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Discussions

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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.

M. Crippa et al.

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Answers to Referee 1 comments We thank the reviewer for the valuable comments that helped improving the manuscript. This manuscript provides an overview of organic aerosol components obtained from AMS data across 25 European sites. The new aspect of this work is that it uses multilinear engine (ME-2) to specifically extract and apportion the observed OA due to primary organic aerosol components from traffic (HOA), burning (BBOA) and cooking (COA). Marine organic aerosol is also extracted in certain sites. I commend the authors on their work compiling all this information together and I think the subject matter is suitable for ACP. However, I think that there

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are several details that the authors need to fully address before the manuscript is published. These details deal with the two goals that the authors lay out in the abstract: 1) To propose a standardized methodology for using ME-2 for extraction of organic aerosol components from AMS data 2) to provide a large overview of organic aerosol sources in Europe.

We agree partially on the criticism of the standardized methodology. We answer below in detail.

As we agree with the Referee that this study does not provide a systematic study on the variation of the a-value and on the different constrained factor profiles, we changed the title to: "Organic aerosol components derived from 25 AMS datasets across Europe using a consistent ME-2 based source apportionment approach". The main point we emphasize here is that we use a consistent approach that allows for better comparison between measurements and models. By our approach we ensure that we look at a very similar HOA and a reasonably similar BBOA component throughout all datasets. We improve the source apportionment compared to using PMF and although we are on the way towards a more standardized methodology, we still need more investigation on how ME-2 can be used in an optimum way to develop a standardized methodology. To investigate the robustness of our results, this revision of the manuscript includes some additional sensitivity analyses. In order to fully address the very important and emerging task of a systematic study on the aforementioned parameters, we are already planning a next study that will take place using more suited datasets with key collocated measurements, such as NOx, BC, gas-phase data etc.

STANDARDIZED METHODOLOGY

1) Justification of a-priori information

Since the ME-2 method depends on a-priori information, the authors need to provide more justification for how and why they constrained the ME-2 runs in the ways they did. More information needs to be provided about how the standard spectra were

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chosen, the uncertainties associated with them, and also how the a-values were chosen. Currently there is very little context for this. Even if this information is in other manuscripts that are referenced, it should be summarized in this one to make this manuscript clearer.

a) The authors choose the Crippa et al. HOA and COA and the Ng et al. BBOA. How do the results change if a different set of starting mass spectra was used? For example, how stable are the results if the Ng et al. or other HOA was used? How similar are the Crippa et al. HOA to direct vehicle emission source mass spectra that have been observed for European vehicles?

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 much 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 is already in planning that will address this very important task using more suited datasets with key collocated data".

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 averaged 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. For most of the cases the variation in the relative contribution of different factors is only a few percent. In order to fully address this critical topic, a more systematic study is planned using more suited datasets with more external constraints to judge which solution performs better or provide a range of results that provide similarly good performance.

b) There is very little discussion of the a-factor and why the values that are used were chosen. Are the a-factor values chosen for HOA reasonable when considering the variabilities among HOA across the world? In the spectral database, Ng et al. HOA reference spectrum mass spectrum, for example, has reported standard deviations for most of the key ions that are at least 20% if not greater of the measured ion intensity. How does the a-factor that you have chosen compare to these variabilities? Why were the a-factors that are being used chosen? What happens to the extracted HOA loadings if the a-factors are increased to 0.3 as in the case of the BBOA a-factors?

