sup>b</sup> MOBILE=GAS+DIES

<sup>c</sup> BURN=BURN-H+BURN-S

Case 1: Data generated with BURN-H (hardwood) and BURN-S (softwood), no organics in CMB.

Case 2: Data generated with BURN-H (hardwood) and BURN-S (softwood), organics in CMB.

Case 3: Data generated with BURN-H (hardwood) and BURN-S (softwood), no organics in CMB.

Case 4: Data generated with BURN-H (hardwood) and BURN-S (softwood), organics in CMB.

Case 5: Data generated with BURN-H (hardwood) and BURN-S (softwood), organics in CMB, no BURN-S in CMB.

Case 6: Data generated with BURN-H (hardwood) only, organics in CMB.

concentrations greater than their uncertainties) was 1.1 compared with a pure sea salt ratio of 1.8. This depletion results from reactions of sea salt particles with strong acids like  $\text{HNO}_3$ , where  $\text{NO}_3^-$  substitutes for Cl (Mamane and Gottlieb, 1992). To account for this, a “reacted” sea salt profile (MARINE) was used in which half of the Cl was replaced by  $\text{NO}_3^-$  on a molar basis (Chow et al., 1996). Secondary  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were represented by pure ammonium nitrate (AMNIT;  $\text{NH}_4\text{NO}_3$ ) and ammonium sulfate [AMSUL;  $(\text{NH}_4)_2\text{SO}_4$ ] profiles, respectively.

### 3 Results and discussion

#### 3.1 CMB feasibility analysis

Simulated data were generated with methods described by Javitz et al. (1988), Lowenthal et al. (1992), and Chow et al. (2004b). Average true source contributions from PVRD, GAS, DIES, BURN-H, BURN-S, COOK, MARINE, AMSUL, and AMNIT of 1, 3, 10, 30, 10, 10, 0.1, 5, and  $30 \mu\text{g}/\text{m}^3$ , respectively, were based on previous SJV source apportionments studies. True  $S_{ji}$  were created by randomly perturbing the average values (above) with a coefficient of variation (CV) of 50%, assuming a lognormal distribution. Synthetic concentrations were calculated for each “sample” using Eq. (1). Random lognormal variation for the source profiles (F) and measurement uncertainty was introduced to the derived concentrations (C) in two ways: 1) assuming measurement uncertainty and source profile variations of 10 and 30%, respectively; and 2) using the root-mean squared uncertainties of ambient concentrations and the actual standard deviations of the composite source profiles. The latter approach may be more realistic because some species

are measured more precisely than others. Cholesterol levels were below lower quantifiable limits (LQLs) in many of the samples owing to the short sample durations and periods of the day when cooking contributions were not expected. Cholesterol has also been reported to react with ozone under ambient conditions (Dreyfus et al., 2005). However, cholesterol was well-determined in the meat cooking emissions samples. To allow this compound to act as a useful marker for cooking in the simulations, its uncertainty in the ambient measurements was assumed to be 10%.

The CMB model was applied to the two data sets, each with 100 simulated samples using the average source profiles with weighting based on the uncertainties described above. The variance of the  $S_{ji}$  is the precision attainable for a particular source mix for a model with specified random errors. This precision is expressed as the average absolute error (AAE %), which is the average ( $N=100$ ) of the absolute percent differences between the estimated and true  $S_{ji}$ . Results are summarized in Table 2.

Case 1 represents fixed uncertainty without organics. The  $S_{\text{MARINE}}$  AAE was large (107%) because the true average  $S_{\text{MARINE}}$  was only  $0.1 \mu\text{g}/\text{m}^3$ . The AAEs for  $S_{\text{DIES}}$  and  $S_{\text{BURN-H}}$  were less than 20% while the AAEs for  $S_{\text{GAS}}$ ,  $S_{\text{BURN-S}}$ , and  $S_{\text{COOK}}$  were 84, 34 and 45%, respectively. When organics were included (Case 2), the AAEs were much lower for  $S_{\text{GAS}}$ ,  $S_{\text{DIES}}$ , and  $S_{\text{COOK}}$ , but they did not change as much for  $S_{\text{BURN-H}}$  and  $S_{\text{BURN-S}}$ . Including organic compounds reduced collinearity (similarity) among profiles for the vehicle exhaust and cooking sources. Except for  $S_{\text{BURN-H}}$ ,  $S_{\text{AMSUL}}$ , and  $S_{\text{AMNIT}}$ , the AAEs for Case 3 (no organics) were considerably larger than for Case 1: 72, 178, 29, 108, 70, and 268% for contributions from PVRD, GAS, DIES, BURN-S, COOK, and

