

## ***Interactive comment on “Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite” by J. C. Chow et al.***

**J. C. Chow et al.**

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We thank the reviewers for their thoughtful comments. Our responses are in the order that they appeared on-line. The comments are shown in *italics* with our responses below.

### **Anonymous Reviewer #2**

*One of the aspects open to criticism is the excessive utilization of abbreviations throughout the manuscript, which forces the reader to keep in mind the source codes of Table 2 and other definitions provided in the text.*

The abbreviations for the source profile names defined in Table 1 are used for brevity.

We noticed that the column headings for the continuation of Table 1 on-line are repetitions of the headings in the first part of the table. The table as originally submitted shows headings for the second part of the table that describe the following source profiles: charbroiled chicken (CHCHICK); propane chicken (PRCHICK); charbroiled hamburger (CHHAMB); meat cooking (COOK); seasalt (MARINE); and ammonium sulfate (AMSUL). The revised table also contains the profile for ammonium nitrate (AMNIT).

*Another aspect deserving consideration is the omission of comparative results pertaining to the diverse sampling periods (00:00-05:00, 05:00-10:00, 10:00-16:00, and 16:00-24:00) to evaluate different source contributions. The source profiles for the 00:00-05:00 sampling period are the only that have been discussed.*

There are two issues: 1) the use of the 0000-0500 period for initial CMB testing; and 2) the diurnal variation of source contributions. As stated in the text, we chose the average ambient concentrations for the 0000-0500 period for initial CMB testing because concentrations were high during this period.

In the revised text, a discussion and figure are presented describing average diurnal variations of source contributions (percent of estimated  $PM_{2.5}$ ) for mobile, burning (RWC), cooking, and secondary ammonium nitrate (AMNIT) source contributions.

Ammonium nitrate increases in the afternoon period (1000-1600) as transported pollutants are mixed to the surface. Cooking and burning contributions display similar diurnal variations, with the highest relative contributions in the evening (1600-2400) and early morning hours (0000-0500). The mobile contribution varies least during the day although the percent contributions are highest in the evening and mid-morning (0500-1000) periods.

#### *Specific comments*

*- Page 10344, Methods. A general description of the sampling site is completely missing.*

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The revised text (section 2.1) contains the following sentence. The Fresno Supersite is located at 3425 First Street, approximately five km from the downtown district. Air quality monitors are operated on the roof of a two-story building.

- Page 10345, lines 2-4. *“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 Eq 7. Generally, hydrocarbons of low molecular weight, e.g., methane, ethane, and propane, are gases; those of intermediate molecular weight, e.g., hexane, heptane, and octane, are liquids; and those of high molecular weight are found in the particulate phase. It is important to define the partition between the gaseous and the particulate phases in a more rigorous way.*

The definition and description of semi-volatile organic compounds (SVOC) is clear.

Although hexane, heptane and octane are liquid in a pure form, there are present in the gas phase in ambient air. Semi-volatile organic compounds (SVOC) are defined as compounds having vapor pressures between  $10^{-4}$  and  $10^{-11}$  atm. They exhibit significant gas and particle concentrations in the atmosphere. Nearly all classes of organic compounds contain semi-volatile species: alkanes, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), nitro-aromatics, terpenes, acids, carbonyls, and lipids, for example.

- Page 10345, line 7. *“samples were extracted in DCM and 10% diethyl ether in hexane”. How were the extractions done (Soxhlet, ultrasonication)? Also, give information on the solvent volumes.*

All samples were extracted with an Accelerated Solvent Extractor (ASE-300, Dionex). The solvent volumes were generally 150 ml. (As noted in the revised text, section 2.1)

- Page 10345, lines 26-27. *“Organic compounds included PAHs, polar compounds, hopanes, steranes and long-chain alkanes.”. The type of organic compounds analyzed*

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*was previously given at the beginning of the paragraph.*

This sentence is redundant and is deleted in the revised text.

*- Page 10346, line 5. Samples were collected based on forecasts of high PM<sub>2.5</sub> conditions. What were the criteria for classifying the PM levels as high? How was done the forecast? Was this done based on EPA models and standards?*

The following description is added to the revised text after the first sentence of the last paragraph of section 1. Forecasting was done by San Joaquin Valley Air Pollution Control District meteorologists using a regression-based prognostic model that predicts 5-day PM<sub>10</sub> and PM<sub>2.5</sub> concentrations based on variables including atmospheric stability, wind speed, upper-air temperature, and continuous nitrate 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 PM<sub>2.5</sub> concentrations exceeded the national PM<sub>2.5</sub> standard of 65  $\mu\text{g}/\text{m}^3$ .

