Atmos. Chem. Phys. Discuss., 10, C5984–C5995, 2010
www.atmos-chem-phys-discuss.net/10/C5984/2010/

Atmospheric Chemistry and Physics Discussions

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.

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Received and published: 3 August 2010

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.

Response) Our sensitivity tests show that while some mass can switch between different SOA factors when using different rotations, the same four SOA factors remain in the different solutions. Each SOA factor has a unique composition profile and time series. The authors believe it is meaningful to investigate the differences between these factors, although when speaking of SOA mass, it is also appropriate to sum all SOA factors as has been done in the abstract and conclusions. More information on this topic is included in the following responses.

(2) More analysis, including additional PMF modeling, is needed to evaluate uncertainties in the PMF solution and the effect of such uncertainties on the apportionment results.

Response) More work on uncertainties has been included. See responses below and responses to Reviewer #1.

(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.

Response) Addressed in response to comment #10.

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.

Response) References added (Appel et al., 1979; Pandis et al., 1992; Turpin and Huntzicker, 1995). A sentence has been added to address the observed discrepancy: "This discrepancy is likely due to problems in the methods applied to obtain previous estimates (EC tracer method and SOA modeling in particular) and potentially changes in the fraction of SOA in the South Coast Air Basin due to a larger decrease in POA emissions compared to SOA precursor emissions, as discussed by Docherty et al. (2008)."

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

Response) Further text has been added to the figure caption to help readers differentiate the traces. (differentiating them by abundance in addition to shade)

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.)

Response) Questions regarding detector drift have been addressed in responses to Reviewer# 1 (e.g., comment#3). Detector drift has been incorporated in the calculation of IP for each compound.

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.

Response) See discussion below regarding division of SOA into 3 factors. The 9 and

7-factor solutions were chosen to minimize factor splitting, while maximizing what the authors have determined to be meaningful factors. By adding more factors, some factors begin to split into multiple factors with very similar chemical profiles. By using fewer factors, relevant factors are summed into a more general factor, diminishing the strength of TAG's high time and chemically-resolved data.

5. P6585L13: "Of 300 bootstraps, and of the resulting 2700 factors, only 124 factors (i.e. 4.6%) did not match the factor profiles defined in the base case." What is the criteria for determining whether a factor matches? How much variability is allowed in the profile/time series while still considering the factor to be a "match?" Are the nonmatches 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).

Response) Bootstrapping settings are explained on page 6579. The criteria for a match is a correlation > 0.6, as used as a default in the EPA method. The "unmatched" factors are distributed amongst all of the factors, but occur slightly more for factors that have other factors with similar diurnal trends (e.g. SOA factors).

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.

Response) Due to the large number of figures already supplied, this information has been summarized for the summer PMF and fall PMF analysis in two new figures (Fig. S3d and Fig. S5d, respectively). These new figures show the change in factor concentrations over a selected fPeak range. The same factors were obtained with each solution, profiles changed very little, and time series remained fairly stable, with the largest changes observed for swapping of some mass between SOA factors during midday.

7. Fig. S8: I'm not sure I understand the values displayed. Is this sum(residuals)/sum(total)-1? In the legend, it says sum(residual)/sum(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.

Response) The values shown are sum(residual)/sum(total). Values are summed individually for each compound. A fraction of each compound's fixed timeseries is attributed to each factor. This plot (fig. S8) is to show how much of each compound's timeseries has been used to create all the factors. Any deviation from 0 means that the compound was either used too much (<0, making it over-explained) or not enough (>0, making it under-explained). A value of 1 on this scale would mean that the compound was not used at all to create the factors. A value of 0 on this scale would mean that there was no residual and the reconstructed signal equals the measured signal.

See section 3.3 for clarification and examples. A explanation of "under-explained" has been added to the text: "Individual compounds that remained nearly 50% under-explained (i.e., the reconstructed signal from the chosen PMF solution is only half of the measured signal) during the summer included monopalmitin,...."

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- 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.

Response) Here, mass is only attributed to factors after the PMF analysis. It is the variability of TAG compounds alone that is driving our PMF solution. The primary biogenic factor still has a large contribution from TAG compounds. It is only after fitting the PMF factors to the AMS organics mass that this factor becomes a "low-mass" factor.

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

Response) Corrected.

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.

