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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.

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Answers to Referee 2 comments We thank the reviewer for the valuable comments that helped improving the manuscript. 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".

Following the suggestions of both Referees, we included a paragraph in the supplementary material to discuss the importance of the selection of a reference mass spectrum. A complete answer to this point is provided in the detailed technical comments at point 2.

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.

The main goal of our work is to provide a technical support to source apportionment users, in order to reduce the subjectivity in this analysis performing ME2 in a consistent way. We agree with the Referee that a huge amount of scientific information is included in 25 datasets, but we cannot deeply discuss all the features and differences occurring among the sites (both in terms of source features and quantification, and meteorological patterns happening during the campaigns). The overview on all these data is provided by the work of Nemitz et al. (in preparation). Model evaluation papers integrating the information on the emissions, aging and the measurements are underway (e.g. Li et al., 2013)

A table reporting the sites list, together with their location (longitude and latitude) as well as the site classification (urban, rural, remote, high altitude), is now included in the supplementary material (Table SI-4) to drive the reader in the results visualization

and interpretation. Few sentences are also added to explain why specific features are observed at some sites. For example:

"Although Puijo is classified as rural site, it has nearly the largest HOA fraction since located on a hill at 2 km from the city center of Kuopio (population 97000) which is a source of HOA and few point sources (Leskinen et al., 2012;Hao et al., 2013). However, in absolute terms, HOA concentrations in Puijo are rather low (0.2 μg/m3), while in sites with high total OA concentrations the absolute HOA amount is higher compared to rural sites."

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)

As reported in the manuscript, the a-value represents the allowed variability given to the algorithm to fit a mass spectrum from the constrained one (refer to equations 3a and 3b). Therefore, low a-values are close to 0 while a=1 means represents a variability of 100%. This concept is defined in the manuscript as following:

"The a-value (ranging from 0 up to values larger than 1) determines how much the resolved factors (fj,solution and gi,solution) are allowed to vary from the input ones (fj, gi), as defined in eq. 3a and 3b (Canonaco et al., 2013). In our work we only constrained the mass spectra represented by f.

(3a) (3b)

For example, if a=0.1 when constraining a mass spectral profile, all of the m/z's in the fit profile can vary as much as -10% to +10% of the input constraining mass spectrum profile".

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

As reported by Mohr et al. (2012), enhanced ratios of f55/f57 during specific hours of the day (meal hours) suggest the presence of a cooking source. So, looking at the presence of a temporal structure of the f55 vs f57 plot the user can identify the presence of cooking activities.

This concept is clarified in the manuscript with the following sentences:

"To interpret the retrieved factor as a cooking-related source, its diurnal pattern should show two peaks corresponding to the meal hours at least in urban or semi-urban sites. As demonstrated in Fig. 6 of the work by Mohr et al. (2012), the f55 vs. f57 plot can provide further evidence of COA in urban sites strongly affected by cooking activities. In fact, the triangular space defined by Mohr et al. (2012) allows the identification of cooking influenced OA for points laying on the left hand side of this triangle which are dominated by f55 (and therefore cooking emissions) compared to points dominated by the traffic source (laying on the right hand side of the triangle)."

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?

As pointed out by the Referee, the selection of the reference mass spectra to be constrained when running the ME-2 approach is critical and it might affect the source apportionment output. However, the correlation coefficient between the HOA MS of Crippa et al. and Ng et al. is high (R2=0.99), as well as with those of direct vehicle emissions (R2=0.94 and 0.96, considering gasoline and diesel emission spectra, respectively, reported by Mohr et al. (2009)). Therefore, the choice of the Crippa et al. HOA MS to run ME2 did not influence the output MS. However, for more variable mass spectra, like for the BBOA case, the selection of a starting BBOA MS might affect more the output MS. In order to take into account the uncertainty and variability of the input MS, a larger a-value is assumed. In this way the reference MS gives the algorithm an indication of the features of the source mass spectrum it should retrieve, while a larger a-value gives the algorithm the freedom to better fit the measured data. Moreover, our study is consistent with Canonaco et al., (2013) who tested and evaluated good ranges of a-value for HOA, BBOA and COA for the case of Zurich (identified a-value range = 0-0.2). In order to partly address the importance of the selection of a reference MS when using ME2, we included a section in the supplementary material (see below) reporting the different OA apportionment obtained using 2 reference HOA MS for a selection of datasets.