A good value of the a-value is hard to determine objectively. The problem is that most PMF solutions published may suffer from imperfect unmixing of the sources, especially if cooking could not be extracted because the cooking mass spectrum is highly similar to HOA. So the variability in the published HOA spectra likely does not reflect variability in the actual source profiles but imperfections in the solution. Directly measured emission profiles are also not ideal as they reflect only individual vehicles and very highly specific operating conditions and likely would not represent the mixture found in the atmosphere, also including e.g. off-road emissions. Measurements in a tunnel

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with a bigger fleet are more representative. However, there are still several issues. In such a case the concentrations are often high and the partitioning between gas and aerosol is often not representative leading to different chemistry. Also the emissions during other driving conditions are missing, e.g. cold start, and off-road engines with usually much older technology and less after treatment are missing. Still, the HOA spectra usually found are very similar to spectra found in the literature. Our experience indicates that in cases where we found contributions of cooking (COA), HOA values of around 0.1 needed to be used to be able to distinguish between these two sources (e.g. Canonaco et al., (2013)). This is the main reason we chose to investigate the sensitivity to a rather narrow a-value range. For completeness, we will show also the results for 7 campaigns using an a-value range of 0.05-0.2 for two distinct HOA MS (refer to the aforementioned section SI-6 of the supplementary material). In general, datasets with more external data available should be used to investigate the ideal a-value range. This will be the task of future investigations. A detailed sensitivity analysis investigating the impact of the input MS on the final solution is topic of another work in progress (Canonaco et al., in preparation b, 2014). Here it is important to us to use a consistent approach for all sites including the selection of source specific a-values.

In addition to section SI-6 introduced in the supplementary material, the following sentence is added into the manuscript for clarification:

"A detailed sensitivity analysis investigating the impact of the input MS on the final solution is already ongoing and will be fully addressed in Canonaco et al. (in preparation b, 2014)."

c) Is the a-factor applied uniformly across the entire mass spectrum? What uncertainties does this introduce given that the spectral database reference mass spectra clearly have standard deviations that vary with m/z.

The a-factor is here applied uniformly, although it is possible to change the a-value for different m/z's. This is an interesting suggestion and should be investigated in depth in

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the future, although the quality of the reference spectra can be doubted as discussed above. Also in the pulling approach (Paatero and Hopke, 2009; Brown et al., 2012) available in SoFi (Canonaco et al., 2013) one may try to scale the pulling weight with the standard deviation of different variables. The sensitivity of using such alternative approaches should be systematically tested for individual datasets with good external data available.

In this work only the a-value approach is explored, while the other methods, and especially the pulling one, are described and applied in a separate work (Canonaco et al., in preparation a, 2014). In the context of defining a standardized source apportionment procedure, we consider the pulling approach as a separate method which needs a careful and detailed analysis which cannot be provided in this work. Anyway, we agree with the Referee that mz specific a-values could be also applied. We clarified that we applied a constant a-value to all the mz for a spectrum in the following sentence:

"In our work, a constant a-value is applied to the entire constrained MS; however a softer constraining technique is provided by the pulling approach (Paatero and Hopke, 2009; Brown et al., 2012), which is available within the SoFi package (Canonaco et al., 2013) and which is explained in more detail in Canonaco et al. (2013)."

d) The authors mention in the first paragraph of p. 23348 that the a value of 0.3 is found to be reasonable for the BBOA MS. They further mention that it is hard to determine when the BBOA factor fails when increasing the a-value. This sounds troubling. If you don't have a metric to judge whether the results that are obtained from the analysis is reasonable, how do you choose an a-value? Could you not use the variabilities observed in source BBOA signatures to define the a value? The authors mention the variabilities, but don't quantify them in any way. How does the a-value that you have chosen for BBOA compare with the observed variabilities in BBOA, particularly since the BBOA factor accounts for all kinds of burning.

As reported in ambient and chamber studies, the BBOA MS varies depending on burn-

ing 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. 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 0.45-0.46 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 - -

2) Validity of extracted components

a)The technical guidelines for standardized strategy should include more details on how to validate whether the extracted components are reasonable or not. In step 3 the authors recommend looking at diurnal increases to identify wood burning. Isn't this going to be complicated by the diurnal changes in boundary layer height as well? Also, if PMF could not extract the components distinctly, there is likely not enough distinct temporal variation between the components to start with that can be used for this purpose.

