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

J. C. Chow[1], J. G. Watson[1], D. H. Lowenthal[1], L.-W. A. Chen[1], B. Zielinska[1], L. R. Rinehart[2], and K. L. Magliano[3]

[1]Desert Research Institute, Reno, NV, USA
[2]Colorado State University, Fort Collins, CO, USA
[3]California Air Resources Board, Sacramento, CA, USA

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Correspondence to: J. C. Chow (judy.chow@dri.edu)

Abstract

Sources of $PM_{2.5}$ at the Fresno Supersite during high $PM_{2.5}$ 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 combustion 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 most significant source, contributing 29–31% of the measured $PM_{2.5}$. 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 $PM_{2.5}$. Fresno source apportionment results were consistent with those estimated in previous studies.

1 Introduction

According to the California emission inventory, area-wide sources account for about 76% of the statewide emissions of directly emitted $PM_{2.5}$ (582 out of 765 t/day) (California Air Resources Board, 2004). Approximately half of the remaining directly emitted $PM_{2.5}$ (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 $PM_{2.5}$ and PM_{10} (Chow et al., 1992; Magliano et al., 1999; Schauer and Cass, 2000). Primary $PM_{2.5}$ and PM_{10} 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 (Watson et al., 1998a; Zheng et al., 2002, 2006; Manchester-Neesvig et al., 2003; Hannigan et al., 2005; Labban et al., 2006[1]). Applying the CMB to three multiday episodes during winter 1995/1996 detected contributions from diesel and gasoline exhaust, hardwood and softwood combustion, cooking, and natural gas combustion at four SJV locations (Schauer et al., 2000), including the Fresno Supersite (Watson et al., 2000) where $PM_{2.5}$ carbon levels are high during 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 $PM_{2.5}$ episodes in winter 2000/2001 as part of the California Regional Air Quality Study (CRPAQS; Watson and Chow, 2002; Chow et al., 2005c; Rine-

[1] Labban, R., Veranth, J. M., Watson, J. G., and Chow, J. C.: Feasibility of soil dust source apportionment by pyrolysis- gas chromatography/mass spectrometry method, J. Air Waste Manage. Assoc., in review, 2006.

hart 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 with and without the inclusion of organic 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., 2005c) and summarized here. Samples were collected at the Fresno Supersite with Desert Research Institute (DRI; Reno, NV) sequential filter samplers (SFS) preceded by $PM_{2.5}$ size-selective inlets (Sensidyne Bendix 240 cyclones) and aluminum oxide tubular nitric acid (HNO_3) denuders (Chow et al., 2005c). Teflon-membrane (Pall Sciences, R2PJ047, Ann Arbor, MI) filters were analyzed for $PM_{2.5}$ 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 (Cl^-), nitrate (NO_3^-), and sulfate ($SO_4^=$) by ion chromatography (Chow and Watson, 1999), ammonium (NH_4^+) by automated colorimetry, and water-soluble sodium (Na^+) and potassium (K^+) by atomic absorption spectrometry. OC and EC were analyzed by the IMPROVE thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001, 2004a, 2005b). 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 (O_2) atmosphere. EC is the sum of EC1–EC3 minus OP.

$PM_{2.5}$ 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

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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. For SVOC analysis (Zielinska and Fujita, 2003; Rinehart, 2005, 2006[2]), 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. 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.) column connected to a Varian Saturn 2000 Ion Trap. Polar compounds (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 a chemical ionization GC/MS technique 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 and Fujita, 2003; Rinehart, 2005, 2006). Organic compounds included PAHs, polar compounds, hopanes, steranes, and

[2]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, 2006.

long-chain alkanes that have been found to be useful for distinguishing among contributing sources.

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 $PM_{2.5}$ conditions. 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 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:

$$C_{it} = \Sigma F_{ij} S_{jt} + E_{it} \tag{1}$$

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., 2002; Watson and Chow, 2004), which have also been applied to $PM_{2.5}$ data in central California. (Chen et al., 2006[3]). The effective variance weighted least squares minimization solution (Watson et al., 1984) is most commonly used for obtaining source

[3] Chen, L.-W. A., Chow, J. C., Watson, J. G., Lowenthal, D. H., and Chang, M. C.: Quantifying $PM_{2.5}$ source contributions for the San Joaquin Valley with multivariate receptor models, Environ. Sci. Technol., in review, 2006.

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 (R2) and chi-square (CHI) and the percentage of measured mass (PMASS) 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 post-2000 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 (Pechan, 2006).

Composite diesel (DIES) and gasoline (GAS) exhaust profiles were derived from many dynamometer tests on a wide range of vehicles (Fujita et al., 2005). 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 over-loaded. 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 (Zielinska et al., 2004; Fujita et al., 2006[2]). 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). Emissions inventories suggested that there was more hardwood than softwood combustion in Fresno during 1995 (Magliano et al., 1999). Water soluble potassium (K^+) and polar organic compounds including levoglucosan, syringols, and guaiacols are markers for wood burning emissions (Rinehart et al., 2003, 2006).

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 levoglocosan 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 et al., 2003). 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 (AGRI), dairy and feed lot (CATTLE), lake deposits (SALT), and construction (CONST). OC and EC were measured in these samples but their specific organic compounds were not measured and they are set to zero in the profile.

Examination of the ambient data for sodium (Na) and chlorine (Cl) (sea salt markers) showed that Cl was depleted with respect to Na in pure sea salt, even at a coastal site like Bodega Bay where the average ratio of Cl/Na (for 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 HNO_3, where 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 NO_3^- on a molar basis (Chow et al., 1996). Secondary NO_3^- and $SO_4^=$ were represented by pure ammonium nitrate (AMNIT; NH_4NO_3) and ammonium sulfate [AMSUL; $(NH_4)_2SO_4$] 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 μg/m^3, respectively, were based on previous SJV source apportionments studies. "True" S_{jt} were created by randomly perturbing the average values (above) with a coefficient of variation (CV) of 50%, assuming a log-normal 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.

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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 determined well 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_{jt} 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_{jt}. Results are summarized in Table 2.

Case 1 represents fixed uncertainty without organics. The S_{MARINE} AAE was large (107%) because the true average S_{MARINE} was only 0.1 $\mu g/m^3$. The AAEs for S_{DIES} and S_{BURN-H} were less than 20% while the AAEs for S_{GAS}, S_{BURN-S}, and S_{COOK} were 84, 34 and 45%, respectively. When organics were included (Case 2), the AAEs were much lower for S_{GAS}, S_{DIES}, and S_{COOK}, but they did not change as much for S_{BURN-H} and S_{BURN-S}. Including organic compounds reduced collinearity (similarity) among profiles for the vehicle exhaust and cooking sources. Except for S_{BURN-H}, S_{AMSUL} and S_{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_{GAS}, S_{DIES}, S_{BURN-H}, and S_{COOK} AAEs to 52, 21, 13, and 20%, respectively. While the S_{BURN-H} AAE improved somewhat (from 17% to 13%) when organics were included, the S_{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, 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_{BURN-H} AAE was only 8%.