*- Page 10346, lines 8-9. It is stated that the 10:00-16:00 PST period was chosen to evaluate mixing down of aged/secondary aerosols, and that the 16:00-24:00 PST period was for assessing the evening traffic, cooking, and home heating. The 10:00-16:00 period includes the lunch time. Previsibly, it is also very affected by cooking operations. Why was it considered that only the 16:00-24:00 period was influenced by cooking? On the other hand, the time zone abbreviation (Pacific Standard Time) may not be obvious to all the readers.*

“PST” on page 10346 is redefined in the revised text as “Pacific Standard Time, GMT-8”. The basis for expected diurnal variations of the source contributions is described in the references cited in the text. The afternoon period (1000-1600) may contain cooking emissions (although not residential cooking) but primary emissions and concentrations are low during this period because of the deepening mixed layer. This dynamic can significantly increase the concentration of secondary ammonium nitrate (as seen in the figure (above)) which is advected aloft and mixed to the surface during the afternoon.

- Page 10347, lines 16-28. *Its is stated that indeno(123-cd)pyrene, benzo(ghi)perylene, and coronene are useful components for distinguishing diesel from gasoline exhaust contributions. However, it is not clear how this separation is done. Are the 3 PAHs only emitted by gasoline exhaust? Do the concentration ratios between the 3 PAHs differ from gasoline to diesel emissions? The paper of Zielinka et al. (2004) does not clarify this matter with objectiveness and the one of Fujita et al. (2006) is not yet available.*

- Page 10348, 2nd paragraph. *Hardwood and softwood profiles were determined from oak, eucalyptus, almond, and tamarack. It is not obvious why the emission profiles from wood burning of these species were chosen. Are these frequently burned species in Fresno? There are other emission profiles for white oak, red maple, sugar maple, Douglas fir, loblolly pine (Fine et al., 2004, Env. Eng. Sci.), and other temperate climate conifers (Oros and Simoneit, 2001, Appl. Geochem., 16, 1513) or deciduous trees (Oros and Simoneit, 2001, Appl. Geochem., 16, 1545) abundant in the USA.*

- Page 10348. Lines 252-23. *Rogge et al. (1991) and Simoneit (1989). These citations are not listed in the Reference list, at the end.*

The reference to Zielinska et al. (2004) and the data in Table 1 clearly show that the three PAH's, indeno(123-cd)pyrene, benzo(ghi)perylene, and coronene are emitted by gasoline- but not diesel-powered vehicles. The following references in the revised text provide additional support:

Miguel, A. H., Kirchstetter, T.W., Harley, R.A., and Hering, S.V., 1998: On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon soot from gasoline and diesel vehicles. *Environ.Sci.Technol.*, 32, 450-455.

Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney K., Lawson D.R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *J. Air & Waste Manage. Assoc.*, 54, 1138-1150.

As described in the first paragraph of section 2.3, source profiles were chosen that

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were based on sampling and analytical methods that were consistent with those applied to the CRPAQS ambient samples. The profiles developed by Fine et al. (2004), for example, represent particulate organic compounds while our source profiles and ambient measurements represent SVOC (gas plus particle) concentrations. Fine et al. (2004) did not measure hopanes and steranes. Fine et al. (2004) used the method of Birch and Cary (1996) to measure OC and EC and their thermal fractions while the IMPROVE protocol was used in our source profile and ambient measurements. Chow et al. (2001, *Aerosol Sci. Technol.*, 34,23-34.) reported significant differences between the two methods, as noted in section 2.3 with reference to Watson et al. (2005).

The Rogge and Simoneit references were inadvertently omitted and are included in the revised text.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1991). Sources of fine organic aerosol - 1. Charbroilers and meat cooking operations. *Environ.Sci.Technol.* 25, 1112-1125.

Simoneit, B.R.T., 1989. Organic matter of the troposphere — V. Application of molecular marker analysis to biogenic emissions into troposphere for source reconciliations. *J.Atmos.Chem.* 8, 251-275.