MARINE, respectively. Including organics (Case 4) reduced the  $S_{\text{GAS}}$ ,  $S_{\text{DIES}}$ ,  $S_{\text{BURN-H}}$ , and  $S_{\text{COOK}}$  AAEs to 52, 21, 13, and 20%, respectively. While the  $S_{\text{BURN-H}}$  AAE improved somewhat (from 17% to 13%) when organics were included, the  $S_{\text{BURN-S}}$  AAE remained high (98%).

These results verify that organic markers can help distinguish contributions from gasoline exhaust, diesel exhaust, and cooking by increasing the differences between their source profiles. However, organics were not needed to estimate the wood burning contribution. Organics did not appear to separate hardwood and softwood contributions, even though there are noticeable differences between their source profiles. For example, the OC, EC,  $\text{K}^+$ , levoglucosan, 4-allyl-guaiacol, and syringaldehyde compositions of hardwood smoke were 58, 5.2, 2.9, 2.3, 0.12, and 0.46%, respectively, compared with 35, 27, 0.81, 0.16, 0.055, and 0.025%, respectively, for softwood smoke. Case 5 demonstrates the collinearity between the hardwood and softwood profiles by removing BURN-S from the CMB fit. Even though softwood combustion emissions contributed to the simulated concentrations, the hardwood profile (BURN-H) was sufficient to estimate the total burning contribution to within 20%. When all of the actual burning contribution came from hardwood combustion, the  $S_{\text{BURN-H}}$  AAE was only 8%.

The CMB8 model output contains the diagnostic MPIN (modified pseudo-inverse normalized) matrix (Kim and Henry, 1999). The MPIN identifies the influence of the fitting species on the source contribution estimates. An MPIN value of one indicates the highest influence. Average concentrations from Case 4, Table 2 were subjected to CMB analysis and the MPIN was calculated. The influential species in the source profiles were as expected: Al and Si for PVRD (paved road); benzo(ghi)perylene, coronene, and indeno[123-cd]pyrene for gasoline vehicles; the EC2 thermal fraction for diesel vehicles;  $\text{K}^+$ , levoglucosan, and syringaldehyde for hardwood combustion; EC for softwood combustion; and cholesterol for cooking.

These tests with simulated data demonstrate the feasibility of identifying and quantifying gasoline- and diesel-exhaust contributions with reasonable precision using organic markers. This is also the case for cooking contributions. Organics were not necessary to estimate the RWC contribution and it was not feasible to distinguish hardwood and softwood contributions from the source profiles used in this study, even when organics were included in the CMB model.

### 3.2 Initial source contribution estimates

Following the CMB applications and validation protocol (Watson et al., 1998b), the stability of the  $S_{jt}$  to different selections of source profiles and fitting species was evaluated for the average concentrations for the 00:00–05:00 PST sampling period. Ambient concentrations during this interval, including those of levoglucosan and cholesterol, markers for RWC and cooking, respectively, were relatively high

**Table 3.** Fitting species<sup>a</sup> used in CMB modeling for Fresno winter intensive samples.

Traditional species	Organic species
$\text{NO}_3^-$	Indeno[123-cd]pyrene (INCDPY)
$\text{SO}_4^{2-}$	Benzo(ghi)perylene (BGHIPE)
$\text{NH}_4^+$	Coronene (CORONE)
$\text{Na}^+$	17a(H),21b(H)-29-Hopane (HOP17)
$\text{K}^+$ (soluble K)	Levoglucosan (LEVG)
OC3	Syringaldehyde (SYRALD)
OC4	Palmitoleic acid (PALOL)
OC	Oleic acid (OLAC)
EC2	Cholesterol (CHOL)
EC3	Norfarnesane (NORFAR)
EC	Farnesane (FARNES)
Al	Norpristane (NORPRI)
Si	Pristane (PRIST)
Cl	Phytane (PHYTAN)
K (total K)	
Fe	
Se	
Br	
Pb	

<sup>a</sup> See Table 1 for chemical species.