These tests with simulated data demonstrate the feasibility of identifying and quantifying gasoline- and diesel-exhaust contributions with reasonable precision using the organic markers. This is also the case for cooking contributions. Organics were not necessary to estimate RWC contribution and it is not feasible to distinguish hardwood and softwood contributions from the source profiles used in this study, even when organics are 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 is 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 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. 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 (pyrolized 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 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 the S_{BURN-H} and S_{BURN-S} ($22\pm7\,\mu g/m^3$). Similarly, while GAS and DIES contributions were resolved, the uncertainty of S_{GAS} ($1.9\pm1.3\,\mu g/m^3$) was large (68%). The cooking contribution was large ($20\pm5\,\mu g/m^3$) as was the secondary NH_4NO_3 contribution ($18\pm2\,\mu g/m^3$). Zero values for S_{PVRD} and S_{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 (PMASS=92) and the included sources explained the ambient chemical concentrations well (R2=0.96, CHI=0.6).

The distinguishing chemical markers for the sources in Case 1 were examined with the MPIN (modified pseudo-inverse normalized) matrix, a feature of the CMB8 model, shown in Table 5. The MPIN identifies the influence of the fitting species on source contribution estimates. A value of one indicates the highest influence. 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 K^+ and syringaldehyde. Levoglucosan was also a significant marker with a value of 0.5. The MPIN shows that the most influential marker for softwood combustion (BURN-S) was Fe. This is not reasonable and probably results from the fact that the geological profile (PVRD) was dropped from the fit and that the BURN-S profile was somewhat collinear with BURN-H or other combustion profiles. While EC (0.8) was also an influential significant marker for BURN-S, none of the organic species were.

Case 2 (Table 4) was the same as Case 1 except that organic species were excluded from the fit. Except for a S_{GAS} of zero, the solution was very similar to Case 1 (with organics) although S_{COOK} was 3 $\mu g/m^3$ 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_{GAS} and S_{DIES} slightly and increased S_{BURN-H} and S_{COOK} by 2 and 1 $\mu g/m^3$, respectively. In Case 4 (without organics), all of the vehicle exhaust contribution was assigned to DIES, as in Case 2, and S_{COOK} increased from 23±6 (Case 2) to 25±6 $\mu g/m^3$. Removing BURN-S in Cases 3 and 4 reduced PMASS 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±3 and 36±3 $\mu g/m^3$, with and without organics, respectively, and an overestimation of measured mass by 10 and 9%, respectively. Both S_{GAS} and S_{DIES} were reduced by about a factor of 2 and S_{COOK} increased by 3 $\mu g/m^3$ compared with Case 1. R2 decreased and CHI 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_{GAS} and

S_{DIES} increased somewhat while the total burning contribution increased from 22±7 to 29±7 μg/m^3. The solution changed dramatically without organics (Case 8). All of S_{BURN-S} and S_{COOK} were assigned to S_{GAS} (30±7 μg/m^3). Both DIES and BURN-S were eliminated from fit. Note that while mass was underestimated by 15%, this model fit the non-organic concentrations well (R2=0.97, CHI=0.4). However, the previous results suggest that this solution was not realistic and that cooking should be included in the model.

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 K^+ and not organics. The cooking contribution was most influenced by OC and OC3, probably because cholesterol was lower than LQLs in most samples. However, when the 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.

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

Table 6 shows that source contribution estimates were calculated 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 results of the CMB 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 $PM_{2.5}$. For Case C (average sample), DIES (4.7 μg/m^3) was more than twice GAS (2.2 μg/m^3). The combined vehicle exhaust contribution was 9% of measured $PM_{2.5}$. BURN-H was 16–17% in all cases, averaging 11.5 μg/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 μg/m^3 for Case B (29%) to 22 μg/m^3 for Case A (31%). COOK was the most variable, ranging from 3.6 μg/m^3 (5% of $PM_{2.5}$) for Case A to 13.9 μg/m^3 (19% of $PM_{2.5}$) for Case 3. AMSUL ranged from 1.2–1.5 μg/m^3 (2% of $PM_{2.5}$), while AMNIT (22–24 μg/m^3), accounted for 31–33% of $PM_{2.5}$. The MARINE contribution was not significant in any of the cases. Overall, $PM_{2.5}$ 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).

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

Figure 1 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 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 emissions 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 (11%) 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 the CMB (29 and 12%, 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^+.

RWC was the largest contributor to measured $PM_{2.5}$ (29–31%). Harwood 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 $(NH_4)_2SO_4$ 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 and was variable, 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 short time scales (5–8 h). Despite this variability, 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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6, 10341–10372, 2006

References

Ashbaugh, L. L., Carvacho, O. F., Brown, M. S., Chow, J. C., Watson, J. G., and Magliano, K. L.: Soil sample collection and analysis for the Fugitive Dust Characterization Study, Atmos. Environ., 37, 1163–1173, 2003.

California Air Resources Board: Climate Change Emissions Inventory, Draft Report, prepared for California Environmental Protection Agency Air Resources Board, Sacramento, CA, 2004.

Chow, J. C.: Critical review: Measurement methods to determine compliance with ambient air quality standards for suspended particles, J. Air Waste Manage. Assoc., 45, 320–382, 1995.

Chow, J. C. and Watson, J. G.: Ion chromatography in elemental analysis of airborne particles, in: Elemental Analysis of Airborne Particles, edited by: Landsberger, S. and Creatchman, M., Gordon and Breach Science, Amsterdam, 1, 97–137, 1999.

Chow, J. C. and Watson, J. G.: $PM_{2.5}$ carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites, J. Geophys. Res., 107, ICC 6-1–ICC 6-9, 2002.

Chow, J. C., Watson, J. G., Lowenthal, D. H., Solomon, P. A., Magliano, K. L., Ziman, S. D., and Richards, L. W.. PM_{10} source apportionment in California's San Joaquin Valley, Atmos. Environ., 26A, 3335–3354, 1992.

Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies, Atmos. Environ., 27A, 1185–1201, 1993.

Chow, J. C., Watson, J. G., Lowenthal, D. H., and Countess, R. J.: Sources and chemistry of PM_{10} aerosol in Santa Barbara County, CA, Atmos. Environ., 30, 1489–1499, 1996.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T. M.: Comparison of IMPROVE and NIOSH carbon measurements, Aerosol Sci. Technol., 34, 23–34, 2001.

Chow, J. C., Watson, J. G., Ashbaugh, L. L., and Magliano, K. L.: Similarities and differences in PM_{10} chemical source profiles for geological dust from the San Joaquin Valley, California, Atmos. Environ., 37, 1317–1340, 2003.