We believe that the analysis of the source diurnal pattern is very important to interpret and evaluate a source apportionment solution since it represents the temporal variability of each source. If the unconstrained PMF run was not able to clearly discriminate some sources, this does not necessarily mean that these sources did not have a specific temporal variability. As mentioned in the manuscript (paragraph 4.1):

"Our methodology combines the advantages of the chemical mass balance and the

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positive matrix factorization approach. In fact, the a-priori knowledge of well-known source profiles (e.g. from primary sources) drives the source apportionment algorithm in finding an optimal solution for the model, while less constrained components (e.g. secondary OA) are allowed to freely vary (similarly to the unconstrained PMF case). However, our approach should provide consistent results with the unconstrained PMF case, where an optimal solution could be also identified by the means of other techniques such as e.g. a significant number of seeds, individual rotations or by reweighting specific uncertainties, etc., although requiring often very high time efforts and a lot of expertise on the user's side. " As discussed by the Referee, the evolution of the boundary layer height affects the source diurnal pattern too. In order to remove the effect of the boundary layer evolution, the user can look at the source diurnal pattern in relative terms (evaluating the relative contribution of each source to total organic and then their diurnal pattern). This concept is introduced in the manuscript with the following sentence:

"In order to remove the effect of boundary layer height evolution, we recommend that users investigate the relative source contribution diurnal pattern in addition to the absolute source contribution."

Since the extracted components are primary components, couldn't source emission ratio information be used to help guide the interpretation of whether component apportionments are reasonable or not? For example, HOA/CO, HOA/BC and HOA/NOx values for source emissions exist in the literature. What are these ratios for the extracted components in the various sites and how do they compare to these known values? A compilation of at least some of these values for the dataset you have could be very useful.

We perfectly agree with the Referee regarding the possibility to interpret a source apportionment solution based on specific ratios, like HOA/BC or HOA/NOx. However, these ratios must be carefully calculated, for example the HOA/BC ratio should be evaluated considering only the BC fraction emitted by traffic and not the part emitted

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by wood combustion (or other sources like coal burning, etc.). Therefore one should apply additional source apportionment approaches to the BC component before calculating the HOA/BC ratio, like the aethalometer approach reported by Sandradewi et al. (2008). In our study the lack of external data availability reduced the possibility to systematically evaluate all these ratios. Difficulties in estimating such ratios due to the presence of multiple sources can be performed using bilinear regression, as shown in some literature works (allan, 2010). However, this method is more applicable to a single dataset rather than an overview of 25 datasets across Europe.

We included in the manuscript the following sentence to summarize this concept:

"To further evaluate the interpretation of primary sources within the selected solution, source specific ratios can be calculated (e.g. HOA/CO, HOA/BC and HOA/NOx) and compared with literature studies. However, in our work this approach could not be systematically applied due to the lack of external data. Bilinear regression (Allan et al., 2010) can be used to estimate these ratios also in the presence of multiple sources; however, this method is more applicable to a single dataset rather than an overview of 25 datasets across Europe."

Similar information can likely be obtained for BBOA/CO and BBOA/BC. The f60/BBOA ratio is a good start at this as well, but isn't this correlation primarily driven by the allowed variability in the f60 of the assumed BBOA mass spectrum in the first place?

As reported in literature (Heringa et al., 2011), the BBOA/CO and BBOA/BC ratio is highly variable, therefore it is difficult to define a reference value for these ratios to compare with. Moreover, as just mentioned, BC can be emitted by several sources, so specific measurements or assumptions should be made in order to be able to define the BBOA/BC ratio. We believe that the relationship between f60 and fBBOA shows the consistency of the results applying the systematic procedure to 25 datasets.

a) Uncertainties in Source Apportionment

The sensitivity analysis to the a-value that is presented in section 4.5 does not seem to be complete since it really only tests for the sensitivity to small changes in the a-value used for HOA and does not really address the variability in the BBOA factor MS which could be large at many of the sites. Some suggestions on how the uncertainties could be quantified:

a) It is not clear to me how the mass is redistributed as additional factors are added to the analysis. For example, how much cross talk is there between HOA and BBOA vs. HOA and SV-OOA etc.. It would be good to see for at least one case study (likely Barcelona) how the mass apportionment changes as you go through the steps suggested in your methodology.