and it is expected that this period is not dominated by a single source contribution. Chemical species whose concentrations were less than their uncertainties in most samples (more than 40 out of 51 total sampling periods in Fresno) were not included in the CMB model. While cholesterol did not fit this criterion, it was included because of its potential value as a cooking marker. Initial model runs indicated that other species were not adequately accounted for in the CMB. Calcium (Ca), whose concentrations were greater than twice their uncertainties in only 15 out of 51 samples, was overestimated by a factor of 5. Copper (Cu) and zinc (Zn) could not be explained by the available source profiles, including municipal incineration and brake wear. These species may be enriched by exhaust from the sampling equipment (Hoffman and Duce, 1971; King and Toma, 1975; Patterson, 1980). Guaiacol and 4-allyl-guaiacol, potential RWC markers, were underestimated by factors of 2 to 10. This could be attributed to differences between the profile fuels and burning conditions and those used in Fresno. Thermal carbon fractions were included except for OP (pyrolyzed OC), OC1 and OC2, which are believed to contain much of the adsorbed organic vapors on quartz filters, and EC1, which may contain some pyrolysis products. Table 3 shows the 19 traditional and 14 organic species included in subsequent CMB analyses.

Case 1 in Table 4 gives the CMB solution for the “best fit”, which included organic species and both hardwood and softwood RWC source profiles. In a statistical sense, it is not clear that the BURN-S contribution was resolved because its

**Table 4.** Source contribution estimates from the CMB trial runs for average Fresno winter intensive samples during the early morning (00:00–05:00 PST) period, with and without organics for various source mixes.

Case	PVRD	Source contributions ( $\mu\text{g}/\text{m}^3$ )										
		GAS	DIES	BURN-H	BURN-S	COOK	MARINE	AMSUL	AMNIT	PCMASS	R SQR	CHI SQR
1 <sup>a</sup>	0	1.9±1.3	6.6±2.2	16±3	5.8±6.2	20±5	0	1.1±0.4	18±2	92	0.96	0.6
2 <sup>b</sup>	0	0	7.1±2.3	15±3	7.0±6.4	23±6	0	1.3±0.3	18±2	94	0.98	0.7
3 <sup>a</sup>	0	2.2±1.4	7.6±2.2	18±2	–	21±6	0	1.1±0.4	18±2	89	0.96	0.6
4 <sup>b</sup>	0.04±0.3	0	8.5±2.2	17±2	–	25±6	0	1.3±0.4	18±2	91	0.97	0.7
5 <sup>a</sup>	0	1.0±0.9	3.0±1.6	–	37±3	23±5	0.49±0.12	1.3±0.3	18±2	110	0.88	3.0
6 <sup>b</sup>	0	0	3.2±1.6	–	36±3	24±6	0.49±0.12	1.4±0.3	18±2	109	0.91	4.1
7 <sup>a</sup>	0	2.4±1.4	8.2±2.4	19±3	10±6	–	0	1.0±0.4	18±2	77	0.92	1.2
8 <sup>b</sup>	0	30±7	0	18±2	0	–	0.05±0.20	0	17±2	85	0.97	0.4

<sup>a</sup> With organics.

<sup>b</sup> Without organics.

value was lower than its uncertainty. On the other hand, including this source accounted for a larger percentage of the measured mass. The best estimate of the RWC contribution may be the sum of  $S_{\text{BURN-H}}$  and  $S_{\text{BURN-S}}$  ( $22\pm7\ \mu\text{g}/\text{m}^3$ ). Similarly, while GAS and DIES contributions were resolved, the uncertainty of  $S_{\text{GAS}}$  ( $1.9\pm1.3\ \mu\text{g}/\text{m}^3$ ) was large (68%). The cooking contribution was large ( $20\pm5\ \mu\text{g}/\text{m}^3$ ) as was the secondary  $\text{NH}_4\text{NO}_3$  contribution ( $18\pm2\ \mu\text{g}/\text{m}^3$ ). Zero values for  $S_{\text{PVRD}}$  and  $S_{\text{MARINE}}$  indicate that their contributions became negative in the iterative solution and that their respective source profiles were dropped from the model. Most of the measured mass was accounted for (PCMASS=92) and the included sources explained the ambient chemical concentrations well (R SQR=0.96, CHI SQR=0.6).

The distinguishing chemical markers for the sources in Case 1 were examined with the MPIN matrix, a feature of the CMB8 model, shown in Table 5. According to the MPIN, the most important markers for cooking were OC, OC3, and palmitoleic acid. Cholesterol exhibited a relatively low value because its average ambient concentration was smaller than its uncertainty. The MPIN indicated that the most important GAS markers were coronene and benzo(ghi)perylene, as expected. The EC2 fraction was the most important DIES marker. The principal hardwood (BURN-H) markers were  $\text{K}^+$  and syringaldehyde. Levoglucosan was also an important marker with a value of 0.5. The MPIN shows that the most influential marker for softwood (BURN-S) was Fe, but this should not be the case.