The following paragraph has been added to the manuscript (in section 4.5) as well as chapter SI-6 of the supplementary material:

"Finally, we recognize that the selection of the reference mass spectra to be constrained when running the ME-2 approach is critical and it might affect the source apportionment output. Therefore, in Sect. 6 of the Supplementary Material, the effect of the choice of specific mass spectrum as reference when running ME-2 on the source apportionment output is investigated. However, a future study using more suited datasets with more external constraints on the validity of the retrieved sources will be performed to fully address this important task."

SI-6 Effect of a-priori information on the ME-2 output In this section we briefly introduce a critical aspect of our work that is the influence of a specific mass spectrum taken as reference when running ME-2 on the source apportionment output. Here we test the effect of fixing the HOA MS presented by Crippa et al. (2013) and the average one provided by Ng et al. (2011) for the Northern Hemisphere on the ME-2 output. Table SI-6 reports the relative contribution of OA sources to total organics varying the constrained HOA MS. We report these results for a range of a-values (0.05-0.2).

Table SI-6: Comparison of OA source apportionment results (mass fractions) constraining in ME-2 two reference HOA MS (HOA from Crippa et al., 2013 (this study) and from Ng et al., 2011). Relative contribution of OA sources to total organics is reported for 7 case studies considering an a-value range for HOA of 0.05-0.20. In the table, the first number refers to the solution obtained with an a-value of 0.05 and the second one to with a-value of 0.2.

reference MS HOA BBOA SV-OOA LV-OOA COA BCN spring 09 HOA Ng et al. 2011 0.21-0.22 0.08-0.08 0.19-0.14 0.38-0.39 0.14-0.16 HOA (this study) 0.24-0.25 0.09-0.07 0.13-0.10 0.37-0.34 0.17-0.14 MPZ spring 08 HOA Ng et al. 2011 0.04-0.07 - 0.44-0.39 0.53-0.54 - HOA (this study) 0.07-0.06 - 0.37-0.34 0.56-0.60 - MPZ fall 08 HOA Ng et al. 2011 0.10-0.11 0.19-0.19 0.28-0.23 0.42-0.47 - HOA (this study) 0.08-0.08 0.14-0.15 0.34-0.31 0.44-0.46 - MPZ spring 09 HOA Ng et al. 2011 0.06-0.07 0.11-0.11 0.25-0.25 0.58-0.57 - HOA (this study) 0.10-0.10 0.17-0.10 0.30-0.28 0.43-0.52 - VAV fall 08 HOA Ng et al. 2011 0.16-0.17 0.19-0.16 - 0.69-0.67 - HOA (this study) 0.20-0.22 0.13-0.13 - 0.67-0.65 - VAV spring 09 HOA Ng et al. 2011 0.11-0.09 0.15-0.17 0.23-0.34 0.51-0.41 - HOA (this study) 0.10-0.13 0.15-0.16 0.26-0.20 0.49-0.51 -

As shown in Table SI-6, varying the constrained reference HOA MS in ME-2 has an influence on the OA source attribution. However, for most of the cases, only a variation of few percent in the relative contribution of OA sources to total OA can be observed. In order to fully address this critical topic, a more systematic study is planned using more suitable datasets with the full complement of external measurements to constrain and

validate the solution.

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.

The following paragraph is introduced in the supplementary material to discuss the results presented in table SI-2:

“Table SI-2 shows the comparison between OA sources retrieved with the unconstrained PMF run and with our methodology. For some datasets high resolution data were available and the PMF algorithm was able to separate the same type of sources as in our approach (see for further details section SI-3). This is the case of Barcelona, Helsinki, Mace Head, Montseny and San Pietro Capofiume. For most of the other sites, we were able to identify more primary sources and/or determine the split between OOA components following the standardized procedure here introduced (e.g. Hyytiala, Jungfraujoch, K-Puszta, Melpitz, Puijo, Puy de Dome, Vavihill, Harwell). In the case of Chilbolton, the HOA MS was constrained to get better separation of the other components, although both POA and SOA sources were retrieved by the unconstrained run too.”