*- Page 10350. First paragraph. The reaction of cholesterol with ozone is pointed out as a possible cause for detecting this tracer at very low levels. The estimated cooking contribution was done by using palmitoleic acid as organic tracer. However, this unsaturated fatty acid has a double bond, which is subjected to a faster attack of ozone than that of cholesterol. Thus, the explanation given for cholesterol is not entirely valid.*

The relative rates of ozone reaction with palmitoleic acid and cholesterol are not known. Palmitoleic acid appears to be emitted in higher quantities than cholesterol during cooking. The reviewer raised the issue of the importance of marker species in the CMB. We presented the CMB with a set of fitting species (see Table 3) in the source profiles and

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ambient concentrations. While there may be expectations as to which species should be important markers for different sources, the CMB results are based on the matrix algebra of the solution and not those expectations. The CMB output contains the MPIN (modified pseudo-inverse) matrix (Table 5) which informs us what the model “thought” were the most important source markers. As shown in Table 5, the most influential species for distinguishing the cooking profile in the CMB were OC, the OC3 thermal fraction, and palmitoleic acid. We noted that cholesterol was not identified as a key species because of its large measurement uncertainty in the ambient samples.

- Page 10355, last paragraph. Provide the linear regression equations and  $r^2$  for both graphs of Figure 1. How many samples were averaged for each time period?

The following regression statistics are included in the revised figure.

For the upper graph in Figure 1,  $Y = 60 \pm 6 X - 1.91 \pm 2.3$ ,  $R^2 = 0.98$ .

For the lower graph in Figure 1,  $Y = 1828 \pm 267 X + 0.59 \pm 0.59$ ,  $R^2 = 0.96$ .

The following sentence is added to the revised text.

There were 13, 13, 12, and 13 samples included in the averages for the 0000-0500, 0500-1000, 1000-1600, and 1600-2400 PST periods, respectively.

#### *Technical corrections*

- Page 10346, line 22. “aE central California. (Chen et al., 20063)”. Delete the dot after California.

Changed in the revised text.

- Page 10347, line 6, and throughout the text. Change  $R^2$  to  $r^2$ .

Changed in the revised text.

- Footnote of Table 2. Change hard wood to hardwood.

Changed in the revised text.

- Which was the CMB version that has been used? Was it the CMB 8.2?

It was noted on p. 10347, line 1, that CMB version 8 was used.

### **Anonymous Referee #1**

#### *General Comments:*

*This paper investigated the application of organic markers to better distinguish some sources of aerosols, especially those from combustion sources using simulated data. The sources of high PM<sub>2.5</sub> episodes at Fresno in winter (2000-2001) were also studied using CMB and organic tracers. The study concluded that “organics were not required to estimate hardwood combustion. The important RWC marker was the water soluble potassium ion.” Resin acids are known to be enriched in softwood combustion including pimaric, isopimaric, and sandarapimaric acids, but they were not included as the fitting species in this study. With the simulated data, it showed that softwood was overestimated by the model (Table 2). Table 4 also showed that the softwood source estimates were either highly uncertain or overestimated. Adding these known softwood tracers may lead to a better estimate of contributions from softwood source. Therefore, without confidence in the estimation of softwood source contribution, it is hard to conclude that the most important marker is potassium ion. The authors stated in the Conclusions section that “The cooking contribution did not depend on cholesterol..”. Cholesterol has been detected in meat cooking sources (McDonald et al., 2003, Vol 53, 185-194, J. Air Waste Manage. Assoc.). Because cholesterol in most samples in this study was under detection limit or with high uncertainty, cholesterol was not used as a tracer. But it does not necessarily mean that cholesterol is not a good tracer for meat cooking. More evidence is needed if the authors want to question if cholesterol is a good tracer for meat cooking or not. I recommend this paper to be published after modification and clarification. Specific comments are listed below.*

The three softwood markers (pimaric, isopimaric, and sandarapimaric acids) noted above weren't measured in this study so this point is moot. Reviewers #1 and #2 have



read more into the paper than is there. This results from confusing expectations about source markers, which are discussed in section 2.3, and how the CMB model keys on influential species in its solution for the source contributions.

This confusion can be addressed in part with the MPIN results for the average sample from Case 4 in Table 2 (simulated data based on actual uncertainties, all sources and organics included, with the cholesterol ambient uncertainty set at 10%). Since the synthetic data represent an idealized case, the MPIN results are as expected. The key species are Al and Si for PVRD, benzo(ghi)perylene, coronene, and indeno[123-cd]pyrene for gasoline vehicles, the EC2 thermal fraction for diesel vehicles, soluble K, levoglucosan, and syringaldehyde for hardwood combustion, EC for softwood combustion, and cholesterol for cooking. Thus, our expectations are met with ideal data. A paragraph describing these results was added before the last paragraph in Section 3.1.