Case 2 (Table 4) was the same as Case 1 except that organic species were excluded from the fit. Except for a  $S_{\text{GAS}}$  of zero, the solution was very similar to Case 1 (with organics) although  $S_{\text{COOK}}$  was  $3\ \mu\text{g}/\text{m}^3$  higher. Cases 3 and 4 were analogous to Cases 1 and 2, respectively, except that BURN-S was removed from the model. In Case 3, with organics, removing BURN-S increased the  $S_{\text{GAS}}$  and  $S_{\text{DIES}}$  slightly and increased  $S_{\text{BURN-H}}$  and  $S_{\text{COOK}}$  by 2 and  $1\ \mu\text{g}/\text{m}^3$ , respectively. In Case 4 (without organics), all of the vehicle

exhaust contribution was assigned to DIES, as in Case 2, and  $S_{\text{COOK}}$  increased from  $23\pm6$  (Case 2) to  $25\pm6\ \mu\text{g}/\text{m}^3$ . Removing BURN-S in Cases 3 and 4 reduced PCMASS by 3% and most of this decrease came from the burning source contribution.

Case 5 (with organics) and Case 6 (without organics) were analogous to Cases 3 and 4, respectively, except that BURN-S was included and BURN-H was excluded from the model. This caused a large increase in the burning contribution, to  $37\pm3$  and  $36\pm3\ \mu\text{g}/\text{m}^3$ , with and without organics, respectively, and an overestimation of measured mass by 10 and 9%, respectively. Both  $S_{\text{GAS}}$  and  $S_{\text{DIES}}$  were reduced by about a factor of 2 and  $S_{\text{COOK}}$  increased by  $3\ \mu\text{g}/\text{m}^3$  compared with Case 1. The R SQR decreased and CHI SQR increased dramatically compared with previous cases, indicating that BURN-S did not explain the traditional or organic species concentrations as well as BURN-H.

Finally, the cooking profile was removed while BURN-H and BURN-S were retained. In Case 7 (with organics), the solution was similar to that of Case 1 although  $S_{\text{GAS}}$  and  $S_{\text{DIES}}$  increased somewhat while the total burning contribution increased from  $22\pm7$  to  $29\pm7\ \mu\text{g}/\text{m}^3$ . The solution changed dramatically without organics (Case 8). All of  $S_{\text{BURN-S}}$  and  $S_{\text{COOK}}$  were assigned to  $S_{\text{GAS}}$  ( $30\pm7\ \mu\text{g}/\text{m}^3$ ). Both DIES and BURN-S were eliminated from the fit. Note that while mass was underestimated by 15%, this model fit the non-organic concentrations well (R SQR=0.97, CHI SQR=0.4). However, the previous results suggest that this solution was not realistic and that cooking should be included in the model, even though its uncertainty is large.

The solutions for Cases 1 through 4 were relatively stable with or without organics. Gasoline and diesel contributions were not resolved without organics. The overall burning contribution (hardwood plus softwood) depended mainly on  $\text{K}^+$  and not on organics. The cooking contribution was most influenced by OC and OC3, probably because cholesterol was lower than LQLs in most samples. However, when the



**Table 5.** Modified pseudo-inverse normalized (MPIN) matrix in the CMB model for Case 1 of Table 4. Key species for each source are underlined.