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 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?

The authors do not claim that their solution is better than the one obtained with the HR-PMF, since actually the exact mass information available within the high resolution dataset is much more detailed compared to the unit mass resolution data. The algorithm in the HR-PMF uses the covariance of specific ions to identify OA sources, while this is only employed within ratios of the UMR variables. Moreover, in this paper we showed the possibility to use ME-2 to extract more information from the UMR spectra that is often not otherwise possible with unconstrained UMR PMF and the comparison to more information-rich HR PMF is meant as one assessment of how well it works and not to show which solution is better or more correct. The motivation of our work is due to the fact that often HR spectra are not available (e.g. in many air quality monitoring stations ACSMs, etc. are deployed and not HR-AMS) and thus the utility/need for this method.

The following sentences are now included as discussion in the supplementary material:

“In this section the comparison between source apportionment solutions retrieved with our standardized method and UMR/HR-PMF results available for some field campaigns is reported. In our work we showed the possibility to use ME-2 to extract more information from the UMR spectra that is often not otherwise possible with unconstrained UMR PMF and the comparison to more information-rich HR PMF is only meant as one assessment of how well it works. The motivation of our work is due to the fact that often HR spectra are not available (e.g. in many air quality monitoring stations ACSMs, etc. are deployed and not HR-AMS) and thus the utility/need for this method. This analysis shows that our source apportionment procedure produces quite comparable results with UMR/HR-PMF in the cases of Montseny (Fig. SI-3.1). However, Fig. SI-3.2 highlights some issues with the quantification of OA sources in Barcelona, in fact despite the good agreement in terms of temporal correlations for all sources between the two methods, the slopes of the linear fit look quite different. A slope of 1.9 is found for HOA, which appears to be lower in our approach, while more comparable results are found for COA (slope 1.09). This is possibly due to the exact attribution of the reduced ions at mass 41, 43, 55 and 57 to the HOA MS and the oxygenated part to COA by the HR-PMF making use of the high resolution information. On the other hand, both BBOA and SV-OOA are underestimated by our methodology while LV-OOA is here overestimated. This underlines the uncertainty associated with the attribution of specific masses like m/z 43 and m/z 44 to BBOA and to the oxygenated components, which are not characterized by constant mass spectra over the world and the season. Some discrepancies are also observed for the Cabauw case (Fig. SI-3.3) since our solution additionally includes a BBOA factor compared to the work of Paglione et al. (2013).“ Below, the MS of the HR-PMF solution presented in Fig.2 by Mohr et al., (2012) for the Barcelona dataset is reported, as well as the source MS retrieved with our methodology.

The comparison of these two set of MS shows that within the primary sources some ratios between the most important m/z for each spectrum, as well as their contribution to the total signal, are partly different. As expected, major differences can be observed for the ratios within the BBOA MS. Moreover, different degree of oxygenation is observed for SV-OOA and LV-OOA comparing the 2 solutions (higher m/z44 to m/z43 ratio is found for LV-OOA and SV-OOA for the HR-PMF solution).

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.

We agree with the Referee comment that a comparison between the unconstrained PMF run and the chosen ME2 solution should be reported. However, this task is not realistic and sometimes it is not even meaningful. In fact, we cannot provide for 25 campaigns having on average 3 sources for each site the R2, slope and intercept for the MS and time series of each source when comparing the two methods. Moreover, these values (R2, slope and intercept) should be reported for a solution having the same number of factors between the 2 methods, but in the case of PMF some of the factors are not meaningful. Finally, this comparison would not take into account the residuals, which are in some cases reduced when running ME2 compared to the unconstrained PMF. These are the reasons for which we did not report a systematic comparison, but only the number and type of factors we were able to retrieve with the two methods. Factor time series and mass spectra of ME2 and PMF solutions will be available on the AMS spectral database (http://cires.colorado.edu/jimenez-group/AMSsd/#Ambient), so that everyone can compare differences for a specific site. Moreover, an unconstrained run is simply one shot in the solution space, whereas by the means of the constrained information we rotate the solution in a more specific way. Hence, it is not relevant in many cases to compare the two approaches, since the unconstrained run might not contain a useful solution. More systematic intercomparisons should be done for individual data sets where also lots of additional external data is available to constrain the data.