Chow, J. C., Watson, J. G., Chen, L.-W. A., Arnott, W. P., Moosmüller, H., and Fung, K. K.: Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414–4422, 2004a.

Chow, J. C., Watson, J. G., Kuhns, H. D., Etyemezian, V., Lowenthal, D. H., Crow, D. J., Kohl, S. D., Engelbrecht, J. P., and Green, M. C.: Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study, Chemosphere, 54, 185–208, 2004b.

Chow, J. C., Chen, L.-W. A., Lowenthal, D. H., Doraiswamy, P., Park, K., Kohl, S., Trimble, D. L., and Watson, J. G.: California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) – Initial data analysis of field program measurements, California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV, 2005a.

Chow, J. C., Watson, J. G., Chen, L. W. A., Paredes-Miranda, G., Chang, M.-C. O., Trimble, D., Fung, K. K., Zhang, H., and Yu, J. Z.: Refining temperature measures in thermal/optical carbon analysis, Atmos. Chem. Phys., 5, 2961–2972, 2005b.

Chow, J. C., Watson, J. G., Lowenthal, D. H., and Magliano, K.: Loss of $PM_{2.5}$ nitrate from filter samples in central California, J. Air Waste Manage. Assoc., 55, 1158–1168, 2005c.

Chow, J. C., Chen, L.-W. A., Watson, J. G., Lowenthal, D. H., Magliano, K., Turkiewicz, K., and Lehrman, D.: $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS), J. Geophys. Res., 111, D10S04, doi:10.1029/2005JD006457, 2006a.

Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L. W. A., and Magliano, K. L.: Particulate carbon measurements in California's San Joaquin Valley, Chemosphere, 62, 337–348, 2006b.

Fitz, D. R., Chow, J. C., and Zielinska, B.: Development of a gas and particulate matter organic speciation profile database, prepared for Draft Final Report June 2003, prepared for San Joaquin Valleywide Air Pollution Study Agency, California Regional $PM_{10}/PM_{2.5}$ Air Quality Study, by The University of California CE-CERT, Riverside, CA, 2003.

Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Air quality model evaluation data for organics 6. C3–C24 organic acids, Environ. Sci. Technol., 37, 446–453, 2003.

Fujita, E. M., Campbell, D., Zielinska, B., and Chow, J. C.: Kansas City PM Characterization Study, Round 1 Testing Report – Addendum A, Chemical Speciation, prepared for U.S. Environomental Protection Agency, Desert Research Institute, Reno, NV, 2005.

Hannigan, M. P., Busby Jr., W. F., and Cass, G. R.: Source contributions to the mutagenicity of urban particulate air pollution, J. Air Waste Manage. Assoc., 55, 399–410, 2005.

Hidy, G. M. and Friedlander, S. K.. The nature of the Los Angeles aerosol, in: Proceedings of the Second International Clean Air Congress, edited by: Englund, H. M. and Beery, W. T.,

Academic Press, New York, pp. 391–404, 1971.
Javitz, H. S., Watson, J. G., and Robinson, N. F.: Performance of the chemical mass balance model with simulated local-scale aerosols, Atmos. Environ., 22, 2309–2322, 1988.
Lowenthal, D. H., Chow, J. C., Watson, J. G., Neuroth, G. R., Robbins, R. B., Shafritz, B. P., and Countess, R. J.: The effects of collinearity on the ability to determine aerosol contributions from diesel- and gasoline-powered vehicles using the chemical mass balance model, Atmos. Environ., 26A, 2341–2351, 1992.
Magliano, K. L., Hughes, V. M., Chinkin, L. R., Coe, D. L., Haste, T. L., Kumar, N., and Lurmann, F. W.: Spatial and temporal variations in PM_{10} and $PM_{2.5}$ source contributions and comparison to emissions during the 1995 Integrated Monitoring Study, Atmos. Environ., 33, 4757–4773, 1999.
Mamane, Y. and Gottlieb, J.: Nitrate formation on sea-salt and mineral particles – A single particle approach, Atmos. Environ., 26A, 1763–1769, 1992.
Manchester-Neesvig, J. B., Schauer, J. J., and Cass, G. R.: The distribution of particle-phase organic compounds in the atmosphere and their use for source apportionment during the Southern California Children's Health Study, J. Air Waste Manage. Assoc., 53, 1065–1079, 2003.
McDonald, J. D., Zielinska, B., Fujita, E. M., Sagebiel, J. C., Chow, J. C., and Watson, J. G.: Fine particle and gaseous emission rates from residential wood combustion, Environ. Sci. Technol., 34, 2080–2091, 2000.
McDonald, J. D., Zielinska, B., Fujita, E. M., Sagebiel, J. C., Chow, J. C., and Watson, J. G.: Emissions from charbroiling and grilling of chicken and beef, J. Air Waste Manage. Assoc., 53, 185–194, 2003.
Park, K., Chow, J. C., Watson, J. G., Trimble, D. L., Doraiswamy, P., Arnott, W. P., Stroud, K. R., Bowers, K., Bode, R., Petzold, A., and Hansen, A. D. A.: Comparison of continuous and filter-based carbon measurements at the Fresno Supersite, J. Air Waste Manage. Assoc., 56, 474–491, 2006.
Pechan, E. H. and Associates: SPECIATE Project Web Site, prepared for E.H Pechan and Associates, Springfield, VA, 2006.
Rinehart, L. R.: The origin of polar organic compounds in ambient fine particulate matter, Ph.D. University of Nevada, Reno, 2005.
Rinehart, L. R., Cunningham, A., Chow, J. C., and Zielinska, B.: Characterization of $PM_{2.5}$ associated organic compounds of emission sources collected during the California Regional