*Specific Comments:*

1. *Page 10343: RWC is common in winter. Are emissions from prescribed burning and wild fires important in this area?*

Agricultural burning can be important but not during winter.

2. *Page 10345, line 4: “..while hopanes, steranes, and high molecular weight molecular weight organic acids and alkanes are present mainly in particle phase.” References should be cited.*

The reference to Zielinska et al., 2004 (in response to Reviewer #2) was inserted.

3. *Page 10345, line 7: Dichloromethane and 10% diethyl ether in hexane were used for extraction of ambient samples. Is the analytical method applied for the ambient samples in this study the same as those source samples including solvent system, quantification method, GC/MS analysis (e.g. chemical ionization in this study)? If not, would the author expect any impact on the CMB results?*

The analytical methods were the same for ambient and source samples.

4. *Page 10345, line 9: The extracts from the PUF plugs and filter-XAD pairs were combined. Any special reason for the authors to combine the extracts? Only species that are considered as conservative (from sources to receptors) are normally used as fitting species.*

We are interested in SVOC composition. Thus, we combined the measured gas and particle SVOC concentrations and assumed that the sum was conserved. We restricted the CMB to [relatively] unreactive compounds.

5. *Page 10345, Lines 14-21: One half of extract was analyzed for non-derivative SVOC. Was the other half analyzed for polar compounds with derivatization? If so, state it clearly.*

Yes, the other half was analyzed for polar compounds with derivatization. This was clarified in the revised text.

6. *Page 10345: It would be helpful to indicate QA/QC of the organic tracer analysis including recovery and blank etc.*

The reader is referred to Rinehart et al. (2006).

7. *Page 10346: Lines 7-10: The authors collected samples during different periods. This paper should include discussions of the CMB results during different periods. What are the dominant sources for each period from this study? Do the results correspond well to the authors' speculations, e.g., more emissions from evening traffic, cooking, and home heating during 16:00-24:00 PST? The readers do not have these information since the averaged values are presented in Table 6.*

Diurnal source contributions are discussed in response to Reviewer #2 and in section 3.3 of the revised text.

8. *Page 10347, Line 2: The authors present the criteria for evaluating the CMB re-*

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*sults. Are the fitting species well explained in this study? What about the C/M ratios (calculated to measured ratios)?*

The following was inserted at the beginning of section 3.3. 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. Thus, organics were not fit as well as the traditional species but including organics accounted for more of the measured mass.

*9. Page 10347, Line 13: “post-2000 vehicle exhaust”: When were these source tests conducted exactly?*

The revised text indicates that the source tests were conducted during summer, 2001 but were not limited to post-2000 vehicles.

*10. Page 10347, Line 25: The Teflon filters were over-loaded. Was it significantly overloaded or not? Say 200% or more?*

The text was revised as follows. 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 or because of VOC absorption by the quartz-fiber filter. It isn't possible to quantify these potential artifacts.

*11. Page 10347, Line 28: The authors stated that three PAHs (i.e., indeno[123-cd]pyrene, benzo[ghi]perylene, and coronene) can be used to separate diesel exhaust from gasoline exhaust. Since PAHs can be emitted from sources with incomplete combustion such as coal combustion, appropriate references or more supporting evidence should be cited or provided to demonstrate the power of three PAHs in diesel and gasoline split.*

There is no coal combustion in Fresno. Discussion and additional references on motor vehicle emissions were provided in the response to Reviewer #2.

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12. Page 10348, Line 29: *In the road dust profile, specific organic compounds were not measured and they are set to zero in the profiles. Table 7 shows the huge difference between the CMB estimate of road dust (zero) compared to the inventory (22%). Is it possibly due to the source profile or other reasons?*

One possible explanation why the inventory and the CMB results disagree is that the inventory reflects the entire San Joaquin Valley. Note that the inventory does not contain secondary ammonium nitrate, which accounts for nearly a third of the wintertime  $\text{PM}_{2.5}$  mass in Fresno.

13. Page 10350, Lines 1-3: *Cholesterol was below detection limit in most samples. Does the highest cholesterol concentration occur during the 16:00-24:00 period?*

The cholesterol concentration was higher than its uncertainty in only 6 out of 51 cases in Fresno. Three of these occurred during the 1600-2400 PST period and one each during the 0000-0500, 0500-1000, and 1000-1600 PST periods.