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?

Barcelona, together with Helsinki, is the only urban site (as reported in Table SI-4), therefore it is not surprising that we are able to quantify the cooking source only in Barcelona characterized by numerous restaurants, open air barbecues, etc. (while reduced cooking activity is expected in Helsinki, especially during wintertime). Besides the less intense cooking activity in Helsinki, also the station is located ∼5 km from the downtown. There's a big road near (significant contribution from traffic) but almost no restaurants. In fact, the station is defined as urban background (Järvi et al., 2009).

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?

The Barcelona site is the only urban site together with Helsinki. However, only for the Barcelona dataset it was possible to separate a cooking source. That is why we reported this case in a separate panel (since it was not possible to average it with any other dataset). Moreover, Barcelona can be representative of typical urban sources (traffic, cooking, wood burning, etc.), as discussed in the text, but not necessarily for the secondary components.

"For an urban site like Barcelona (see Fig. 5b), traffic is a significant source both at low and high OA concentrations, while the semi-volatile oxygenated component is rather low. However, the differentiation between SV- and LV-OOA is highly dependent on the oxidation processes in the atmosphere, geographical position of the measurement site, season, meteorological conditions, etc., therefore our conclusions for the Barcelona site might not have general validity."

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?

At rural sites, the major fraction of the OA component is expected to derive from secondary formation processes, involving for example the oxidation of primary emissions and gas into particle conversion. Transport of air masses plays also an important role depending on the site location. When higher OA concentrations are observed at rural sites, the major contribution does not derive from primarily emitted OA particles but it is mainly associated with transported air masses (e.g. from polluted areas, cities, etc.) with an increased fraction of SOA compared to urban sites. Also the semi-volatile fractions of HOA will slowly degrade and the low volatile fractions of HOA may change due to heterogeneous or condensed phase reactions.

b. 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 LVOOA?) 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.

We do not observe the pattern identified by the Reviewer. In Fig.5 (panel b), the relative contribution of LV-OOA to total OA mass is higher at lower OA concentrations and then it increases. Above 20 ug/m3 of OA, LV-OOA relative contribution is instead quite constant.

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.

As shown in Figure 6, the LV-OOA diurnal pattern is rather flat, although a relatively small afternoon increase can be observed especially during the late spring measurement campaign of 2008. However, no relevant daily features are observed for this component possibly due to the sampling time and/or atmospheric processes.

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. Usually it is expected that secondary OA components temporally co-vary with secondary inorganic fractions, however in our work we distinguish between SV-OOA and LV-OOA just because of their different degree of oxidation (which can be represented in their mass spectrum by the mz43 to mz44 ratio) and the possible anti-correlation of SV-OOA with temperature. There are many reasons why SV-OOA may not correlate well with nitrate or LV-OOA with sulfate. The NOx, SO2 and VOC emissions leading to the components are often not collocated. So if advection of air masses from different regions with different ratios occurs, one would not expect good correlations. One could e.g. assume that marine air masses and more urban air masses should have different ratios; also air masses from Poland with higher SO2 emissions from coal would be expected to provide different ratios. If ammonia is limited, then nitrate might not form at all because ammonia is used to neutralize sulfuric acid but SV-OOA is still formed. Processing in clouds may also change the ratios and the removal of the components by rain may not be equal if the components are partially externally mixed. So the correlations are actually only expected to be high in a region where the ratios of precursors do not vary very much upwind of the station.

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.

As already discussed, in order to distinguish the SV-OOA and LV-OOA fractions we think the correlation with NO3 and SO4 as external tracers is not the only metric to be considered. It does not seem to make much sense and would be tiresome for so many datasets to discuss here the PMF solutions in detail that could obviously not unmix the components. It would in our opinion not mean much if e.g. an SV-OOA or LV-OOA in Melpitz derived from PMF without being able to extract a primary component would have a slightly better or worse correlation with nitrate or sulfate than the ME-2 solution.