$PM_{10}/PM_{2.5}$ Air Quality Study, 23 June 2003, San Diego, CA. 96th Annual Meeting of the Air & Waste Management Association, 2003.
Rinehart, L. R., Fujita, E. M., Chow, J. C., Magliano, K., and Zielinska, B.: Spatial distribution of $PM_{2.5}$ associated organic compounds in central California, Atmos. Environ., 40, 290–303, 2006.
Schauer, J. J. and Cass, G. R.: Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers, Environ. Sci. Technol., 34, 1821–1832, 2000.
Wang, D. and Hopke, P. K.: The use of constrained least-squares to solve the chemical mass balance problem, Atmos. Environ., 23, 2143–2150, 1989.
Watson, J. G. and Chow, J. C.: A wintertime $PM_{2.5}$ episode at the Fresno, CA, supersite, Atmos. Environ., 36, 465–475, 2002.
Watson, J. G. and Chow, J. C.: Receptor models for air quality management, EM 10, 27–36, 2004.
Watson, J. G. and Chow, J. C.: Receptor models, in: Air Quality Modeling – Theories, Methodologies, Computational Techniques, and Available Databases and Software. Vol. II – Advanced Topics, edited by: Zannetti, P., Air and Waste Management Association and the EnviroComp Institute, Pittsburgh, PA, pp. 455–501, 2005.
Watson, J. G., Cooper, J. A., and Huntzicker, J. J.: The effective variance weighting for least squares calculations applied to the mass balance receptor model, Atmos. Environ., 18, 1347–1355, 1984.
Watson, J. G., Chow, J. C., Lowenthal, D. H., Pritchett, L. C., Frazier, C. A., Neuroth, G. R., and Robbins, R.: Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles, Atmos. Environ., 28, 2493–2505, 1994.
Watson, J. G., Robinson, N. F., Lewis, C. W., Coulter, C. T., Chow, J. C., Fujita, E. M., Lowenthal, D. H., Conner, T. L., Henry, R. C., and Willis, R. D.: Chemical mass balance receptor model version 8 (CMB) user's manual, prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV, 1997.
Watson, J. G., DuBois, D. W., DeMandel, R., Kaduwela, A. P., Magliano, K. L., McDade, C., Mueller, P. K., Ranzieri, A. J., Roth, P. M., and Tanrikulu, S.: Field program plan for the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS), prepared for California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV, 1998a.
Watson, J. G., Robinson, N. F., Lewis, C. W., Coulter, C. T., Chow, J. C., Fujita, E. M., Conner, T.

L., and Pace, T. G.: CMB8 applications and validation protocol for $PM_{2.5}$ and VOCs, prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV, 1998b.

Watson, J. G., Chow, J. C., and Frazier, C. A.: X-ray fluorescence analysis of ambient air samples, in: Elemental Analysis of Airborne Particles, edited by: Landsberger, S. and Creatchman, M., vol. 1. Gordon and Breach Science, Amsterdam, pp. 67–96, 1999.

Watson, J. G., Chow, J. C., Bowen, J. L., Lowenthal, D. H., Hering, S., Ouchida, P., and Oslund, W.: Air quality measurements from the Fresno Supersite, J. Air Waste Manage. Assoc., 50, 1321–1334, 2000.

Watson, J. G., Zhu, T., Chow, J. C., Engelbrecht, J. P., Fujita, E. M., and Wilson, W. E.: Receptor modeling application framework for particle source apportionment, Chemosphere, 49, 1093–1136, 2002.

Watson, J. G., Chow, J. C., and Chen, L.-W. A.: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, Aerosol and Air Quality Research, 5, 65–102, 2005.

Watson, J. G., Chow, J. C., Lowenthal, D. H., Kreisberg, N., Hering, S. V., and Stolzenburg, M. R.: Variations of nanoparticle concentrations at the Fresno supersite, Sci. Total Environ., 358, 178–187, 2006a.

Watson, J. G., Chow, J. C., Park, K., and Lowenthal, D. H.: Nanoparticle and ultrafine particle events at the Fresno Supersite, J. Air Waste Manage. Assoc., 56, 417–430, 2006b.

Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E. S.: Source apportionment of $PM_{2.5}$ in the southeastern United States using solvent-extractable organic compounds as tracers, Environ. Sci. Technol., 36, 2361–2371, 2002.

Zheng, M., Ke, L., Edgerton, E. S., Schauer, J. J., Dong, M. Y., and Russell, A. G.: Spatial distribution of carbonaceous aerosol in the southeastern United States using molecular markers and carbon isotope data, J. Geophys. Res., 111, D10S06, doi:10.1029/2005JD006777, 2006.

Zielinska, B. and Fujita, E. M.: Characterization of ambient volatile organic compounds at the western boundary of the SCOS97-NARSTO modeling domain, Atmos. Environ., 37, S171–S180, 2003.

Zielinska, B., McDonald, J. D., Hayes, T., Chow, J. C., Fujita, E. M., and Watson, J. G.: Northern Front Range Air Quality Study, Volume B: Source measurements, prepared for Colorado State University, Fort Collins, CO, by Desert Research Institute, Reno, NV, 1998.

Zielinska, B., Rinehart, L. R., and Goliff, W. S.: California Regional $PM_{10}/PM_{2.5}$ Air Quality Study - Organic compound measurements, prepared for California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV, 2003.

Zielinska, B., Sagebiel, J., Arnott, W. P., Rogers, C. F., Kelly, K. E., Wagner, D. A., Lighty, J. S., Sarofim, A. F., and Palmer, G.: Phase and size distribution of polycyclic aromatic hydrocarbons in diesel and gasoline vehicle emissions, Environ. Sci. Technol., 38, 2557–2567, 2004.

Table 1. Source profiles (percent of emitted $PM_{2.5}$) used in CMB receptor modeling for samples acquired during the Fresno CRPAQS winter intensive study.

