

Interactive comment on “Primary to secondary organic aerosol: evolution of organic emissions from mobile combustion sources” by A. A. Presto et al.

Anonymous Referee #3

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This work used PMF analysis to determine separate factors from the organics formed in the photooxidation of diluted gasoline and diesel exhaust in chamber experiments. In most cases, two factors were obtained: POA and SOA. It was found that the POA mass spectra are similar to ambient HOA, while the SOA mass spectra are markedly different from ambient OOA factors. The authors did not observe substantial change in f44 with aging and suggested that only the first generation oxidation chemistry was achieved in these experiments. The authors also attempted to use the PMF factors and a basis set model to infer mixing of POA/SOA, where they concluded that in most cases the POA and SOA seem to mix and form a single phase.

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I think the manuscript is well-written overall, but I found it lacking substantial new insights. This work is similar to a previous publication by the same group (Sage et al.), one of the main differences was that PMF was used in this analysis while residual spectrum method was used in Sage et al. The authors pointed out that the assumption in Sage et al. where all the OA mass at m/z 57 was attributed to POA could lead to an erroneous split between the POA and SOA mass in that study. However, it appears in this work that all the OA mass at m/z 57 is associated with the POA factor (e.g., Fig. 2) and the assumption made in the residual method in Sage et al could be appropriate. Further, the authors observed some differences in this work and Sage et al. but did not provide sound explanations regarding these differences. Hence, it is not clear what the causes of such differences are.

The authors used the PMF factors and a basis set model to infer the mixing of POA/SOA. The analysis could potentially be interesting. However, I do not think that their conclusions are well-supported by the data. Neither results from “ideal mixing” nor “no mixing” seem to fit the data particularly well given the noisiness in the data.

This work belongs to a large body of publications from the same set of experiments. While the analysis was carefully done and well-presented in general, this work does not appear to offer substantial new insights to warrant a separate publication. I do not recommend publication at this stage. I suggest the authors either incorporate the results from this work into another manuscript to provide a more detailed, in depth analysis of the results from these experiments, or, they will have to expand this work substantially, and at the same time offer and emphasize the new scientific insights in addition to what are known from their previous publications.

Specific comments:

1. Page 24266, line 17. It should be f44 vs. f43.
2. Page 24267, lines 6-7. The authors stated that Sage et al. demonstrated that the mass spectra of SOA formed from photooxidation of dilute diesel engine exhaust are

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similar to ambient OOA. In this regard, it seems that the results from the current study are not consistent with Sage et al. The authors need to comment on this, given both the Sage et al. study and the current study are from the same group.

3. Page 24270, line 22. How are the VOCs measured and what are the specific VOCs identified?

4. Page 24270, line 27-28. The authors wrote that VOC:NOx ratio was adjusted by adding propene to investigate the effect of VOC/NOx ratio on aerosol formation. I do not understand how adding propene can provide useful information regarding the effect of VOC/NOx ratio on aerosol formation from the primary vapors. Please explain further. The authors noted that individual VOCs in the chamber were typically less than 1ppb. This would seem to suggest that propene will be the dominant precursor hydrocarbon. The radical chemistry in the system will then be dominated by peroxy radicals from the photooxidation of propene. How can this provide any insights into the aerosol formation from the vehicle exhaust (either with or without POA)? Further, the authors did not actually discuss the effects of VOC/NOx in the subsequent parts of the manuscript.

5. Page 24275, line 6. The authors noted that AMS still has 0.3 ug/m³ of organics with a HEPA filter upstream. This would seem to suggest that either the HEPA filter was not working or the authors did not adjust the fragmentation table correctly, or there was something else that was wrong with the instrument. If it is the fragmentation table, it could potentially affect all the mass spectra presented in the manuscript as well as the subsequent discussions/conclusions.

6. Page 24276, line 19. The authors should also show the mass spectra of the "pure SOA" systems. Are those mass spectra similar to the SOA factor shown in Fig. 2?

7. Page 24276, line 27. The authors should show the mass spectrum of the nitrate factor. It is unusual that almost half of the OA mass is at m/z 30. What is the source of this factor?

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8. Page 24277. The authors offered two explanations regarding the differences in the change of the mass spectra with further oxidation in Sage et al. and the current study. Neither explanation is sound. The authors discarded their first explanation and offered an alternative explanation that perhaps the difference could arise from the apportionment of all OA mass at m/z 57 to POA in Sage et al. However, from Fig. 2a it appears that all the OA mass at m/z 57 is assigned to POA in the current study as well. As noted in point #3, the authors need to reconcile the differences between this work and their previous study.

9. Page 24278, line 6. It should be f44 vs. f43.

10. Page 24279, line 24 The slope of -1 in Heald et al. is for all ambient data (including different OA types) while the slope of ~-0.5 in Ng et al. corresponds to OOA components from the ambient data. This should be clearly stated when citing these two publications.

11. Page 24279, line 28. The authors wrote that the Van Krevelen diagram results suggested that the SOA chemistry observed in gasoline vehicle experiments is atmospherically relevant. However, earlier they emphasized that the SOA mass spectra for the vehicles are markedly different from ambient OOA factors. These two statements seem contradictory. If the oxidation chemistry in their experiments is similar to ambient environments, shouldn't one expect the mass spectra to be similar as well?

12. Page 24280. The authors should also show the mass spectra of the SOA from diesel so readers can compare those with the mass spectra from gasoline SOA directly.

13. Page 24281, section 3.3. I think the use of the basis set model and PMF factors to infer the POA/SOA mixing in the experiments is not as informative as the authors suggested. The data points in Figure 6 are extremely noisy. What are the uncertainties? It is difficult to tell from Fig. 6 whether ideal mixing or no mixing would represent the data better.

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14. Supplementary info. I do not understand the context of Figure S5. More explanations of the figure and how it relates to the present work are needed.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 24263, 2013.

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