

## ***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.***

**Anonymous Referee #2**

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This paper presents results of PMF analysis and factor apportionment of chemically speciated compounds measured by a thermal desorption aerosol gas chromatograph (TAG) system. Such measurements and analysis show great promise for improving current understanding of aerosol sources and aging processes. The study should be published in ACP after several issues are resolved. My major concerns are as follows. (1) The distinction between SOA and SOA4+SV seems clear. However, I am not sure of the validity or benefits in using a 3-factor description of the remaining SOA vs. a single SOA factor. (2) More analysis, including additional PMF modeling, is needed

C2578

to evaluate uncertainties in the PMF solution and the effect of such uncertainties on the apportionment results. (3) Some aspects of the data presentation (esp. Table 2) should be revised to provide the reader with sufficient data to interpret the study results. Detailed comments follow.

1. P6571L12-15: “These results contrast strongly with previous studies carried out in Riverside and nearby locations, as well as modeling studies, which have consistently found SOA/OA <50% during the summer.” References for these studies should be added. Also, a brief comment on factors contributing to the discrepancy would be welcome.

2. Fig. 3: It is difficult to distinguish the different shades of grey. Consider using colored traces.

3. P6579L1: The detector drift mentioned previously (P6574L17) also contributes to measurement uncertainty, but does not seem to be accounted for here. Because this drift was observed to be species-dependent, incorporating it into the uncertainties will affect the PMF factors and apportionment results. The sensitivity of the results to this uncertainty should be investigated. (This is in contrast to the sensitivity test performed by the authors, i.e. application to the data matrix of a uniform detector drift correction across all compounds vs. no correction. Because such a method treats the data uniformly, it would not be expected to significantly affect the PMF results.)

4. P6584L22: I would like to see more discussion of why the 9 and 7-factor solutions were selected, and the implications of this selection on factor identification and apportionment results. As discussed in more detail below, it is not clear to me whether the division of SOA into 3 factors is meaningful. Also, the sensitivity of the apportionment results to the solution selection is not discussed. Because the selection of a specific PMF solution is inherently somewhat suggested, such uncertainties should be directly addressed.

5. P6585L13: “Of 300 bootstraps, and of the resulting 2700 factors, only 124 factors

C2579

(i.e. 4.6%) did not match the factor profiles defined in the base case.” What is the criteria for determining whether a factor profiles matches? How much variability is allowed in the profile/time series while still considering the factor to be a “match?” Are the non-matches distributed evenly across all factors, or are certain factors more prone to being unmatched? For a 9-factor solution, 4.6% could be quite significant if the a particular factor is consistently unmatched (e.g. if all the unmatched factors occurred in the (very weak) primary biogenic factor, this would indicate that the factor was only resolved ~half of the time).

6. Fig. S3: The plot of Q/Qexp as a function of fPeak does not really show the solution to this parameter. Because the conclusions presented in the paper depend strongly on the specific characteristics of the factor profiles and time series, the reader needs to see the extent to which these features change with fPeak. Consider adding a plot showing the range of profile and time series values obtained for each factor over a selected fPeak range.

7. Fig. S8: I'm not sure I understand the values displayed. Is this  $\text{sum}(\text{residuals})/\text{sum}(\text{total})-1$ ? In the legend, it says  $\text{sum}(\text{residual})/\text{sum}(\text{total})$ , but this cannot be right. Also suggest the “under-explained/over-explained” terminology in the caption be revised. To me this suggests that the solution is explaining too much/too little of the variability. If I understand the plot, it is instead the case that the reconstructed time series of each species is greater than/less than the original data. It might be clearer to state that the PMF solution overestimates/underestimates the concentrations of the designated species.

8. P6595L20+: The “primary biogenic” factor has very low mass. The tracer compounds discussed in the body of the paper (section 3.1.5) support the authors' identification of this factor. However most of the factor mass is contained in compounds occurring in multiple factors (e.g. benzo(e)anthracene, 2-methylpyrene, cyclopenta(d,e,f)phenanthrene); from Fig. 6, I would estimate that 15% of the mass is contained in the designated “biogenic” compounds (green shading). Therefore state-

C2580

ments such as “ Further, previous studies suggest that low-mass factors may not be accurately resolved by PMF (Ulbrich et al., 2009). A more rigorous of the robustness of this factor as a function of solution parameters is necessary.