		Profile and code					
Chemical species	Species Abbreviation	Paved road PVRD	Gasoline vehicle GAS	Diesel vehicle DIES	Hardwood combustion BURN-H	Softwood combustion BURN-S	Smoked chicken SMCHICK
Chloride	Cl^-	0.1027±0.1839	0.4769±0.4318	0.2371±0.3495	1.4719±1.8146	0.1061±0.0323	1.2589±0.7814
Nitrate	NO_3^-	0.0435±0.1817	1.6545±1.2115	0.1351±0.3835	0.6803±0.0567	0.1534±0.0293	0.4196±0.1199
Sulfate	$SO_4^=$	0.2787±0.1881	6.7749±6.9651	3.5862±2.9797	1.4179±0.6204	0.5794±0.0597	0.4235±0.2699
Ammonium	NH_4^+	0.3233±0.2305	3.0173±3.1377	1.1804±1.1875	0.4565±0.3963	0.2122±0.0312	0.1407±0.1188
Soluble sodium	Na^+	0.0789±0.0351	0.0000±0.0010	0.0000±0.0010	0.3045±0.0252	0.1544±0.0117	0.2170±0.0291
Soluble Potassium	K^+	0.1509±0.0899	0.0699±0.0682	0.1552±0.0529	2.9389±0.3286	0.8124±0.0594	0.3454±0.0354
Organic carbon	OC	6.8950±3.7295	58.7720±21.5960	61.9970±24.9550	58.3350±4.6528	34.8740±2.7827	62.6800±9.5480
OC fraction 1	OC1	0.2746±0.2973	24.3710±18.1950	20.8160±7.6162	18.2440±5.3407	4.3149±0.3811	10.3330±4.9033
OC fraction 2	OC2	0.8838±0.6051	12.4740±4.9880	12.7670±6.2938	10.2400±1.2550	3.0070±0.3695	10.4480±2.4690
OC fraction 3	OC3	2.6704±1.3216	13.3020±6.0825	18.8010±7.2890	21.2100±3.4685	7.5739±0.6666	26.7180±12.7580
OC fraction 4	OC4	1.9571±0.8353	7.3284±2.8507	9.5810±5.4608	8.6300±1.2041	4.4939±0.6265	8.7359±1.2399
Pyrolized OC	OP	1.1091±0.6952	1.2972±2.5596	0.0318±0.1382	0.0117±0.0399	15.4830±5.4853	5.7697±2.9909
Elemental carbon	EC	0.9946±0.9520	28.5650±13.8100	78.3140±16.5500	5.1909±0.7901	27.2360±2.2356	11.8760±1.4911
EC fraction 1	EC1	1.0781±0.7091	13.8680±6.1435	26.0500±5.9936	4.8393±0.9385	41.2150±3.0776	13.0800±3.1538
EC fraction 2	EC2	1.0257±0.9381	15.5220±12.9970	51.9030±12.6890	0.3017±0.0576	1.3362±0.1858	3.9735±2.6549
EC fraction 3	EC3	0.0000±0.0823	0.4739±0.3534	0.3886±0.3840	0.0606±0.0342	0.1676±0.0525	0.5915±0.5020
Total carbon	TC	7.8897±4.6815	87.3370±25.6330	140.3100±29.9440	63.5260±5.0335	62.1100±4.9180	74.4750±10.7590
Aluminum	Al	10.0008±3.0147	0.1073±0.0736	0.1717±0.1715	0.0944±0.0112	0.2013±0.0176	0.0508±0.0102
Silicon	Si	28.1663±8.9603	4.7878±4.1119	1.2029±0.3647	0.2912±0.0230	1.0151±0.0724	0.5602±0.4483
Phosphorus	P	0.3877±0.3543	0.3479±0.5129	0.1782±0.0555	0.0000±0.0073	0.0000±0.0057	0.0000±0.0061
Sulfur	S	0.3516±0.2100	2.6670±2.4785	1.4845±1.1969	0.4240±0.0331	0.2352±0.0169	0.2427±0.0239
Chlorine	Cl	0.1006±0.1422	0.2491±0.2978	0.0768±0.0424	1.3544±1.5612	0.1160±0.0090	1.6225±1.1894
Potassium	K	2.8206±0.5488	0.0579±0.0474	0.1096±0.0910	2.9511±0.6782	1.0675±0.0758	0.5008±0.2895
Calcium	Ca	3.4850±1.1771	0.7865±1.4028	0.7045±0.2820	0.1873±0.0225	0.5216±0.0376	0.1621±0.0436
Titantium	Ti	0.4553±0.1348	0.0030±0.0569	0.0153±0.0914	0.0129±0.0197	0.0880±0.0096	0.0108±0.0287
Manganese	Mn	0.0759±0.0054	0.0042±0.0042	0.0013±0.0066	0.0067±0.0007	0.0129±0.0011	0.0550±0.0049
Iron	Fe	5.2254±1.0428	0.4226±0.3424	0.6570±0.4100	0.1402±0.0114	0.5172±0.0367	0.5990±0.5467
Copper	Cu	0.0168±0.0119	0.0519±0.0537	0.0157±0.0066	0.0067±0.0006	0.0392±0.0028	0.0617±0.0067
Zinc	Zn	0.0965±0.0467	0.4335±0.4056	0.3771±0.0872	0.1368±0.0135	0.0925±0.0066	0.0507±0.0049
Arsenic	As	0.0016±0.0027	0.0001±0.0052	0.0004±0.0077	0.0007±0.0017	0.0006±0.0016	0.0019±0.0019
Selenium	Se	0.0002±0.0010	0.0002±0.0027	0.0022±0.0041	0.0001±0.0007	0.0000±0.0007	0.0001±0.0009