14. Page 10350, Line 4: *This reference (Dreyfus et al., 2005) is not found in the References section.*

The citation is included in the revised text.

Dreyfus, M.A., M.P. Tolocka, S.M. Dodds, J. Dykins and Johnston, M.V., 2005. Cholesterol ozonolysis: kinetics, mechanism and oligomer products. *J. Phys. Chem. A*, 109, 6242-6248.

15. Page 10350, Line 7: *The uncertainty of the ambient measurement was assumed to be 10%. Why was the uncertainty of 10% assumed and used? Is it based on experimental results? Schauer et al. estimated the average uncertainty of 20%.*

This was only done for the feasibility analysis with the simulated data to allow cholesterol to act as a useful marker. Schauer et al. were able to measure cholesterol because they collected 24-hour duration samples with high volume (500 lpm) samplers. Our samples were of 5-8 hour duration and were collected at a flow rate of 20 lpm.

16. Page 10350, Lines 14-26: Explain the difference between Case 1 and Case 3. What does the “actual” in Table 2 mean? If that represents “actual uncertainty”, present the value.

The term “actual” uncertainties” is defined on page 10349, lines 24-25. Case 3 used actual uncertainties while Case 1 used fixed uncertainties.

17. Page 10351, Lines 20: The 00:00-05:00 period was used in the discussion. What not using the 16:00-24:00 period when evening traffic, meat cooking, and residential heating are active? Or at least a comparison between different periods should be made.

The purpose of this section was to show how changing the combination of source profiles and fitting species affected the stability of the CMB results. We used the 0000-0500 PST period simply because concentrations were relatively high during this period. As shown in the response to Reviewer #2 on diurnal variations, the average contributions for traffic, meat cooking, and RWC were similar during the 0000-0500 and 1600-2400 PST periods.

18. Page 10352, Lines 3-4: “These species may be enriched by exhaust from the sampling equipment.” Any references or supporting evidence for this? For example, there are studies to show that Cu can be a contaminant due to pump exhaust of high vol sampling.

High volume brush pumps have been shown to produce copper contamination (Hoffman and Duce, 1971; King and Toma, 1975; Patterson, 1980). It is reasonable to assume that the medium-volume rotary vane pumps may also produce copper contamination but we are not aware of references to zinc contamination by brush or vane pumps.

The following references are cited in the revised text.

Hoffman, G.L., and Duce, R.A., 1971. Copper contamination of atmospheric particu-

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late samples collected with Gelman Hurricane air sampler. Environ. Sci. Technol., 5, 1134-1136.

King, R.B., and Toma, J. 1974. Copper emissions from a high-volume air sampler. NASA technical memorandum, NASA-TM X-71693.

Patterson, R.K., 1980. Aerosol contamination from high volume sampler exhaust. JAPCA, 30, 169-171.

*19. Page 10353, Line 18: Cooking contribution seems large (e.g., as high as 30% of mass in some cases) during 00:00-05:00 period. One would imagine it should be higher during the active cooking period in the evening. Is it likely that cooking source was overestimated? Could it be due to the tracers used such as palmitoleic acid?*

The figure in the response to Reviewer #2 shows that while the highest average cooking contribution was during the 0000-0500 PST period (12.4%), the relative contributions were more similar during the 0500-1000 PST (6.4%) and 1600-2400 PST (5.0%) periods. It is possible that the cooking contribution was overestimated. If the source profiles were not representative, the CMB results would be biased. A systematic high bias could be caused by uniformly low-biased profile compositions of marker species like palmitoleic acid and cholesterol. This would not explain diurnal biases unless the true source profiles also varied diurnally.

*20. Page 10366: In Table 2, the number of samples (n) used in the statistics should be shown.*

The text on page 10305, lines 8 and 12, notes that  $N=100$ .

*21. Page 10367: Why are some lighter (in molecular weight) species such as pristane and phytane used in the fitting species? They are found in petroleum, but they are not as heavy as other organic species. Are they conservative?*

Since we use the sum of gas and particle concentrations (SVOC), it is reasonable to include pristine and phytane, which are not very reactive, especially in winter.

22. *Figure 1 should include the standard deviation of the average concentration.*

Regression parameters and the 95% confidence interval of the expected values of the dependent variable are included in the revised Figure 1.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10341, 2006.

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