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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Organic aerosol components derived from 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy" *by* M. Crippa et al.

Anonymous Referee #2

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The manuscript utilized a ME-2 based source apportionment approach to analyze 25 AMS datasets collected during the EUCAARI campaign and provided an overview of the organic aerosols in Europe. Four organic components were retrieved at most sites: HOA, BBOA, SV-OOA, and LV-OOA. It is suggested that with the PMF/ME-2 approach, one can better resolve the HOA and BBOA factors generally, especially in resolving the HOA factor at rural/remote sites.

Analyzing 25 AMS datasets is not a trivial task and this manuscript succeeded in providing a comprehensive overview of the OA factors resolved at different sites across Europe. One of the main objectives of the manuscript is to demonstrate the use of

PMF/ME-2 technique in source apportionments across multiple sites, ranging from urban to rural sites. While the details regarding this technique have been documented in some previous publications, I think it is important to provide some basic information in this manuscript as well. The use of ME-2 requires a-priori information. However, there are very little information and discussion in the manuscript regarding how the choice of a particular source profile will affect the source apportionment results. Further, a parameter referred to as "a-value" is used to allow for variations in the source profiles. However, the significance of this "a-value" is not discussed. The authors listed some ranges of "a-values" but they should provide more justification regarding the choice of the "a-value".

One of the advantages of the method outlined in the manuscript is the ability to resolve HOA factor even at remote/rural sites, and/or to provide a "cleaner" separation between the HOA and BBOA factor. This is an improvement over the unconstrained PMF analysis. However, I have some concerns regarding how the a-priori information could affect source apportionment results. In their analysis, OOA components are not fixed. Technically, one should expect the OOA components to be fairly stable and comparable between this PMF/ME-2 analysis and the unconstrained PMF analysis. The authors provided a comparison for the results at a few sites in the Supplementary information (S1-3). There is a fairly large discrepancy between the SVOOA and LVOOA factors resolved by the two methods in the Barcelona dataset, where it appears that the contributions from SVOOA and LVOOA are swapped in the two analyses. This large discrepancy is quite concerning but there is no discussion regarding this. If the OOA source apportionments are so different between the two methods, what does this actually mean? What does this infer about the robustness of their approach? How does one decide which approach gives more "accurate" source apportionment results? This is a critical issue that needs to be addressed. Without further information, it is not possible to tell how the source apportionment results from the two methods compare at other sites. But, I urge the authors to perform a systematic analysis about this and provide justification/guidelines on how to interpret their results when compared to traditional

unconstrained PMF analysis.

As it stands now, the manuscript provides information such as what factors are resolved at each site and how much each factor contributes to the total OA at each site. There is no discussion regarding what all these mean. While this manuscript provides a nice overview of the source apportionments of OA in Europe, I think this would have been a much more impactful paper if the authors could also discuss their data in the context of the sources and atmospheric processing of the OA across Europe, i.e., providing more scientific context in addition to the source apportionment results.

Overall, I think the manuscript is well-written and provided tremendous information regarding the sources of OA in Europe. However, there are a fairly amount of issues that should be addressed prior to the publication of this manuscript, as noted in the previous paragraphs as well as the more detailed comments provided below.

Detailed technical comments:

1. Page 23335. The authors presented the sequential steps of the methodology. I understand that the details of using PMF with ME-2 have been documented in some previous publications. However, more information needs to be included in the current manuscript to provide context.

a. What is a – value? What is the significance of it? How are the ranges chosen for different OA types? How does one define whether a particular "a-value" is low or high? (e.g., the authors referred to a "a-value" to 0.05 as "low", but no context was provided)

b. How does one determine from the f55 vs f57 plot whether to constrain COA or not?

2. Page 23338. The authors used the HOA and COA MS identified in Paris by Crippa et al. and BBOA from Ng et al. as their source spectra. As choosing a particular source profile to fix is an important step in their methodology, more justification is needed regarding how they chose the reference MS. Further, how sensitive are their results with respect to the input MS? Did the authors use other MS as inputs and examine

how that affects the source apportionment results?