Bromine	Br	0.0016±0.0012	0.0375±0.0384	0.0451±0.0711	0.0045±0.0004	0.0014±0.0003	0.0166±0.0016
Rubidium	Rb	0.0139±0.0046	0.0005±0.0022	0.0007±0.0038	0.0046±0.0005	0.0019±0.0003	0.0007±0.0011
Strontium	Sr	0.0305±0.0016	0.0009±0.0023	0.0029±0.0039	0.0025±0.0004	0.0060±0.0006	0.0011±0.0011
Lead	Pb	0.0109±0.0074	0.0257±0.0241	0.0086±0.0119	0.0039±0.0009	0.0030±0.0008	0.0082±0.0025
Retene	RETENE	0.0000±0.0000	0.0042±0.0132	0.0002±0.0009	0.0272±0.0039	0.0140±0.0012	0.0059±0.0014
Indeno[123-cd]pyrene	INCDPY	0.0000±0.0000	0.0340±0.0278	0.0000±0.0014	0.0028±0.0004	0.0033±0.0005	0.0053±0.0027
Benzo(ghi)perylene	BGHIPE	0.0000±0.0000	0.0941±0.0827	0.0000±0.0017	0.0029±0.0008	0.0028±0.0008	0.0018±0.0035
Coronene	CORONE	0.0000±0.0000	0.0836±0.0920	0.0000±0.0005	0.0011±0.0003	0.0008±0.0003	0.0001±0.0010
20S-13β(H),17α(H)-diacholestane	STER35	0.0000±0.0000	0.0068±0.0060	0.0060±0.0036	0.0016±0.0005	0.0038±0.0009	0.0000±0.0010
C_{29}20S-13β(H), 17α(H)-diasterane	STER45	0.0000±0.0000	0.0182±0.0162	0.0040±0.0036	0.0001±0.0001	0.0000±0.0001	0.0000±0.0011
C_{29}20S-13α(H), 17β(H)-diasterane	STER48	0.0000±0.0000	0.0031±0.0037	0.0000±0.0009	0.0000±0.0001	0.0000±0.0001	0.0000±0.0010
C_{28}20R-5α(H), 14α(H),17α(H)-ergostane	STER49	0.0000±0.0000	0.0431±0.0978	0.0011±0.0027	0.0000±0.0001	0.0000±0.0001	0.0000±0.0010
17α(H), 21β(H)-29-Norhopane	HOP17	0.0000±0.0000	0.0146±0.0262	0.0118±0.0075	0.0001±0.0002	0.0000±0.0001	0.0009±0.0011
17α(H), 21β(H)-29-Hopane	HOP19	0.0000±0.0000	0.0446±0.0791	0.0062±0.0046	0.0006±0.0002	0.0008±0.0003	0.0026±0.0054
22S-17α(H),21β(H)-30,31,32-Trishomohopane	HOP24	0.0000±0.0000	0.0026±0.0054	0.0000±0.0009	0.0005±0.0003	0.0005±0.0003	0.0000±0.0013
22R-17α(H),21β(H)-30,31,32-Trishomohopane	HOP26	0.0000±0.0000	0.0025±0.0052	0.0000±0.0009	0.0001±0.0002	0.0001±0.0002	0.0001±0.0028
Guaiacol	GUAI	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000	0.3721±0.0309	0.2409±0.0170	1.6752±0.4991
4-allyl-guaiacol	ALGUAI	0.0000±0.0000	0.0000±0.0027	0.0000±0.0006	0.1195±0.0085	0.0548±0.0055	0.0067±0.0067
Levoglucosan	LEVG	0.0000±0.0000	0.0000±0.0120	0.0000±0.0175	2.2778±0.5924	0.1552±0.0172	1.1505±0.4381
Syringaldehyde	SYRALD	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000	0.4631±0.0307	0.0247±0.0017	0.1871±0.0224
Palmitoleic acid	PALOL	0.0000±0.0000	0.0082±0.0117	0.0263±0.0217	0.0069±0.0005	0.0000±0.0002	0.0261±0.0234
Palmitic acid	PALAC	0.0000±0.0000	0.0000±0.0486	0.0000±0.1507	0.0562±0.0041	0.0000±0.0323	0.0000±0.1940
Oleic acid	OLAC	0.0000±0.0000	0.0000±0.0152	0.0000±0.0422	0.0652±0.0051	0.0000±0.0289	0.0000±0.1385
Stearic acid	STEAC	0.0000±0.0000	0.0000±0.0173	0.0000±0.0358	0.0174±0.0013	0.0000±0.0289	0.0000±0.1574
Cholesterol	CHOL	0.0000±0.0000	0.0000±0.0011	0.0000±0.0020	0.0000±0.0000	0.0000±0.0002	0.0003±0.0012
Phthalic acid	PHTHAC	0.0000±0.0000	0.1026±0.2018	0.1864±0.1740	0.0141±0.0010	0.0000±0.0002	0.0065±0.0012
Norfarnesane	NORFAR	0.0000±0.0000	0.0365±0.3020	0.0285±0.0236	0.0020±0.0010	0.0002±0.0002	0.0007±0.0014
Farnesane	FARNES	0.0000±0.0000	0.0344±0.5172	0.0750±0.0914	0.0011±0.0008	0.0005±0.0005	0.0000±0.0012
Norpristance	NORPRI	0.0000±0.0000	0.0422±0.3857	0.1178±0.0372	0.0006±0.0004	0.0000±0.0004	0.0025±0.0034
Pristane	PRIST	0.0000±0.0000	0.0032±0.2887	0.0119±0.0145	0.0008±0.0005	0.0010±0.0004	0.0352±0.0086
Phytane	PHYTAN	0.0000±0.0000	0.0139±0.4463	0.0974±0.0656	0.0015±0.0005	0.0004±0.0002	0.0041±0.0021

