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Interactive Comment

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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Anonymous Referee #3

General comments:

Chow et al. present a sensitivity analysis of CMB models applied to simulated data. The authors carefully investigated if source profiles with organic tracers improve the capability of CMB models to resolve the contribution of emission sources. The conclusions obtained from the sensitivity analysis are used in a CMB source apportionment for PM2.5 at the Fresno supersite. I recommend this paper to be published after clarification and correction of the issues listed below.

Specific comments:

1. One of the main conclusions of the paper is that organics are not required to estimate hardwood combustion sources and the most important and sufficient residential wood combustion marker was water-soluble potassium (no organic markers required). This is surprising and should be discussed in more detail: One could argue, that emissions of water-soluble potassium and organics from wood combustion sources are not necessarily highly correlated and may represent different states of wood combustion processes. For example, it can be deduced from Khalil and Rasmussen (Atmos. Environ., 37, 1211-1222) that the potassium emission factor is three orders of magnitudes lower in cold wood burning as compared to hot wood combustion. In contrast, emission factors

of OC are considerably higher under cold burning conditions than during hot wood combustion. In the same study, about 80% of the air pollution at Olympia-Lacey Washington) could be attributed to wood burning dominated by emissions at low-temperature combustion. Those findings question that potassium is a good and sufficient tracer for the total emissions of primary particles (inorganic and organic) from wood combustion. One could expect that beside potassium (tracer for inorganic particles) a second organic tracer (for organic aerosols) is required to determine the contribution of the total primary particle emissions from wood combustion sources at a receptor site.

It is difficult to draw conclusions relevant to Fresno from the Khalil and Rasmussen study. They did not attempt to distinguish gasoline from diesel vehicle emissions. Apparently, their air shed did not contain cooking emissions. Their hot and cold RWC source characterizations were based on data obtained during forest fires. It isn't clear how this might relate to residential wood combustion (RWC) in Fresno. As described by McDonald et al. (2000), our wood-burning profiles were determined by burning hardwoods and softwoods in fireplaces and stoves under real-world conditions. We presented hardwood and softwood profiles to the CMB model with the expectation from Magliano et al. (1999) that hardwood emissions would dominate, as they did in the analysis.

Again, the reviewers have read more into our results and conclusions than is warranted from the paper. We did *not* conclude that organic compounds are not needed to quantify wood combustion emissions. We demonstrated that for what we consider to be a representative set of source profiles applied in the CMB model to ambient concentrations in Fresno, the addition of organic compounds to the model did not significantly change the wood burning contribution. This was confirmed with CMB applied to synthetic data generated from the same source profiles. We therefore concluded that the wood burning contribution to PM2.5 did not depend on organic compounds. This is logically follows from our results but implies nothing about the general value of organics as tracers or their utility in other air sheds and modeling applications.

2. Evaluation of the different CMB models applied to the simulated data showed that "it is not feasible to distinguish hardwood and softwood contributions from the source profiles used in this study" (page 10352 lines 14-15) because of collinearity of the hardwood and softwood profiles. Nevertheless, in the CMB models used for PM2.5 source apportionment at the Fresno supersite the collinear hardwood and softwood source profiles are used, and the contribution of hardwood and softwood combustion is determined (e.g. abstract line 15-16, and table 6). This is contradictory and I suggest do redo the CMB modelling for the Fresno PM2.5 data using only the hardwood source profile since this one is "sufficient to estimate the total burning contribution within 20%" (page 10351, lines 8-9).

When two source profiles are collinear, one or both of their source contribution estimates can have inflated variance, depending on the degree of collinearity. This is evident from the high AAE for the softwood contribution in Table 2, Case 4 and the large uncertainty of the softwood contribution in Table 4, Case 1. While it may not be possible to precisely estimate each contribution, the sum of those contributions, which in this case represents hardwood plus softwood, may be precisely estimated. In the revised text, we added and discussed two columns to Table 2 which present AAE's for

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the sum of gasoline and diesel contributions (MOBILE) and the sum of hardwood and softwood contributions (BURN). The AAE for BURN in Case 4, Table 2, where both hardwood and softwood profiles were included, was 16%. When only hardwood was included (Case 5, Table 2), the BURN AAE increased to 20%. Thus, better results were obtained by including the softwood profile.

3. The authors mention that "PVRD contributions became negative in the iterative solution and that their respective source profiles were dropped from the model" (p. 10352, lines 19-21). On the next page (p. 10353, lines 5-8) the authors state that Fe was the most influential marker for BURN-S and add "This is not reasonable and probably results from the fact that the geological profile (PVRD) was dropped from the fit" Thus, on one hand, PVRD is dropped from the set of source profiles (is considered insignificant), on the other hand, the authors guess that PVRD species cause the unreasonable BURN-S markers in the MPIN matrix (has significant influence on the results in that case). This is again contradictory and requires clarification.

This point is clarified in the revised text. The MPIN shows that the most influential marker for softwood combustion (BURN-S) was Fe. Table 1 indicates that the source profiles used in the CMB with the highest Fe were PVRD (5.2%), BURN-S (0.52%), DIES (0.44%), and GAS (0.42%). When PVRD was removed from the model, BURN-S had the highest Fe composition. EC (MPIN = 0.8) was also an influential marker for BURN-S, although none of the organic species were.

4. Page 10348, line 4: Reference source profiles from almond and eucalyptus, oak and tamarack were used. Please comment if these woods are the ones that are dominantly used for residential wood combustion in the Fresno region.

The choice of woods for RWC testing (done by DRI) was based on previous surveys of RWC in California. For example:

Houck, J.E., Chow, J.C., Watson, J.G., Simons, C.A., Pritchett, L.C., Goulet, J.M., and Frazier, C.A. (1989) Determination of particle size distribution and chemical composition of particulate matter from selected sources in California. Volume I (final report). Prepared under agreement no. A6-175-32 for California Air Resources Board, Sacramento, CA, by OMNI Environmental Services, Inc., Beaverton, OR, and Desert Research Institute, Reno, NV.

Houck, J.E., and Crouch, J. (2002) Residential wood combustion emission inventory South Coast Air Basin and Coachella Valley portion of Salton Sea Air Basin, 2002 base year, OMNI Environmental Services, Inc. 5465 SW Western Ave., Suite G Beaverton, OR 97005.

5. Source contributions are compared to results of a previous study (SJV study). Those are called "true" (10349, lines 15 and 18) source contributions. Unfortunately, the quotation marks get lost as of p. 10349 (incl. Tables), which is misleading.

The quotes were unnecessary and were removed from the revised text.

6. A reference for the MPIN diagnostic (p. 10352, line 25) should be given: Kim and Henry, 1999, J. Air & Waste Manage. Assoc., 49, 1449-1455.

This reference was added to the revised text.

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