Species code <sup>a</sup>	Source code						
	GAS	DIES	BURN-H	BURN-S	COOK	AMSUL	AMNIT
NO <sub>3</sub> <sup>-</sup>	0.00	0.00	0.01	-0.01	0.00	-0.10	<u>1.00</u>
SO <sub>4</sub> <sup>=</sup>	0.00	0.00	0.00	0.00	0.00	<u>1.00</u>	-0.18
NH <sub>4</sub> <sup>+</sup>	0.00	0.00	-0.01	0.01	0.00	0.10	<u>0.92</u>
Na <sup>+</sup>	-0.07	-0.06	0.04	0.09	0.10	0.01	0.00
K <sup>+</sup>	-0.04	0.00	<u>1.00</u>	0.00	-0.30	-0.06	0.00
OC3	-0.04	0.02	0.10	-0.20	<u>0.52</u>	0.00	0.00
OC4	0.00	0.04	0.12	0.00	0.14	-0.02	0.00
OC	-0.07	-0.03	-0.01	-0.10	<u>1.00</u>	0.00	0.00
EC2	0.06	<u>1.00</u>	0.37	-0.64	-0.15	-0.16	0.00
EC3	0.01	0.00	-0.03	0.03	0.03	0.00	0.00
EC	-0.23	0.22	-0.51	<u>0.80</u>	-0.17	-0.01	0.00
Al	-0.09	-0.07	-0.20	0.43	-0.10	0.01	0.00
Si	<u>0.55</u>	-0.17	-0.27	0.44	-0.10	-0.08	-0.01
Cl	0.03	0.02	0.21	-0.12	0.01	-0.02	0.00
K	-0.09	-0.07	<u>0.58</u>	0.23	-0.24	-0.03	0.00
Fe	-0.19	-0.12	-0.59	<u>1.00</u>	-0.14	0.03	0.00
Se	0.00	0.01	0.01	-0.01	0.00	0.00	0.00
Br	0.13	0.15	0.12	-0.16	-0.03	-0.05	0.00
Pb	0.03	-0.01	-0.01	-0.03	0.09	0.00	0.00
INCDPY	<u>0.54</u>	-0.14	0.00	0.06	-0.05	-0.08	-0.01
BGHIPE	<u>0.93</u>	-0.16	0.09	-0.16	-0.03	-0.14	-0.01
CORONE	<u>1.00</u>	-0.14	0.13	-0.23	-0.06	-0.15	-0.01
HOP19	<u>0.57</u>	-0.02	0.09	-0.15	-0.07	-0.10	-0.01
LEVGU	0.05	0.06	<u>0.50</u>	-0.25	-0.08	-0.04	0.00
SYRALD	0.08	0.10	<u>0.73</u>	-0.38	-0.11	-0.06	0.00
PALOL	-0.06	0.00	-0.06	-0.19	<u>0.49</u>	0.02	0.00
OLAC	-0.02	-0.01	0.00	-0.08	0.20	0.01	0.00
CHOL	-0.03	-0.02	-0.05	-0.07	0.22	0.01	0.00
NORFAR	0.11	0.07	0.06	-0.09	-0.02	-0.03	0.00
FARNES	0.04	0.11	0.06	-0.09	-0.02	-0.02	0.00
NORPRI	0.04	0.23	0.10	-0.20	0.02	-0.04	0.00
PRISTU	-0.02	0.01	-0.03	-0.06	0.16	0.01	0.00
PHYTAN	-0.02	0.18	0.08	-0.13	-0.02	-0.02	0.00

<sup>a</sup> See Table 1 for chemical species.

cholesterol uncertainty was reduced to 10% of the average concentration, the solution remained similar to that of Case 1, even though cholesterol became the most influential marker for cooking according to the MPIN. The cooking contribution is highly uncertain.

### 3.3 Source apportionment during winter (2000–2001) in Fresno

Each of the 51 samples collected in Fresno was subjected to CMB analysis. The average  $r^2$ , chi-square, and percent mass accounted for were 0.89, 1.78, and 92%, respectively, when organics were included in the CMB and 0.92, 1.23, and 104%, respectively, without organics. Organics did not fit as well as traditional species, but including organics ac-

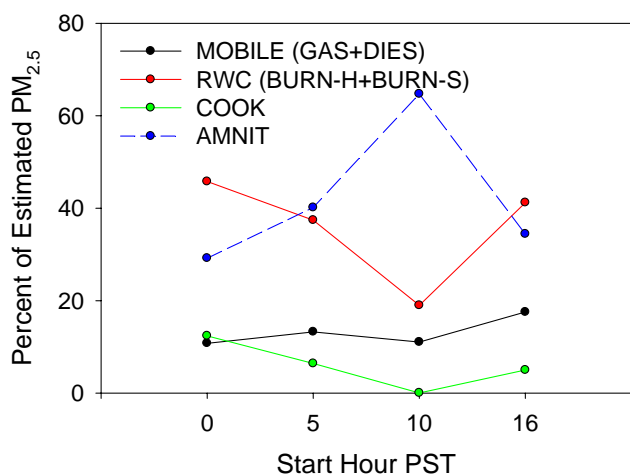
counted for more of the measured mass. Table 6 presents average source contribution estimates (from CMB including organics) based on: 1) the duration-weighted average of the CMB results from the 51 individual samples (Case A); 2) the average of the CMB results from the four intensive periods (Case B); and 3) the CMB result of the duration-weighted average concentrations of the 51 individual samples (Case C). The species in Table 3 were included and CMB8 was run in “auto fit” mode using the “s. elim.” option to constrain the source contribution estimates to positive values.