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Table 1. Continued.

		Profile and code					
Chemical species	Species Abbreviation	Paved road PVRD	Gasoline vehicle GAS	Diesel vehicle DIES	Hardwood combustion BURN-H	Softwood combustion BURN-S	Smoked chicken SMCHICK
Chloride	Cl^-	0.0449±0.0332	0.5209±0.1540	0.0257±0.0180	0.1972±0.2805	23.4880±2.6795	0.0000±0.0000
Nitrate	NO_3^-	0.0637±0.0291	0.0855±0.0911	0.0570±0.0161	0.0687±0.0560	41.6110±4.7469	0.0000±0.0000
Sulfate	$SO_4^=$	0.0950±0.0672	0.2792±0.2123	0.1450±0.0377	0.1731±0.1304	6.5468±0.7468	72.7000±7.2700
Ammonium	NH_4^+	0.0000±0.0289	0.0000±0.0915	0.0000±0.0156	0.0000±0.0561	0.0000±0.1000	27.3000±2.7300
Soluble sodium	Na^+	0.0522±0.0069	0.2508±0.0264	0.0999±0.0083	0.1343±0.0165	26.1870±2.9874	0.0000±0.0000
Soluble Potassium	K^+	0.0157±0.0038	0.2647±0.0255	0.0804±0.0073	0.1203±0.0155	0.9699±0.1106	0.0000±0.0000
Organic carbon	OC	68.8730±6.3751	69.4010±5.8564	70.0080±5.4660	69.4270±5.9109	0.0000±0.0000	0.0000±0.0000
OC fraction 1	OC1	16.4470±3.7353	8.2255±8.1671	13.2710±2.9585	12.6480±5.4591	0.0000±0.0000	0.0000±0.0000
OC fraction 2	OC2	29.4570±6.8492	20.6030±7.3992	31.6790±4.3935	27.2460±6.3499	0.0000±0.0000	0.0000±0.0000
OC fraction 3	OC3	18.3400±2.1696	32.9780±15.9640	21.4670±2.5208	24.2620±9.4146	0.0000±0.0000	0.0000±0.0000
OC fraction 4	OC4	3.6787±0.4984	6.4667±0.9140	2.8861±0.4815	4.3438±1.8807	0.0000±0.0000	0.0000±0.0000
Pyrolized OC	OP	0.7735±0.5627	0.9295±1.0107	0.6110±0.8550	0.7713±0.8305	0.0000±0.1000	0.0000±0.0000
Elemental carbon	EC	2.5938±0.6693	11.8130±3.1734	2.4850±1.8256	5.6306±5.3543	0.0000±0.0000	0.0000±0.0000
EC fraction 1	EC1	2.8265±0.5162	11.5840±4.3242	2.6974±1.0513	5.7025±5.0936	0.0000±0.0000	0.0000±0.0000
EC fraction 2	EC2	0.4571±0.0621	0.9213±0.7199	0.2344±0.0322	0.5376±0.4176	0.0000±0.0000	0.0000±0.0000
EC fraction 3	EC3	0.0843±0.0495	0.2385±0.1675	0.1640±0.0982	0.1623±0.1157	0.0000±0.1000	0.0000±0.0000
Total carbon	TC	71.4450±5.7045	81.1550±7.9406	72.4800±5.7314	75.0270±6.5433	0.0000±0.0000	0.0000±0.0000
Aluminum	Al	0.0291±0.0032	0.0082±0.0121	0.0160±0.0017	0.0178±0.0073	0.0000±0.0000	0.0000±0.0000
Silicon	Si	0.1891±0.0160	0.5620±0.6156	0.0698±0.0055	0.2736±0.3556	0.0073±0.0008	0.0000±0.0000
Phosphorus	P	0.0002±0.0026	0.0083±0.0043	0.0074±0.0009	0.0053±0.0029	0.0001±0.0000	0.0000±0.0000
Sulfur	S	0.0532±0.0059	0.1584±0.0173	0.0797±0.0061	0.0971±0.0111	2.1823±0.2489	24.2700±2.4270
Chlorine	Cl	0.0522±0.0040	0.4478±0.0326	0.0636±0.0047	0.1879±0.0192	23.4880±2.6795	0.0000±0.0000
Potassium	K	0.0386±0.0032	0.3212±0.0236	0.0990±0.0073	0.1529±0.0144	0.9699±0.1106	0.0000±0.0000
Calcium	Ca	0.1658±0.0169	0.0783±0.0336	0.0987±0.0091	0.1143±0.0223	0.9990±0.1140	0.0000±0.0000
Titantium	Ti	0.0030±0.0083	0.0049±0.0235	0.0011±0.0045	0.0030±0.0146	0.0000±0.0000	0.0000±0.0000
Manganese	Mn	0.0098±0.0009	0.0074±0.0011	0.0066±0.0005	0.0079±0.0009	0.0000±0.0000	0.0000±0.0000
Iron	Fe	0.1430±0.0128	0.1049±0.0090	0.0558±0.0041	0.1012±0.0093	0.0000±0.0000	0.0000±0.0000
Copper	Cu	0.0089±0.0008	0.0077±0.0013	0.0033±0.0004	0.0066±0.0009	0.0000±0.0000	0.0000±0.0000
Zinc	Zn	0.0134±0.0010	0.0089±0.0011	0.0051±0.0004	0.0091±0.0009	0.0000±0.0000	0.0000±0.0000
Arsenic	As	0.0002±0.0094	0.0002±0.0015	0.0001±0.0003	0.0002±0.0055	0.0000±0.0000	0.0000±0.0000
Selenium	Se	0.0000±0.0003	0.0001±0.0006	0.0000±0.0001	0.0000±0.0004	0.0000±0.0000	0.0000±0.0000
Bromine	Br	0.0006±0.0007	0.0018±0.0005	0.0010±0.0001	0.0011±0.0005	0.1625±0.0185	0.0000±0.0000
Rubidium	Rb	0.0002±0.0003	0.0005±0.0008	0.0000±0.0002	0.0002±0.0005	0.0000±0.0000	0.0000±0.0000
Strontium	Sr	0.0015±0.0003	0.0004±0.0010	0.0006±0.0002	0.0008±0.0006	0.0192±0.0022	0.0000±0.0000
Lead	Pb	0.0434±0.0044	0.0000±0.0025	0.0000±0.0005	0.0145±0.0029	0.0000±0.0000	0.0000±0.0000
Retene	RETENE	0.0012±0.0004	0.0025±0.0012	0.0006±0.0002	0.0014±0.0007	0.0000±0.0000	0.0000±0.0000
Indeno[123-cd]pyrene	INCDPY	0.0005±0.0007	0.0028±0.0022	0.0003±0.0004	0.0012±0.0014	0.0000±0.0000	0.0000±0.0000
Benzo(ghi)perylene	BGHIPE	0.0003±0.0009	0.0068±0.0034	0.0008±0.0005	0.0026±0.0021	0.0000±0.0000	0.0000±0.0000
Coronene	CORONE	0.0000±0.0003	0.0029±0.0013	0.0000±0.0002	0.0010±0.0008	0.0000±0.0000	0.0000±0.0000
20S-13β(H),17α(H)-diacholestane	STER35	0.0000±0.0003	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
C_{29}20S-13β(H), 17α(H)-diasterane	STER45	0.0000±0.0003	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
C_{29}20S-13α(H), 17β(H)-diasterane	STER48	0.0000±0.0003	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
C_{28}20R-5α(H), 14α(H),17α(H)-ergostane	STER49	0.0000±0.0003	0.0000±0.0008	0.0001±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
17α(H), 21β(H)-29-Norhopane	HOP17	0.0002±0.0003	0.0007±0.0009	0.0001±0.0002	0.0003±0.0006	0.0000±0.0000	0.0000±0.0000
17α(H), 21β(H)-29-Hopane	HOP19	0.0000±0.0011	0.0000±0.0023	0.0003±0.0008	0.0001±0.0015	0.0000±0.0000	0.0000±0.0000
22S-17α(H),21β(H)-30,31,32-Trishomohopane	HOP24	0.0000±0.0004	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
22R-17α(H),21β(H)-30,31,32-Trishomohopane	HOP26	0.0000±0.0004	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
Guaiacol	GUAI	0.0014±0.0013	0.0015±0.0026	0.0060±0.0025	0.0030±0.0026	0.0000±0.0000	0.0000±0.0000
4-allyl-guaiacol	ALGUAI	0.0000±0.0003	0.0000±0.0033	0.0000±0.0006	0.0000±0.0019	0.0000±0.0000	0.0000±0.0000
Levoglucosan	LEVG	0.0135±0.0017	0.0274±0.0036	0.0159±0.0020	0.0189±0.0026	0.0000±0.0000	0.0000±0.0000
Syringaldehyde	SYRALD	0.0016±0.0004	0.0046±0.0010	0.0015±0.0003	0.0026±0.0018	0.0000±0.0000	0.0000±0.0000
Palmitoleic acid	PALOL	0.0694±0.0499	0.1179±0.0795	0.0410±0.0243	0.0761±0.0560	0.0000±0.0000	0.0000±0.0000
Palmitic acid	PALAC	0.0593±0.1499	0.0001±0.2811	0.0508±0.1037	0.0367±0.1934	0.0000±0.0000	0.0000±0.0000
Oleic acid	OLAC	0.1813±0.1632	0.2741±0.3188	0.1965±0.1239	0.2173±0.2188	0.0000±0.0000	0.0000±0.0000
Stearic acid	STEAC	0.0000±0.0565	0.0000±0.2642	0.0027±0.0693	0.0009±0.1610	0.0000±0.0000	0.0000±0.0000
Cholesterol	CHOL	0.0220±0.0058	0.0373±0.0088	0.0283±0.0053	0.0292±0.0068	0.0000±0.0000	0.0000±0.0000
Phthalic acid	PHTHAC	0.0009±0.0003	0.0078±0.0013	0.0000±0.0002	0.0029±0.0008	0.0000±0.0000	0.0000±0.0000
Norfarnesane	NORFAR	0.0000±0.0003	0.0000±0.0008	0.0000±0.0002	0.0000±0.0005	0.0000±0.0000	0.0000±0.0000
Farnesane	FARNES	0.0000±0.0003	0.0000±0.0008	0.0003±0.0004	0.0001±0.0005	0.0000±0.0000	0.0000±0.0000
Norpristance	NORPRI	0.0059±0.0018	0.0010±0.0026	0.0112±0.0022	0.0060±0.0022	0.0000±0.0000	0.0000±0.0000
Pristane	PRIST	0.0112±0.0032	0.0135±0.0043	0.0238±0.0048	0.0162±0.0042	0.0000±0.0000	0.0000±0.0000
Phytane	PHYTAN	0.0018±0.0006	0.0001±0.0013	0.0012±0.0004	0.0010±0.0009	0.0000±0.0000	0.0000±0.0000