Response) 1) This is a good observation. We had originally tried to include a full correlation table within table 2, but it became too busy and crowded (9 factors in summer + 7 factors in fall, w/ correlations to 63 species = over 1000 correlations). We will gladly provide such a table for any readers that are curious enough to contact us for more information. For the case that the reviewer has pointed out, Ox has a correlation with SOA1, 2, and 3 of 0.39, 0.24, and 0.84, respectively. These values have been added to Section 3.1.1, with additional text to explain the meaningful distinction amongst SOA factors. Ox has a clearly increased correlation with SOA3, and we maintain that the three daytime SOA factors are unique enough to retain as separate factors. These results show the usefulness of the higher time resolution TAG measurements.

Response) 2) The highest correlation between summer factors is SOA1 and SOA3, and it is only a correlation of 0.35, which the authors feel is low enough to justify a distinction. During the fall, the highest correlation is between LV and SOA+FC2, with a correlation of only 0.24. A note has been added to the bottom of Table 2: "Note: Summer PMF factors all have correlations < 0.35 with other summer PMF factors, and fall PMF factors have correlations < 0.24 with other fall PMF factors."

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?

Response) The factors are stable. Some mass apportionment can be redistributed amongst SOA factors with different rotations, but the factors remain the same. See response to comment #6.

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

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?

Response) The authors have previously pointed out the uniqueness of each of these factors. These factors are likely not separated in the fall due to the lack of photochemical activity and the higher importance of meteorological transport during that period. It is likely that these summertime SOA factors are actually representative of different stages of photooxidation. Indicators of the photochemical age of atmospheric organic material may be useful in future studies for determining atmospheric reaction pathways and timescales.

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 (subAgedOCSO4) 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.

Response) The argument of diketones will be repeated here. SOA1 and SOA2 also have strong diurnal patterns, however, they peak earlier in the day than SOA3. We agree with the reviewer that there may also be a source-dependent difference between SOA3 and the other SOA factors. We are stating that the source of precursors for SOA3 aerosol is at a location further away than SOA1 and SOA2 sources, and in being further away, has had additional time to oxidize in the atmosphere under elevated oxidation conditions (as is seen by the high correlation between SOA3 and Ox). Less emphasis has been placed on relation of TAG organic compounds and VOCs, as VOCs have their own source dependencies (e.g., location, transport time, meteorological conditions). In our revised manuscript, we have revisited our argument of this case for clarity.

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

Response) They can't be completely decoupled. We do know that summertime meteorological conditions in Riverside were fairly repeatable during the focus period, with high winds from the west during the day, and stable/ very slow winds from the south at night. All we can know is that SOA factors that increase in the early morning have had less time to oxidize in the atmosphere, and have had less time to travel from their source region (meaning their precursors were emitted closer than SOA that shows up later in the day such as SOA3).

New Figure Captions:

Fig. S3. Summer PMF results. A) Q/Qexp values (y-axis) for 3 to 12 factors (x-axis). The chosen solution (9 factors) has a value of 2.9. B) Varying fpeak (x-axis) between ± 2 in increments of 0.5 displays a minimum Q/Qexp at fpeak = 0. C) Using over 60 seeds (starting points) produces identical Q/Qexp values for all solutions of the 9 factor case (p=9). Some fluctuation is observed when going to 10 factors. D) Solutions for 9-factor case, with various rotations (fPeak = -1, -0.5, 0, 0.5, 1). The same factors are found through all rotations, with some redistribution of mass amongst SOA factors.

Fig. S5. Fall PMF results. A) Q/Qexp values (y-axis) for 3 to 10 factors (x-axis). The chosen solution (7 factors) has a value of 3.3. B) Varying fpeak (x-axis) between ± 2 in increments of 0.5 displays a minimum Q/Qexp at fpeak = 0. C) Using over 60 seeds (starting points) produces identical Q/Qexp values for all solutions of the 7 factor case (p=7). Some fluctuation is observed when going to fewer factors (p=6). D) Solutions for 7-factor case, with various rotations (fPeak = -1, -0.5, 0, 0.5, 1). The same factors are found through all rotations, with some redistribution of mass between SOA and SOA+FC2.

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

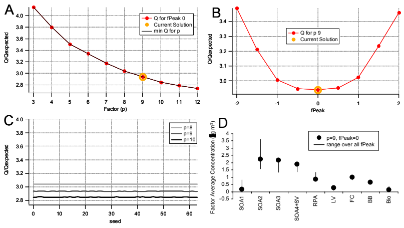

Fig. 1. Fig. S3 - See above for caption

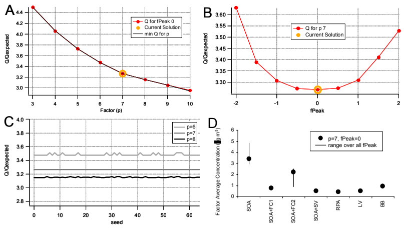

Fig. 2. Fig. S5 - See above for caption