In all cases, PVRD was not detected. GAS was larger than DIES in Cases A and B, although they were equivalent within stated uncertainty levels. The combined vehicle exhaust contributions were 14 and 15% of measured PM<sub>2.5</sub>. For Case C (average sample), DIES (4.7  $\mu\text{g}/\text{m}^3$ ) was more

**Table 6.** CMB source contribution estimates ( $\mu\text{g}/\text{m}^3$ ) for the CRPAQS winter intensive samples in Fresno.

	Case A Average of 51 individual samples	% <sup>a</sup>	Case B Average of 4 IOP average samples	%	Case C Average sample	%
PVRD	0.10±0.20	0.1	0	0	0	0
GAS	5.8±3.6	8	6.9±4.0	10	2.2±1.3	3
DIES	4.2±3.2	6	3.6±3.9	5	4.7±1.9	6
MOBILE (sum)	9.0±4.8	14	10.5±5.6	15	6.9±2.3	9
BURN-H	11.5±2.0	16	11.7±2.5	17	11.4±2.3	16
BURN-S	11.0±4.9	15	8.7±7.2	12	9.7±5.6	13
BURN (sum)	22±5	31	20±8	29	21±6	29
COOK	3.6±2.3	5	7.9±3.3	11	13.9±4.4	19
AMSUL	1.3±0.4	2	1.2±0.3	2	1.5±0.4	2
AMNIT	23±2	32	22±2	31	24±2	33
MARINE	0.09±0.09	0.1	0.11±0.15	0.2	0.08±0.22	0.1
R SQR	0.89		0.94		0.96	
CHI SQR	1.8		0.75		0.67	
PCMASS (%)	93		91		93	
Measured PM <sub>2.5</sub> ( $\mu\text{g}/\text{m}^3$ )	72		70		72	

<sup>a</sup> Percent of measured PM<sub>2.5</sub>.

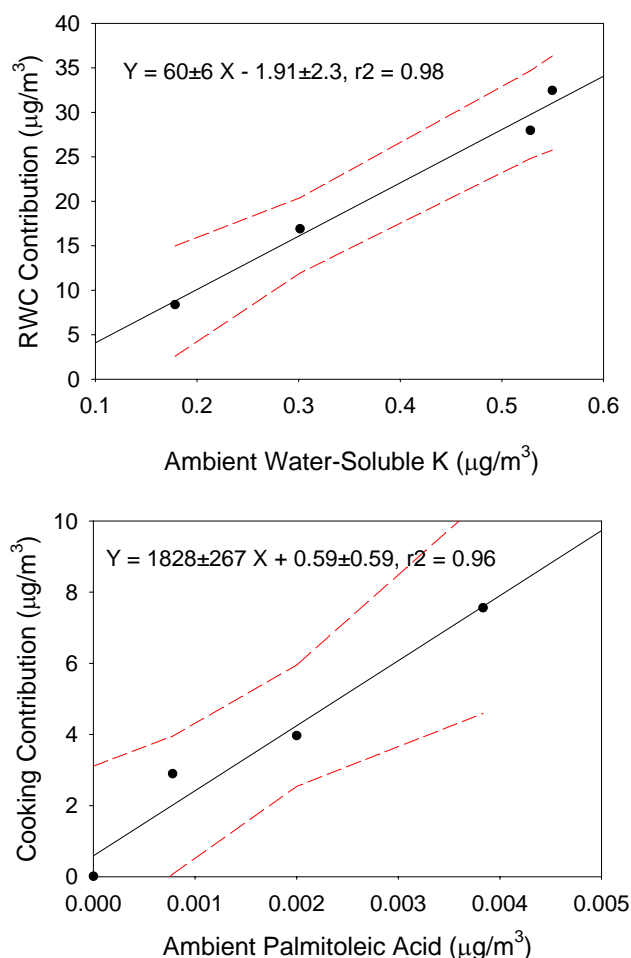


**Fig. 1.** Average diurnal variation of source contributions (percent of estimated PM<sub>2.5</sub>) for mobile (MOBILE = GAS + DIES), residential wood combustion (RWC = BURN-H + BURN-S), cooking (COOK), and secondary ammonium nitrate (AMNIT) during the CRPAQS winter intensive study at the Fresno Supersite in California. The values represent averages from the four sample periods, 00:00–05:00, 05:00–10:00, 10:00–16:00, and 16:00–24:00 PST.