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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[a] PVRD	GAS	DIES	BURN-H	BURN-S	COOK	MARINE	AMSUL	AMNIT
1	N	10%	30%	26	84	19	13	34	45	107	24	18
2	Y	10%	30%	22	10	8	10	29	14	103	23	18
3	N	Actual	Actual	72	178	29	17	108	70	268	18	8
4	Y	Actual	Actual	67	52	21	13	98	20	272	16	8
5	Y	Actual	Actual	76	50	21	20	–	21	282	16	8
6	Y	Actual	Actual	58	50	19	8	–	20	210	16	7

[a] See Table 1 for Source Codes.
Case 1: Data generated with BURN-H (hard wood) and BURN-S (softwood), no organics in CMB.
Case 2: Data generated with BURN-H (hard wood) and BURN-S (softwood), organics in CMB.
Case 3: Data generated with BURN-H (hard wood) and BURN-S (softwood), no organics in CMB.
Case 4: Data generated with BURN-H (hard wood) and BURN-S (softwood), organics in CMB.
Case 5: Data generated with BURN-H (hard wood) and BURN-S (softwood), organics in CMB, no BURN-S in CMB.
Case 6: Data generated with BURN-H (hard wood) only, organics in CMB.

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Table 3. Fitting species used in CMB modeling for samples collected during the CRPAQS winter intensive study.

Traditional species	Organic species
Nitrate (NO_3^-)	Indeno[123-cd]pyrene (INCDPY)
Sulfate ($SO_4^=$)	Benzo(ghi)perylene (BGHIPE)
Ammonium (NH_4^+)	Coronene (CORONE)
Water-Soluble Sodium (Na^+)	17a(H),21ß(H)-29-Hopane (HOP17)
Water-Soluble Potassium (K^+)	Levoglucosan (LEVG)
Organic Carbon at 450 °C (OC3)	Syringaldehyde (SYRALD)
Organic Carbon at 550 °C (OC4)	Palmitoleic acid (PALOL)
Organic Carbon (OC)	Oleic acid (OLAC)
Elemental Carbon at 700 °C (EC2)	Cholesterol (CHOL)
Elemental Carbon at 800 °C (EC3)	Norfarnesane (NORFAR)
Elemental Carbon (EC)	Farnesane (FARNES)
Aluminum (Al)	Norpristane (NORPRI)
Silicon (Si)	Pristane (PRIST)
Chlorine (Cl)	Phytane (PHYTAN)
Total Potassium (K)	
Iron (Fe)	
Selenium (Se)	
Bromine (Br)	
Lead (Pb)	

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Table 4. Source contributed 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 and various source mixes.

	Source contributions ($\mu g/m^3$)											
Case	PVRD	GAS	DIES	BURN-H	BURN-S	COOK	MARINE	AMSUL	AMNIT	PMASS	R2	CHI
1[a]	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[b]	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[a]	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[b]	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[a]	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[b]	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[a]	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[b]	0	30±7	0	18±2	0	–	0.05±0.20	0	17±2	85	0.97	0.4

[a] With organics.

[b] Without organics.

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[a]	GAS	DIES	BURN-H	BURN-S	COOK	AMSUL	AMNIT
	Source code						
NO_3^-	0.00	0.00	0.01	−0.01	0.00	-0.10	1.00
$SO_4^=$	0.00	0.00	0.00	0.00	0.00	1.00	−0.18
NH_4^+	0.00	0.00	−0.01	0.01	0.00	0.10	0.92
Na^+	−0.07	−0.06	0.04	0.09	0.10	0.01	0.00
K^+	−0.04	0.00	1.00	0.00	−0.30	−0.06	0.00
OC3	−0.04	0.02	0.10	−0.20	0.52	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	1.00	0.00	0.00
EC2	0.06	1.00	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	0.80	−0.17	−0.01	0.00
Al	−0.09	−0.07	−0.20	0.43	−0.10	0.01	0.00
Si	0.55	−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	0.58	0.23	−0.24	−0.03	0.00
Fe	−0.19	−0.12	−0.59	1.00	−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	0.54	−0.14	0.00	0.06	−0.05	−0.08	−0.01
BGHIPE	0.93	−0.16	0.09	−0.16	−0.03	−0.14	−0.01
CORONE	1.00	−0.14	0.13	−0.23	−0.06	−0.15	−0.01
HOP19	0.57	−0.02	0.09	−0.15	−0.07	−0.10	−0.01
LEVGU	0.05	0.06	0.50	−0.25	−0.08	−0.04	0.00
SYRALD	0.08	0.10	0.73	−0.38	−0.11	−0.06	0.00
PALOL	−0.06	0.00	−0.06	−0.19	0.49	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

[a] See Table 1 for Chemical Species.

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

	Case A Average of 51 Individual Samples	%[a]	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
Burning (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^2	0.89		0.94		0.96	
CHI	1.8		0.75		0.67	
PCMASS (%)	93		91		93	
Measured $PM_{2.5}$ ($\mu g/m^3$)	72		70		72	

[a] Percent of measured $PM_{2.5}$.

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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 emissions inventory (CARB, 2004).

Source	IMS95[a]	CRPAQS[b]	SJV emissions inventory[c]
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	–

[a] Percent of total estimated $PM_{2.5}$ mass.
[b] Percent of measured $PM_{2.5}$ mass.

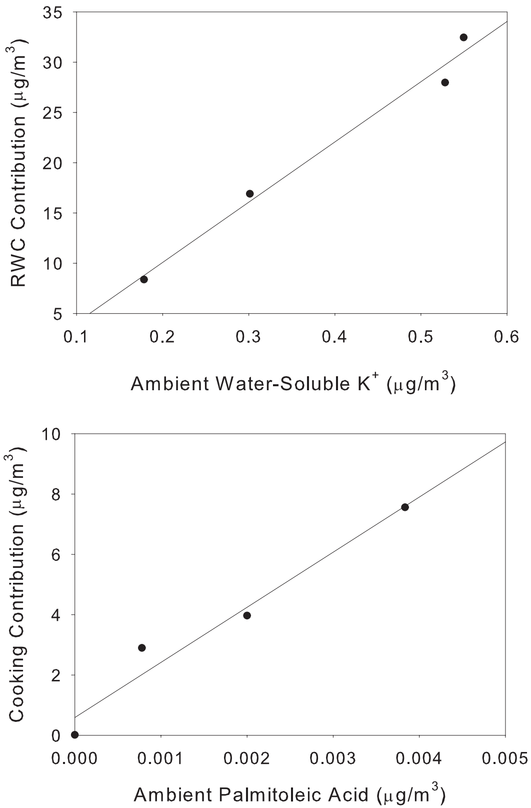

Fig. 1. Comparison of average residential wood combustion (RWC) and cooking contributions and average ambient water-soluble potassium (K^+) and palmitoleic acid concentrations during four CRPAQS winter intensive periods at the Fresno Supersite in California. The values represent averages from the four 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).