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

Anonymous Referee #2

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Review of Presto et al. “Primary to secondary organic aerosol: evolution of organic emissions from mobile combustion sources.”

General Comments

In this manuscript, the authors report results of chamber experiments examining SOA formation from a fleet of both gasoline and diesel-engine vehicles. The authors apply PMF to their quadrupole AMS data to partition OA into a POA factor and an SOA factor. The authors compare the smog chamber PMF factors to ambient HOA and OOA data and they evaluate the mixing of their chamber OOA and POA using the PMF factors and a simple model. The authors reach 3 main conclusions. First, they argue that the PMF analysis improves upon previously described methods to separate SOA and POA in these types of chamber experiments. Second, they argue that the POA factor derived in their experiments strongly resembles the ambient HOA while the SOA factor derived in their experiments does not resemble either ambient SV- or LV-OOA factors. Finally, they argue that the experiments provide evidence of mixing between SOA and POA.

The general topics of SOA formation from diesel or gasoline vehicle emissions and conversion of POA to SOA are certainly relevant and of interest to the readership of ACP. In this manuscript, the authors focus exclusively on analysis of quadrupole AMS data, particularly on PMF analysis of the quadrupole data. No other data is shown. It appears that at least 5 other manuscripts have been written detailing other aspects of the same set of experiments (Gordon et al 2013 a, b; May et al 2013 a,b,c). Therefore, the additional data that one would typically expect to find in a manuscript describing these types of experiments are missing, presumably because they are presented in the other papers (most of which are also in the review process).

The results described in this manuscript would potentially make a nice addition to a larger paper. However, as it reads now, I don't think this manuscript meets the criteria for publication as a stand-alone paper. The scope of the work is very narrow and the conclusions are not sufficiently supported by the data, scientifically novel, or well-developed for this work to stand on its own. As the authors point out, a number of studies have previously reported on SOA formation from dilute vehicle exhaust and it isn't clear what new insights this manuscript provides. I encourage the authors to consider combining the results presented here with some of the other data to make a more robust, novel, and substantive manuscripts. Alternatively, the present manuscript should be substantially revised before publication to 1) further substantiate their conclusions and 2) expand on the presented material and discussion so that is more clear what this study adds to the scientific understanding of the topic and how this study improves upon or is different from previous studies. More specifics are below.

Major Specific Comments

As the authors point out, there have been a large number of chamber studies of SOA formation from vehicle emissions, many of them from their group. There is certainly novel and exciting science that has and will continue to come out of this type of work. In this manuscript, the authors present a narrow slice (PMF analysis of quadrupole AMS data) of data from what appear to be well conducted experiments. The difficulty I have with this paper is identifying what new scientific insights this paper reports. The authors have 3 major points, but I don't find any of these sections sufficiently well developed to warrant a stand-alone publication.

First, the authors make the argument that the PMF method is an improvement over past approaches to separate POA and SOA in these types of experiments. However, they don't show a comparison of their method with previous methods. Furthermore, the majority of the figures show data for which POA does not appear to evaporate and is well described by a simple first-order wall loss. To improve this section, the authors could present some comparisons of the PMF-derived POA and SOA time traces and spectra with similar data using previous methods to show that this method is better and how/why. They could also extend their analysis to data where the POA was observed to evaporate, though the experiment where this was observed appears to be an outlier. In short, the benefits of the PMF analysis are not clear. More comments follow below specific to the figures.

Second, the authors make comparisons of the SOA and POA factors from their chamber experiment to ambient data. They conclude that the diesel SOA does not resemble either ambient SV- or LV-OOA. This contrasts earlier work from the same group (for example Sage et al 2008) (Sage et al., 2008). The authors offer a few short explanations of why this might be the case, but quickly rule them out. It would improve the paper if the authors could offer some reasonable explanation for the difference. I have further technical questions about this comparison detailed below. However, the actual differences between the ambient OOA spectra and the chamber-derived SOA spectra are never presented or discussed, beyond the correlations. I suspect significant insight could be gained from examining the differences in the spectra.

Finally, the authors use the PMF factors and a simple model to infer the miscibility of SOA and POA. The analysis here doesn't seem very robust. First the data are very noisy and appear to agree with either model assumption within the measurement noise. Second, the model is very simple and has many assumptions that aren't well constrained but could change the predictions (for example the POA heat of vaporization and/or mass transfer limitations induced by low-viscosity SOA (Vaden et al., 2011)). Finally, I'm not clear on how the PMF, which is the main data reported in this work, improves the quality of the POA/SOA apportionment. Asa-Awuka et al (2009) provide a much more thorough, robust, and convincing demonstration of POA/SOA mixing state (Asa-Awuku et al., 2009). It isn't clear that the present work is an improvement upon Asa-Awuku or presents new or different results. More specific comments on figure 6 are below.

P24279,L16-30. The relationship between m/z 44 and O:C described in Aiken et al (2008) is based on ambient data. If the chamber SOA spectra really aren't similar to ambient OOA spectra the Aiken parameterization may not work well. Similar to additional comments elsewhere, it would improve the paper if the authors expand the discussion of the differences between the ambient and chamber SOA spectra.