than twice GAS ( $2.2 \mu\text{g}/\text{m}^3$ ). The combined vehicle exhaust contribution was 9% of measured PM<sub>2.5</sub>. BURN-H was 16–17% in all cases, averaging  $11.5 \mu\text{g}/\text{m}^3$ . BURN-S ranged from 12–15% although its uncertainty was large, especially in Cases B and C. BURN-H and BURN-S combined ranged from  $20 \mu\text{g}/\text{m}^3$  for Case B (29%) to  $22 \mu\text{g}/\text{m}^3$  for Case A (31%). COOK was the most variable, ranging from

$3.6 \mu\text{g}/\text{m}^3$  (5% of PM<sub>2.5</sub>) for Case A to  $13.9 \mu\text{g}/\text{m}^3$  (19% of PM<sub>2.5</sub>) for Case C. AMSUL ranged from  $1.2$ – $1.5 \mu\text{g}/\text{m}^3$  (2% of PM<sub>2.5</sub>), while AMNIT ( $22$ – $24 \mu\text{g}/\text{m}^3$ ), accounted for 31–33% of PM<sub>2.5</sub>. The MARINE contribution was not significant in any of the cases. Overall, PM<sub>2.5</sub> mass was underestimated by less than 10%. The CMB performance measures were better for average samples (Cases B and C) than for individual samples (Case A).

Average diurnal variations of source contributions are presented in Fig. 1. Average source contributions derived from CMB analysis, including organics, from mobile (MOBILE = GAS + DEISEL), residential wood combustion (RWC = BURN-H + BURN-S), cooking (COOK), and secondary ammonium nitrate (AMNIT) for the 00:00–05:00, 05:00–10:00, 10:00–16:00, and 16:00–24:00 PST periods were calculated as a percentage of total estimated PM<sub>2.5</sub> mass. AMNIT increased in the afternoon period (10:00–16:00 PST) as transported pollutants were mixed to the surface (Watson and Chow, 2002; Chow et al., 2006a). Cooking and burning contributions displayed similar diurnal variations, with the highest relative contributions in the evening (16:00–24:00 PST) and early morning hours (00:00–05:00 PST). The mobile contribution varied least during the day although the percent contributions were highest in the evening and mid-morning (05:00–10:00) periods. Watson et al. (2002b, 2006b) drew similar conclusions about diurnal variations of source contributions in Fresno from continuous measurements of particle size distributions and NO<sub>x</sub>, CO, and black carbon concentrations.



**Fig. 2.** Comparison of average residential wood combustion (RWC) and cooking contributions and average ambient water-soluble potassium ( $K^+$ ) and palmitoleic acid concentrations during four CRPAQS winter intensive periods at the Fresno Supersite in California. The values represent averages from the four sample periods during the winter intensive study (00:00–05:00, 05:00–10:00, 10:00–16:00, and 16:00–24:00 PST). Included in the figure are the regression parameters and the 95% confidence interval of the expected values of the dependent variable.

While deviations between the measured source profiles and the composition of actual emissions near the Fresno Supersite are probably the largest source of uncertainty, it is difficult to assess the magnitude of these errors. Applying the source profiles to simulated data defines expected estimation error under ideal conditions where such errors are random. CMB analysis of ambient concentrations averaged on various time scales provides bounds on source contribution estimates under real-world conditions. Reported cholesterol and palmitoleic acid concentrations were larger than their measurement uncertainties for only 12 and 25%, respectively, of the Fresno samples. The inability to detect cooking markers probably contributed to large uncertainties for the estimated

**Table 7.** Fresno source contributions (%) from CMB during IMS95 (Schauer and Cass, 2000) and CRPAQS winter intensive study. Also shown are contributions from the California emission inventory (CARB, 2004).

Source	IMS95 <sup>a</sup>	CRPAQS <sup>b</sup>	SJV Emission Inventory <sup>c</sup>
Paved road dust	0	0	22
Vehicle exhaust (gasoline)	3	7	–
Vehicle exhaust (diesel)	10	6	–
Vehicle exhaust (combined)	13	13	8
Wood burning	41	30	11
Cooking	8	12	2
Secondary ammonium sulfate	4	2	–
Secondary ammonium nitrate	30	32	–
Marine	–	0	–

<sup>a</sup> Percent of estimated  $PM_{2.5}$  mass.

