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Interactive comment on “Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds” by B. J. Williams et al.

B. J. Williams et al.

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Comments on “Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds” B. J. Williams, A. H. Goldstein, N. M. Kreisberg, S. V. Hering, D. R. Worsnop, I. M. Ulbrich, K. S. Docherty, and J. L. Jimenez

General comments: This paper presents further results from the 2005 SOAR study, this time with PMF results for organic aerosol (OA) using TAG and AMS data collected

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during the summer and fall campaigns. The TAG instrument is very intriguing in that it can capture ambient trends in organic compounds at high time resolution. TAG is not a direct analog to traditional filter-based GCMS, so the data cannot necessarily be modeled by CMB using published emission profiles. Therefore PMF is the potentially the best means of modeling source contributions using TAG data. However, there are several fundamental issues with the raw dataset and the initial PMF setup which could potentially have significant impact on the results of this study. The correction for drift in the instrument over the course of the field campaigns, the identification and quantification of unverified compounds and the inclusion of said unverified compounds in the PMF, the assignment of uncertainties to TAG compounds, and the use of modeled OA in the fall SOAR campaign. The specific issues have been included below. I will not be as thorough with the examination of the PMF results, as I think that the PMF modeling needs to be redone after addressing the TAG analysis questions. The PMF should ideally be redone with a shortened list of compounds whose identification and quantification can be assured with close surrogate compounds and whose drift correction is at least compound-class specific if not compound-specific. Additionally, I think at least compound-class specific uncertainties are warranted for the PMF modeling. In the end, I am intrigued by the potential of the TAG measurements and future PMF results, but would like to see the authors be more rigorous in their calibration, identification and quantification of organic compounds.

Response) We thank the reviewer for his/her insightful comments, and respond to the specific issues raised below. We disagree with the recommendation that the PMF modeling needs to be redone, and justify below why we stand by the current version of the analysis.

Specific comments:

1) Abstract 6569 ln 17: there needs to be qualifications with this statement of 88% of OA is SOA, considering these are PMF factors. There are many primary hydrocarbon compounds making up the SOA factors (alkanes, PAH, cyclohexane), thus there is

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likely some POA contribution to these SOA-labeled factors. It would be better here to assign a range or at least include an approximation of error for the SOA apportionment.

Response) This is the nature of PMF analysis, and in revising the paper the authors have added statements throughout to acknowledge this limitation and to better estimate the errors of the PMF analysis. Here, we have specified “according to PMF results”.

2) Section 2.2 6574 ln 1 There does need to be a bit more description of the TAG instrument included here. For example, how does TAG deal with gas vs particle phase?

Response) A short description and reference have been added to the start of section 2.2: “Details on TAG operation are provided by Williams et al. (2006). Briefly described, particles are collected by humidification followed inertial impaction and subsequent thermal desorption into a gas chromatograph – mass spectrometer. A separation between gas and particle phase collection is determined through periodic filtration of the particle phase.”

3) Section 2.2 6574 ln 17-26 This is a major concern for this manuscript – using an average detector drift for all compounds. The instrument drift for a selection of compounds is included in Table s1 the range is -60 to +13 or +26 %. To use an average drift of -18% seems a serious over simplification. Ideally drift by compound or compound class should be used. This may introduce serious and uneven bias in the ambient concentrations. The authors did a sensitivity test, but it was also a blanket drift assessment (this time zero drift), so it is not surprising that the results were the same. A better sensitivity test would be to compare PMF results with average drift to compound class-specific drift. On a more general note, there should be another means of assessing accuracy – can daily averages be compared to filter-based GCMS? The Kreisberg paper illustrates TAG accuracy for PAHs, using NIST standard reference material, but that is not sufficient for the variety of compounds and compound classes reported for TAG in this study.

Response) It is true that a compound-by-compound drift would be the best approach,

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and the authors have revised a comment in the revised manuscript regarding this issue: "While the most accurate drift evalutaion would be based on a compound-by-compound drift, it is estimated that biases introduced by appointing surrogate compounds for those not included in the chemical standards inventory will be larger than biases introduced by assuming a constant detector drift across all compounds."