As discussed above, a sensitivity analysis for BBOA (a-value range=0.2-0.4) has been additionally performed and reported in Table 4 of the manuscript to highlight the redistribution of the OA mass through its sources varying the BBOA a-value.

b) In Figure S1-3.2 it seems that the agreement between ME-2 HOA and HR-PMF HOA and BBOA is quite poor (correlation slopes of 1.9 and 0.5 respectively). There is a similar difference in the SV-OOA and LV-OOA assignments as well. It is clear that the apportionment is not unique and there is quite a bit of variability. How do the authors pick which is the most likely apportionment? In this manuscript the authors want to make the case that ME-2 is capable of extracting the more "reasonable" answer. The authors should discuss this in more detail and explain why they think the ME-2 solution is better than the one obtained with HR-PMF.

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. Comparing our ME-2 solutions with HR-PMF results shows that our source apportionment procedure produces quite similar results with UMR/HR-PMF in the case of Montseny (Figs. SI-3.1), although it was necessary to consider a 8-factor HR-PMF solution in order to get an HOA MS and merge all the OOA contributing factors into one single component. 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 underestimated by 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 as-

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sociated 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)."

c) In the extreme case, one limit on the apportionment would be to always run an ME-2 with the constrained (with reasonable a-factors) HOA and BBOA factors and see what comes out compared to what you get from PMF and your methodology for ME-2 that you propose. This would give information about how much error one could potentially have if you constrained both factors in a situation where you didn't need to and would also provide information on how coupled these factors are and also on uncertainties with which zeros in concentrations of either of these factors could be obtained.

Ideally, when constraining a MS spectrum of a fictitious source which is not contributing to the observed OA mass concentration (e.g. BBOA for a specific site), the algorithm should apportion a contribution close to zero for that source. Unfortunately this is true only for very few sources characterized by highly specific MS which are either representative of the considered dataset or they cannot be identified by the algorithm because of their specific features. On the other hand, when considering for example BBOA, its MS can resemble for some features the SV-OOA one meaning that some mz might be co-emitted also by other sources. Therefore, although the source is not present in the dataset, its contribution will be low but not necessarily very close to zero. When fixing BBOA, the algorithm will necessarily return a MS which resembles the imposed BBOA MS (the degree of agreement depends also on the assumed a-value) but its contribution in terms of mass might not be entirely belonging to BBOA but also to other sources. As discussed in our methodology, in order to evaluate whether a solution is acceptable or we are fixing a fictive source, we have to carefully look at the diurnal pattern of the new source (especially in the case of BBOA), correlation with external tracers, introduction of structure in the residuals compared to a previous solution, etc.

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Moreover, it might very well be that the imposed BBOA profile explains SV-OOA and the residual of m/z 60 would be systematically overestimated when in a first approximation m/z 60 is neglected, since the BBOA MS resembles the SV-OOA one. In this case a PMF user should not consider such a solution. Thus, simply estimating the amount of error done when constraining the wrong profile, based on the contribution of such factors, is not straight forward. Comparing ME-2 and PMF results for a case where PMF was producing a reasonable solution is not a trivial task, in fact, the PMF solution might still be mixing factors and ME-2 might be influenced by the choice of a non-ideal reference mass spectrum.

d) The reference MS of the HOA and BBOA appear to correspond to "fresh" emissions. Due to the constraints of the a-factor, presumably aged HOA could appear as an OOA factor rather than as an HOA factor with a larger f44. Similarly aged BBOA could appear as BBOA and another OOA. In order to disentangle this, it would be useful to check correlations between the OOA components and the primary components. Do you see evidence for this at any of the sites?