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.

As reported in ambient and chamber studies, the BBOA MS varies depending on burning conditions, type of wood etc. Therefore it is difficult to define a reference primary BBOA MS and the right a-value range. We surely recommend using a larger a-value than for HOA in general. For individual datasets one can do detailed analyses including correlations of tracers (mostly from external data) of the different sources as a function of the a-value chosen. Also intercomparisons of mass spectra or diurnal cycles are tools to judge the solution. There will always remain some subjectively chosen criteria on why certain solutions are not accepted. In the manuscript, we recommend the users to explore a wide range of a-values for BBOA. Here we chose the concept to provide a consistent approach using one reference profile with an a-value that allows for reasonable adjustment of the factor to the specific conditions of the campaigns. This a-value was chosen from experience after exploration of the solution of previous campaigns. However, we decided to show here in addition a sensitivity analysis to partly investigate the BBOA MS variability using an a-value range of 0.2 and 0.4. In order to see how robust the results remain, a comparison of these results with the ones obtained with an a-value of 0.3 are now reported Table 4.

The following paragraph has been added to section 4.5 (Sensitivity analysis of the a-value approach) of the manuscript:

“Concerning BBOA, an a-value of 0.3 is found to give reasonable freedom to the BBOA MS in the ME-2 model, while it is not possible to define a consistent a-value upper limit for all the sites. In fact it is difficult to define a criterion to determine when the BBOA factor fails when increasing the a-value, due to the variable features of the BBOA MS and the lack of stronger metrics in this study. In our study we present a sensitivity test for BBOA varying the a-value in the range 0.2-0.4 and we report the relative contribution of OA sources to total organic as a function of the a-value extremes of the investigated range (refer to Table 4). However, if a-priori knowledge about wood burning conditions is available for a site, we suggest to constrain the BBOA MS deriving from the same kind of burning conditions, instead of using an average BBOA MS."

Table 4: Sensitivity analysis for the BBOA factor (a-value range=0.2-0.4, a-value for HOA=0.05). The relative contribution of OA sources to the total OA is reported varying the BBOA a-value. In the table, the first number refers to the solution obtained with an a-value of 0.2 and the second one to with a-value of 0.4. site HOA BBOA SV-OOA LV-OOA COA MSA BCN 0.25-0.25 0.07-0.08 0.12-0.11 0.39-0.41 0.16-0.15 - CBW 0.09-0.07 0.08-0.10 0.17-0.19 0.66-0.65 - - 0.20-0.19 0.10-0.10 0.33-0.34 0.36-0.36 - - SMR 0.06-0.06 0.04-0.05 0.55-0.50 0.36-0.38 - - 0.03-0.03 0.04-0.05 0.39-0.26 0.54-0.66 - - JFJ 0.08-0.07 0.10-0.12 - 0.82-0.81 - - KPO 0.12-0.11 0.10-0.14 0.33-0.35 0.45-0.39 - - MH 0.11-0.11 0.14-0.15 0.24-0.15 0.44-0.52 - 0.07-0.07 0.13-0.13 0.27-0.32 - 0.59-0.54 - 0.01-0.02 MSY 0.12-0.12 0.09-0.13 - 0.78-0.75 - - PAY 0.06-0.05 0.10-0.10 0.27-0.35 0.58-0.49 - - 0.08-0.08 0.10-0.09 0.26-0.20 0.57-0.63 - - PDD 0.01-0.01 0.08-0.09 0.45-0.466 0.45-0.44 - - 0.05-0.05 0.15-0.18 0.36-0.37 0.44-0.40 - - SPC 0.11-0.09 0.15-0.20 0.28-0.21 0.46-0.50 - - VAV 0.20-0.21 0.15-0.13 - 0.65-0.67 - - 0.12-0.11 0.14-0.18 0.20-0.22 0.54-0.50 - - HAR 0.07-0.09 0.12-0.10 0.44-0.45 0.36-0.37 - -

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