9. P6598L16: Add citation for the referenced ME-2 paper.

10. To determine whether differences between factors such as summer SOA1-3 are meaningful, comparison with the time series of species not included in PMF is critical. The authors have inspected such correlations with a large number of species (Table 2). However, Table 2 does not allow the reader to evaluate these correlations. Two problems exist. (1) The authors have elected to report only the strongest factor correlated with the selected species. This means that the reader cannot tell, for example, whether during the summer Ox correlates much more strongly with SOA3 than any other factor, or whether the correlations between Ox and SOA1, SOA2, and SOA3 are similar. These two scenarios lead to very different interpretations of factor sources and inform whether two factors can be reliably distinguished! (2) The PMF factors are not included in the table. If factor time series are observed to correlate more strongly with each other than with other species, it may suggest the factors cannot be well distinguished.

11. How sensitive are the apportionment results (section 3.3) to the specific solution selected? That is, if the apportionment is performed at a different fPeak or using a solution containing p+1 or p-1 factors, does the apportionment change significantly?

12. I agree with the authors' conclusion that the SOA4+SV factor is distinct from the other SOA factors. However, it is not clear to me whether the summer SOA1-3 factors are distinct. The authors note in section 3.1.1 (P6587L19+) that summer SOA3 contains significant amounts of compounds found in SOA1 and SOA2. During the fall study, these factors could not be resolved. Instead, factors were obtained such that: fall SOA ~ summer SOA2 + summer SOA3 fall SOA + FC1 ~ summer SOA1 + summer SOA2 + FC fall SOA + FC2 ~ summer SOA3 + FC The mixing between factors may suggest that the SOA factors represent general variations in SOA composition, rather

C2581

than specific sources or processes. Can the authors comment on the extent to which the 3-factor description of SOA contains specific information (vs. serving as an optimized but physically meaningless basis set for describing SOA composition)? That is, how does the 3-factor description of SOA enhance understanding of SOA composition, sources, and/or formation processes in a way that can not be conveyed by a single SOA factor with error bars on the profiles and time series?

13. P6606L24-27: "However, SOA3 does not appear until later in the morning (09:00 PST) [than the other SOA factors], reaches a maximum later in the afternoon (14:00-16:00), and slowly decreases in the evening (22:00 PST), interestingly, at the same time SOA4+SV begins to increase. SOA3 is clearly representative of a different atmospheric age distribution than the other SOA components, and based on wind speeds and wind directions, is likely more representative of an aged regional SOA." I am not sure how this conclusion is reached. It is not clear to me that the later daily increase of SOA3 vs. SOA1 and SOA2 requires that SOA3 be more aged; it may instead be source-dependent. In fact, I would expect aged SOA to exhibit less diurnal variability than fresher SOA and instead be influenced by long-range transport (is this what is meant by "wind speeds and wind directions?"). The authors did previously note that SOA3 contained significant contributions from diketones, which were cited as an indication of aged SOA; if this is considered a crucial point in the age argument, it should be repeated here. I am also not sure that the correlations with non-PMF parameters (Table 2) bears out the authors arguments. Short-lived species such as isoprene, methacrolein, and methyl vinyl ketone correlate most strongly with SOA3, while longer lived VOCs (acetone, methyl ethyl ketone) and aged OC factors (subAgedOC<sub>SO4</sub>) correlate with SOA2. This suggests that SOA2 is the more aged component, although the present form of Table 2 makes the correlations difficult to interpret.

14. SOA factor diurnal patterns are used to infer SOA age and local vs. regional sources (P6606L19-P6607L4). However, there are also significant diurnal patterns in the meteorological conditions at the Riverside site (Fig. 2 and P6572L22+). Such

C2582

conditions could conceivably influence the diurnal patterns of resolved factors. To what extent can such meteorological conditions and sources/processes be decoupled?

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6567, 2010.

C2583