3. Page 23340. Section 4.1. The authors indicated that while unconstrained PMF does not necessarily allow for identification of HOA or separation of HOA and BBOA, the ME-2 methodology allow for retrieval of POA and SOA sources for all of the datasets.

a. When examining Table S1-2, it seems that for a number of sites, HOA and BBOA can already be resolved with the unconstrained PMF analysis. For these datasets, the authors should discuss if and how one can more insights into the sources of OA by performing the PMF/ME-2 analysis instead of just using the unconstrained PMF.

b. In SI-3, the authors compared the factors retrieved with their method and the unconstrained PMF analysis. While the degree of association is reasonable (just judging by looking at the plots, the authors should really include R2 values in their plots), the slopes vary from $\sim$0.3 to 2, which is quite concerning. Take the Barcelona data as an example, both their method and the unconstrained PMF resolved 5 factors. Based on the discussions in the manuscript, one of the main advantages of their approach is the ability to resolve "clean" HOA and BBOA factors. From Figure SI-3.2, it appears the PMF/ME-2 analysis is taking some BBOA resolved from the unconstrained PMF analysis and apportioning that as HOA in the PMF/ME-2 analysis. However, if the PMF/ME-2 is robust, I do not understand how the SV-OOA and LV-OOA apportionments in the PMF/ME-2 and unconstrained PMF analysis are so far off (slope = 0.3 and 1.7 for SV, and LV), given that the OOA components are not fixed. Why? What does this mean in terms of robustness of their analysis? This needs to be carefully addressed. For this dataset, given the SVOOA and LVOOA apportionment is so different between the two methods, I would also be curious in seeing how MS of SV and LVOOA look like for the two methods. Further, in this particular scenario where both approaches resolve the same number of factors, how does one evaluate if one approach is "better" and/or more accurate than the other?

c. Overall, I think the authors should provide a more thorough comparison of the source

apportionment results from their method and the unconstrained PMF approach. I understand with large number of datasets, it is unrealistic to include plots such as Figure S3 for all sites, but at least the authors should provide a table of R value, slope, and intercept for the factors resolved by the two methods at all sites and comment on the differences.

4. Page 23342. It is curious that across all the sites, the COA factor is only resolved from the Barcelona dataset. Many of the sites included in this study are urban sites, where according to the authors, the OA should have some contributions from cooking activities. What does it mean when no COA is resolved at all these other sites even though this source profile is fixed in the analysis?

5. Page 23342. I think Figure 5 is a very interesting figure but more interpretation and discussion are needed.

a. Why is the average plots shown for rural sites and marine sites, but only results from Barcelona are shown? The authors noted "our conclusions for the Barcelona site might not have general validity" so I am not sure why only Barcelona data are shown. How does the average plot for all urban sites look like? Is Barcelona a good representative of all urban sites?

b. The authors noted that "HOA contribution deceases with increasing OA contributions" for rural sites. What does this observation mean? Can the authors provide some discussion regarding what this mean in terms of the sources of OA at rural sites and the processing of OA at these sites?

c. For the Barcelona data, it appears that the fraction of LV-OOA first decreases with OA mass concentration then increases. There is no discussion about this in the manuscript. At low OA concentrations, only the highly oxidized species (likely LV-OOA?) will partition into the particle phase. If so, one should expect the fraction of LV-OOA to be highest at the lowest OA mass concentration? But this is not the case here. Please explain.

6. Page 23343. As noted by the authors, the diurnal pattern for LV-OOA is rather flat. Traditionally, LVOOA is linked to the photochemical production of SOA in mid-afternoon. Is the lack of an afternoon peak in their data simply a result of sampling time (i.e., not summer)? Please elaborate further.

7. Page 23343. The authors noted that the interpretation of the factors is based on comparison with external data, examination of diurnal patterns, and comparison of factor MS with reference MS. These are fairly standard procedures in the unconstrained PMF analysis as well. However, the data from Table S1-3 showed that the correlations of SV-OOA with NO3 and LV-OOA with SO4 are very poor at many sites (some even have a R2 value as low as 0.11). The authors noted that "depending on the specific features of the SV-OOA and LV-OOA components, associated with their origins and processing in the atmosphere, their correlations with the secondary inorganic species might not be very high".

a. What does "specific features of the SVOOA and LVOOA?" mean? If one of the criteria to decide on the number of factors is correlations with external tracers, how did the authors handle the many cases where the correlations of OOA factors with external tracers are so poor? Did the authors simply resolve to using diurnal patterns and comparison of MS only? I think the authors need to clearly justify how their solutions were chosen, given the poor correlation of their OA factors with external tracers.

b. Related to this comment, how do the OA factors resolved from the unconstrained PMF correlate with external tracers? Worse, better? The authors should comment on this.

8. Page 23348. It is not clear to me why sensitivity analysis on the BBOA factor cannot be performed. It appears that the variability of the BBOA factor across all sites is much larger than the HOA factor. If this is the case, I am wondering how robust is the BBOA factor retrieved in their analysis? The BBOA source profile from Ng et al is used to fix their BBOA factor. If fundamentally BBOA has more variations than HOA,

how do the authors justify the choice of a particular BBOA source profile as their input? How would that affect their source apportionment results in terms of the BBOA factor? Further, given that many sites have the BBOA factor, I think the authors should take the opportunity to systematically examine the variations in the BBOA factors resolved at different sites and include the results in this manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 23325, 2013.