<sup>b</sup> Percent of measured  $PM_{2.5}$  mass.

<sup>c</sup> Renormalized to include secondary ammonium sulfate and ammonium nitrate.

cooking contribution, i.e., from 5 to 19% of  $PM_{2.5}$ . On the other hand, the total RWC contribution was stable.

Figure 2 shows the relationships between measured  $K^+$  concentrations and RWC contributions as well as between palmitoleic acid concentrations and cooking contributions. The data were averaged because most of the palmitoleic concentrations in the individual samples were reported as zero. There were 13, 13, 12, and 13 samples included in the averages for the 00:00–05:00, 05:00–10:00, 10:00–16:00, and 16:00–24:00 PST periods, respectively. There are clear relationships between the wood smoke and cooking markers ( $K^+$  and palmitoleic acid, respectively) and the corresponding estimated source contributions. These relationships are insufficient to guarantee that the source contribution estimates are unbiased unless the compositions of the marker species in the source profiles are realistic.

Table 7 compares the average source contributions (%) from Cases A–C in Table 6 with the 1995 Fresno source apportionments reported by Schauer and Cass (2000). In general, the fractions contributed by each source type are similar, although this study estimates slightly higher gasoline-than diesel-exhaust contributions. Schauer and Cass (2000) estimated 37% higher wood burning and this study estimates 50% higher cooking contributions. These differences result from a combination of the different measurement and modeling methods, as well as possible differences in the actual source contributions. In both cases, wood burning dominates the OC contributions.

Also shown in Table 7 are source contributions taken from the California emission inventory (California Air Resources Board, 2004), described above. Because the inventory represents primary  $PM_{2.5}$  emissions, these values were renormalized to include the secondary  $(NH_4)_2SO_4$  and  $NH_4NO_3$  contributions. The biggest difference between the inventory

and these results is the high fugitive dust fraction (22%) in the inventory. The inventory represents all of California for the entire year, and rural agricultural areas may experience higher fugitive dust impacts during drier, non-winter periods (e.g., Chow et al., 2006a). While the CMB (13%) and inventory-based (8%) vehicle contributions were similar, the wood burning and cooking contributions in the inventory (11 and 2%, respectively) were much lower than those estimated by CMB (36 and 10%, respectively). Again, these differences may be related in part to real geographical and seasonal variability in the source impacts.

#### 4 Conclusions

Including organic compounds in the CMB improved the distinction between gasoline and diesel vehicle emissions and allowed a more precise estimate of the cooking source contribution. However, organics were not required to precisely estimate the RWC contribution and did not increase the precision of the softwood burning contribution even though there were significant differences in the hardwood and softwood compositions of RWC markers such as levoglucosan, 4-allyl-guaiacol, and syringaldehyde. The most important RWC marker in the Fresno CMB analysis was water-soluble  $K^+$ , but this was not sufficient to distinguish between hardwood and softwood combustion.

RWC was the largest contributor to measured  $PM_{2.5}$  (29–31%). Hardwood and softwood combustion accounted for 16–17% and 12–15% of  $PM_{2.5}$ , respectively, although the uncertainty of the softwood contribution was large. Secondary  $NH_4NO_3$  represented 31–33% of  $PM_{2.5}$ . Motor vehicle exhaust contributed only 9–15% of  $PM_{2.5}$ . The gasoline-vehicle contribution (3–10%) was comparable to the diesel-vehicle contribution (5–6%). The cooking contribution did not depend on cholesterol, which was not detected in most samples, and was uncertain, ranging from 5–19% of  $PM_{2.5}$ . The most important markers for cooking were OC (specifically OC3, the carbon fraction evolved at 450°C in an inert atmosphere) and palmitoleic acid. However, cholesterol and palmitoleic acid are not unique to meat cooking and more research is needed to identify other markers in the cooking source profiles. Improved sampling and analytic approaches are also needed to accurately measure these species on the short time scales (5–8 h). Despite this variability, this analysis suggests that cooking was an important  $PM_{2.5}$  contributor at Fresno. The current Fresno source contribution estimates are consistent with 1995 receptor modeling using organic markers (Schauer and Cass, 2000).

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