Unfortunately, the data needed to implement such an approach is not available for this study. In fact, a number of issues with the calibration method used during SOAR have been realized through the data analysis and subsequent experiments, and hence a new automated calibration system for TAG is under development (and has now been deployed during the CalNex 2010 study). Here, we are able to achieve injections of deuterated standards onto every single ambient sample that is analyzed. This stands to be the most accurate way of determining drift, as it captures transfer effects from the ambient matrix, which are missed using an external standard. To avoid large, potentially inaccurate corrections, we have chosen to use an average drift for this study.

4) Further on drift/calibration –the r^2 on some of these calibration curves are very low: 0.02 for phthalic acid, for example. Is that the calibration curve used for phthalic acid quantification? Also, the start-finish drift is reported, but what is the standard deviation by compound?

Response) In this analysis, only a drift correction has been applied to observed variations in raw compound signal. Standard deviations by compound based on reproducibility tests average $\sim 10\%$, as is used in our uncertainty estimates here, and as reported by the referenced Williams et al., 2006, 2007, and Kreisberg et al., 2009 papers.

5) Section 2.3.1 Compound identification and quantification is another major concern for this manuscript. Over 300 compounds are reported, many identified based on library matches. Additionally, in Table S2 it becomes apparent that there are whole subsections of compounds which are not represented in the standard mixtures like

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hopanes, substituted guaicols and syringols, terpenes and terpenoids, oxygenated terpenes, and Cl, F and P-containing compounds. I question how the authors can be assured of the identification and quantification of these compounds? In fact many compounds which are not included in the standards and do not have close surrogates in the standards are included in the PMF modeling. The results of the PMF model are only as certain as the input data. I would highly recommend that the authors severely cut down the list of organic compounds to use as PMF inputs. There may be fewer source factors to work with, but the results would likely mean more. I don't think it is necessary to have all quantified compounds in the standard, but a relatively close surrogate in functional group, retention time and molecular weight should be used. This will also help with adjusting for drift over the course of the study, as a reduced list that adheres more closely to the content of the standards should be easier to correct on a compound-by-compound basis.

Response) We believe the reviewer has misinterpreted our approach to the PMF analysis. While the compounds have been identified through either standards or mass spectral matches, their identification does not actually play any role in the PMF results... only in how we interpret the results. The interpretation becomes meaningful when many compounds that have a similar source fall into the same PMF factor (hence, adding additional confirmation of our compound identification). Also, we are not using quantified timelines, but rather relative abundances to limit uncertainties. PMF uses signal-to-noise, not concentration to apportion factors. In our case, the scaling of mass to the factors is based on the concentration of submicron organic aerosols as quantified by the AMS.

6) Is there blank subtraction by compound? What is the carry-over in the instrument after a high OA episode?

Response) Blanks are subtracted by compound, and there is no carry-over in the instrument after high OA episodes. Second desorptions are always clean.

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7) P 6576 Eqn 1 – This is a previously reported equation for calculation of Cwax, but it is an over-simplification. Certainly there is a large difference in CPI between petroleum combustion and biogenic emissions (CPI of 1 and \sim 12, respectively). However, biomass combustion does not necessarily have a CPI of 1.0, as is assumed here. It can have a CPI of 1-3 or even higher for grass and cereal burning. This can actually be seen in the PMF results presented here where the Cwax contribution is higher for biomass burning than primary biogenic. The calculation needs to take into account the potentially higher CPI of biomass burning to effectively separate out the biogenic component of n-alkanes.

Response) While this comment contains very useful information, here the authors do not calculate CPI. We have only used this equation to estimate Cwax, for the purpose of determining how it fits into the factor separation. As we see from our results, Cwax is typically higher for biomass burning and biogenic associated factors, as would be expected, and as indicated by the reviewer's comment.

8) P 6578 In 25 I am unclear, is the instrument precision (IP) and known uncertainty (10%) the same for all compounds? The IP value is not reported. Again, this is very likely an oversimplification. In looking at Table S1, it appears that this might be true for PAHs and medium volatility alkanes, but not for all compounds.