P24275, L3-9. The fact that the AMS measures 0.3-0.5 ug/m3 of organic aerosol when behind a filter suggests the frag table wasn't adjusted properly. Were adjustments made to the frag table based on the filter measurements? If the frag table isn't adjusted properly, it could bias the SOA spectra. It could also explain why the SOA factor doesn't appear to agree with the ambient data.

Figure 1: The POA concentration appears to be well-modeled by simple wall loss in

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this experiment. Will the PMF work as well when POA is lost by evaporation? How does the residual change when the data is more complicated?

Figure 2: Please provide a short description of what exactly is plotted in the correlation plots. The scatter in the SOA correlation plot looks to be dominated by 2 m/z values. What are those m/z's? Is it possible these differences are a result of different frag tables that were used to process the data at m/z 28, 18, etc? It is clear that m/z 28 is not set equal to m/z 44 in the chamber SOA spectrum, which is a common practice in ambient data sets. The manuscript would benefit from a more thorough discussion of the difference between the chamber and ambient OOA factors.

Figure 4: The authors state there is high correlation between gas SOA and diesel SOA (m= 1.11, R2 = 0.94) and gas POA and diesel POA (m= 1.11, R2 = 0.94) yet poor correlation between gas SOA and ambient LV-OOA (m=0.74, R2=.93). The R2 is similar in all cases and the deviation of the slopes from 1 is reasonable in all cases, especially considering the uncertainties. Please expand on why you conclude the correlation is good in two cases, but poor in the third. The high R2 but non-zero slope implies to me that differences in frag tables such that f_m/z is changed equally across the entire spectrum. This could happen for instance by setting m/z 28 = m/z 44 in one case but not the other.

Regarding Figure 6: 1) I don't understand the use of data from test D5.2 in this figure. Figure 5a shows that the POA doesn't evaporate and is well-modeled by a simple first order wall loss. If this is the case, what is the added value of the PMF? It seems PMF is not needed to separate SOA from POA. If instead, the point is to validate the PMF method, shouldn't PMF be challenged with a more difficult experiment? I suggest adding a second panel to Figure 6 showing the same techniques applied to the data from case D4.1or similar.

2) The POA data are very noisy, particularly near the end of the experiments where the models diverge do a significant degree. Why are the data so noisy? The noise appears

to be are on the order of 2-4 ug/m3. Based on the noise, it is easy to imagine either model fitting the data adequately, especially considering all the uncertainties with the model. Please add errors bars to the POA trace. Are the experiments sensitive enough to the effect of mixing to detect a different in the models? Are there other cases where the models diverge to a larger degree relative to the noise the authors can show?

3) The “no chemistry” case suggests that the temperature increase had a substantial effect on the observed POA, relative to the difference between the models. If a larger or smaller temperature correction is applied, how does the data compare to the models? What is the estimated uncertainty in the temperature correction? Can the authors show a simple sensitivity analysis of the temperature correction?

Minor Comments and Technical Corrections

P24286, L20: I suggest changing this to “the answer to the first question may be yes” or something similar. The author points out several conditions where the factors are not physically interpretable.

P24268, L14-17. Please clarify where the results of Asa-Awuka et al (2009) and Song et al (2007) are similar and where they contrast (Song et al., 2007;Asa-Awuku et al., 2009). Both came to similar conclusions about the mixing of SOA with lubricating oil particles. Asa-Awuka et al (2009) observe that diesel POA and SOA do mix while Song et al. do not investigate diesel POA. Both papers are in agreement when comparing similar systems.

P24270, L27. How was the total VOC concentration measured?

P24272, L11. Please clarify what you mean when saying there was no evidence of organic particle signal at m/z 28. The quadrupole doesn’t have sufficient resolution to separate CO+ and N2+. The N2+ signal will be so large that it will completely overwhelm any signal at m/z 28 from the modest amounts of SOA formed in these experiments. Most experiments with SOA find significant particulate CO+, to the extent

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that the “default” frag table has been modified such that org_28 = org_44 (Aiken et al., 2008). Furthermore, the authors argue that oxidation chemistry is proceeding via a combination of carboxylic acid and alcohol/peroxide formation. Studies have shown that organic acids produce signal at m/z 28. So what is different about this SOA?

P24271, L13- 14. If a minor fraction of the nitrate signal is organic nitrate, how is the inorganic nitrate condensing on the particles? The vapor pressure of nitric acid is much too high for condensation (Duisman and Stern, 1969) and it is unlikely that a few monolayers of adsorbed nitric acid would be detectable by the quadrupole AMS. Do the authors have excess ammonia in the chamber? Do you see evidence of ammonium nitrate formation?

P24284, L 9-10. PMF wasn’t performed on the SOA only experiments, so please be specific on what you mean when you say they “produced a single SOA”. The wording implies to me that you only extracted one PMF factor.

Figure 1: I suggest removing the thermodenuder data to make the figure less confusing, since it isn’t used or discussed in the manuscript.

Figure 4. The small panels are very difficult to read and are likely to be even smaller in the final printed version. I suggest splitting F4 into two figures to improve legibility.

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