While aging a primary source, we interpret the change of the mass spectra to be mostly due to addition of SOA than change of POA. Heterogeneous reactions of the primaries by OH is at least on the time scales of a day or two considered to be usually negligible compared to gas phase reactions. There is some fraction of the emitted organics (considering the volatility distribution around 20-30%) that is semi-volatile at typical atmospheric conditions that would age more efficiently in the gas phase and some may call the obtained organics aged POA (May et al., 2013). However, we consider the more oxidized components to be secondary and should be more reflected by SV-OOA than the POAs. In general, but especially at rural sites, we can expect that the primary organics will come together with some secondary organics (initially mostly SV-OOA) that form rather rapidly in 1-2 hours shown in smog chamber experiments by e.g. Carnegie Mellon and the Paul Scherrer Institute in the past. ME-2 makes surer that we are not mixing SV-OOA with the primary emissions which may happen often

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with PMF. As discussed by the Reviewer, larger a-values applied both to HOA and BBOA often enhance the relative contribution of mz44 to these MS. In the case of HOA, we know from literature studies that the amount of mz44 is rather low (being HOA freshly emitted); therefore, we apply a rather low a-value (a-value range=0-0.2) to constrain mz44 as well as the other masses. On the contrary the fraction of mz44 in the BBOA MS can significantly vary; therefore it is not trivial to apportion the exact amount of mz44 in this spectrum. Based on our experience, the use of higher a-values (0.2-0.4) gives enough freedom to the algorithm when trying to optimize the data fit. Table 4 reports the relative contribution of OA sources to total OA varying the BBOA a-value range. Larger a-values would likely apportion secondary mz44 into BBOA and also HOA as discussed above.

INTERCOMPARISON ACROSS EUROPE

4) While data is presented for all the sites, the discussion regarding the overview of organic aerosol sources in Europe is limited. There is a lot of information and it would be useful if the authors presented more context to the trends between sites given overall meteorology and source regions that impact the various sites.

The main goal of our work is to provide an overview of the organic components for European sites using consistent ME-2 approach as a starting point for further investigations. We agree with the Referee that a high amount of scientific information is included in the 25 datasets which can be put into context with many variables. This is however out of the scope of this publication. An overview of the inorganic components and the general meteorology is in preparation by Nemitz et al. Several modelling studies are initiated which allow an easier way of integrating and interpreting the overall results in the context of emission and aging.

a) One way of giving context could be ordering the sites in tables and figures according to some consistent metric along which trends could be discussed (Rural/Remote/Urban or North/South or Loading levels)

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A table reporting the sites list, together with their location (longitude, latitude, altitude) as well as the site typology, is now included in the supplementary material (Table SI-4) to guide the reader in the results visualization and interpretation.

b) It is surprising that Puijo has nearly the largest HOA fraction even though it is classified as rural. Does this make sense with respect to the source regions that are close to this site? A similar question for the rural VHL site where HOA when 0.2 of the mass and CBW where it is 0.15 of the mass. The issue behind these questions is whether HOA is overestimated at these sites perhaps due to misapportionment from BBOA or SV-OOA or due to the chosen HOA profile. As mentioned earlier, one way to check whether the HOA is in a reasonable range would be to check against CO or NOx and see whether the HOA/CO ratios are consistent with vehicle emissions.

Puijo station is on the top of an observation and retransmitting tower, which is a 75m high building on the Puijo hill (elevation 150m), approximately 2 km northwest of the city center of Kuopio (population 97000) which is a source of HOA e.g. traffic and a few point sources (Leskinen et al., 2012;Hao et al., 2013). However, it is important to highlight that, compared to other sites, the amount of HOA is lower in absolute terms (ca 0.2 μg/m3). The absolute amount of OOA is also low so that not much of local/regional HOA is needed to provide a high fraction.

The following sentence is now included in the paper:

"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 at sites with high total OA concentrations the absolute HOA amount is higher compared to rural sites."

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C12638/2014/acpd-13-C12638-2014-supplement.zip

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