Response) The IP calculation is different for each compound. The authors have added text to make this point clear: "for each compound" has been added twice to the paragraph.

9) P 6580 In 10 – It is specified that only the particle-phase component of the TAG compounds are included in the PMF analysis, however this cutoff is set at 35% in the particle phase. This seems quite low in that it includes compounds which are a majority in the gas-phase. What was the rationale for the 35% cutoff?

Response) This value was chosen through a sensitivity analysis of PMF results. Results were stabilized by eliminating compounds that were dominantly gas-phase (in this

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case the threshold was 35%). Text has been added to clarify this point: “a value determined through a PMF sensitivity analysis, wherein PMF solutions were stabilized by eliminating compounds that were dominantly in the gas-phase”

10) P6581 In 4-9 – Is there a reference for this assumption of pm1.0 and pm1.5 being the same? I agree that this is very likely true for the PAHs, hopanes. Is it possible that some of the biogenic or biomass burning particles might be in the 1.0-1.5 range? I'm not sure.

Response) PM1 and PM1.5 organic composition is approximately equal. However, PM1 and PM2.5 organic differences are currently being investigated (full papers may come out on this question from the CalNex 2010 experiment). Typically PM1 contains at least 80% of the organic mass of PM2.5. However, it is true that there could be some deviations for some specific sources.

11) P 6581-2 reconstructed OA: I agree that filling in gaps in the OA using the BAM relationship is acceptable when most of the timeframe is mostly covered by the AMS. However, my only concern is that the beginning of the fall period (11/14-11/18) has very little AMS coverage. This wouldn't be that big of an issue if there weren't very different conditions during the latter half of the fall period, which calls into question whether the AMS to BAM relationship is the same for that initial period. Is there no semi-continuous OCEC for this period? It seems like that would be an even better choice for estimating OA.

Response) There was OCEC data available in the summer, but unfortunately there is no OCEC data for the fall. This is the most direct estimation that we can make, given the available dataset.

12) There are too many very similar presentations of the PMF data. These are of some interest, but the authors need to decide which to focus on as Fig 8-9, 10-11 and 15-16 report very similar data.

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Response) While it is agreed that similar data is reported, the authors feel each has its merits for aiding the interpretation of the data. No change has been made to the manuscript in response to this comment.

13) The biomass burning factor has odd daily trends peaking in the middle of the night/early morning. Additionally, it is highly correlated with terpenes. These two characteristics make it seem that this is a factor with some BB characteristics, but not really a fully BB source factor.

Response) The authors have interpreted it as an increase in concentrations due to a shallow nighttime boundary layer. It is not unreasonable to expect a terpene correlation both due to boundary layer conditions and potential co-location of sources. Biomass burning is also known to emit some terpenes (e.g. Grieshop et al., ACP 2009), which may play a part on the observed correlation.

14) The Biogenic factor also seems a very loose connection as there seems to be a very wide array of compounds which contribute to this factor including PAHs.

Response) Again, there are correlations between factors that are highest at night due to boundary layer conditions. This factor has been interpreted to be dominantly biogenic given the number of correlations with biogenic components (e.g., d-3-carene, a-phellandrene, homomenthylsalicylate, norabieta.4.8.11.13.tetraene, norabietatetraene-mixture, vanillin, and Cwax).

15) Table 3 – the uncertainty would be more inclusive if the authors propagated the uncertainty of the AMS OA measurement and the TAG compound measurements along with the modeling uncertainty.

Response) Agreed. Uncertainty of AMS OA measurements and TAG compound measurements have been included with modeling uncertainty.

16) It would be better not to average the Summer and Fall SOA/POA split in the abstract.

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Response) This split is only reported for the Summer period, and we have retained the split in the abstract, but have clarified it as an “estimated” split.

17) P 6606 ln 8-9: Estimating Fall EC based on the Summer EC/PM2.5 ratio is not a great idea. Since this appears to only be used here, it is unnecessary to include in the manuscript. Reporting just the summer EC is fine.

Response) The authors have included a statement and reference to justify our approximation: “This is the same fraction of total PM2.5 that EC has been observed to contribute in this region during the fall in previous years (Sawant et al., 2004).”

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