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Comment

Interactive comment on “Burning of olive tree branches: a major organic aerosol source in the Mediterranean” by E. Kostenidou et al.

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This paper investigated the composition of organic aerosols in the area of ICE-HT institute. By performing PMF analysis on the organics data collected by HR-ToF-AMS, it is found that olive tree burning contributed a substantial fraction (33.7%) to the total organic aerosols loading. The otBB-OA factor determined has a lower m/z 60 than other BBOA factors previously reported. Based on these results, the authors suggested that olive tree burning is one of the most important aerosol sources in the Mediterranean countries.

Overall, the paper is well written and clear. I found the results from this study very interesting. However, I have some concerns regarding the results from the PMF analysis.

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The authors presented a 3-factor solution (otBB-OA, HOA, OOA) with a $f_{peak} = -0.2$. The f_{peak} value of -0.2 was chosen to obtain the smallest angle between the otBB-OA factor and the chamber otBB spectrum. While one would expect the ambient otBB-OA factor and the chamber otBB spectrum to be strongly correlated, I do not think that it is appropriate to use this as a criterion for choosing the f_{peak} value, especially the chamber otBB spectra have some variations among themselves (Table S1). The authors should first decide on the appropriate number of factors before they explore the rotational freedom of their solution (Ulbrich et al., 2009). Based on all the information provided in the manuscript, it seems that the COA factor should be included in the solution and that a f_{peak} value of zero would be appropriate (please see detailed comments below). This is simply based on my interpretation of the analysis and supporting information provided in the manuscript. I suggest the authors to re-evaluate their PMF solutions again and carefully evaluate the 4 factor solution with $f_{peak} = 0$ in the revised manuscript. While this could be a major revision, I do not see this posing a large amount of extra work since the authors have explored the different solutions in great details. The issue is in choosing the most appropriate solution for their data.

We have followed the reviewer's suggestion and reevaluated the PMF solution using four factors. We discuss the corresponding issues and changes to the manuscript in our reply to Comment 10 below.

Specific comments:

1. *Page 7227, line 14. It is not clear how the "30 g of fine PM per year" is relevant to the context when the authors are discussing PM concentrations in "tons per year".*

In this section we compare the fine PM emitted per year by the burning of olive tree branches to one of major sources of particles in Greece: transportation. The 30 g per car per year is the assumed emission factor for cars in Greece. We have rephrased this sentence to avoid confusion.

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2. *Page 7231, line 15. Is Nafion dryer used at the AMS inlet? The authors cannot simply apply CE from chambers to their ambient data. A CE of 0.5 is recommended if a dryer is used. Otherwise a higher CE might be more appropriate (depending on ambient RH and aerosol composition). Please clarify this.*

We did not use a Nafion dryer in any of our measurements (smog chamber and field). We added this clarification in Sections 2.1 and 2.3.

We tested the accuracy of our assumed CE for the field measurements comparing the AMS results with the SMPS measurements. We assumed organic densities: 1.4 g cm^{-3} for the OOA (Kostenidou et al., 2007), 1.0 g cm^{-3} for the HOA (Canagaratna et al., 2010) and 1.25 g cm^{-3} for the otBB-OA (based on our chamber experiments). The aerosol water was estimated assuming equilibrium and using the AIM model. The CE=0.6 used is consistent with the SMPS volume concentration. The comparison for different values of CE is now shown in Figure S14. The estimated uncertainty is around 20%. We added a paragraph at the end of session 4.4 discussing this issue.

3. *Page 7232, line 19 onwards. It would be clearer if the authors could indicate the positions of the different functional groups in the spectrum shown in Figure 1.*

We modified Figure 1 showing the positions of the different functional groups. We also mention the wavelengths for each functional group in the third paragraph of Section 3.1.

4. *Page 7232, lines 25-26. The sentence “the differences in the alkane group region are expected given that the biomass precursors in Mexico and Texas likely do not include olive trees” is not clear. How would biomass precursors affect alkane contribution?*

One would expect different signatures from different types of biomass burning. So, because in Mexico or Texas the burned biomass does not include olive trees, it is likely

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that their combustion will lead to different products with different “fingerprints”. We have rephrased the above sentence to make it clearer.

5. *Page 7235, line 2. At a first read it seems that the authors injected extra toluene into the chamber as a tracer to estimate OH concentration. Later in page 7236 the authors discussed that toluene is actually present in olive tree burning. It would be clearer if the authors mention this on page 7235 when they discussed how they estimated OH concentration.*

We now mention in the beginning of the discussion that toluene was actually emitted during the burning and was therefore an OH tracer of opportunity.

6. *Page 7235, line 5. The author should include the corresponding O/C calculated from HR analysis in Figure 5.*

Done. We also extended the x-axis (time) to 16 hours.

7. *Page 7235, line 11. “through out” should be “throughout”.*

Done.

8. *Page 7235. Are there any aerosol formed in these chamber experiments? If so, how much? The authors should include this info in the revised manuscript.*

During the chamber experiments no new particle formation was observed as we did not add any additional oxidation agents or use UV radiation. We already include this information in the manuscript (Page 7240, line 25-26). The ratio of organics to sulfate remained practically constant during the experiment suggesting that if there was any organic aerosol mass formation it was minimal. We added this information in the second paragraph of Section 3.2.

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9. Page 7235, lines 19–23. *What about carbonyl functional groups? Did they show a corresponding decrease in intensity?*

The contribution of carbonyl groups was approximately the same in both cases. We made the corresponding addition to the text.

10. Page 7237, PMF analysis:

a. *Figure 9. Since HR PMF is performed, the authors should show the HR spectrum instead of UMR spectrum. This would clearly indicate the contributions of different families (CH, CHO, CHN, etc) at each m/z.*

The HR spectrum has been added indicating the contributions of the different families at each m/z.

b. *Page 7238, last two paragraphs. I think some of the info should be included in the supplementary info instead of the main text. In PMF analysis, various m/z with similar temporal variations are grouped into one factor. One would certainly expect the time series of the individual m/z in each factor to correlate well with the time series of that particular factor. Hence, while it is extremely useful to examine the correlations of factors with external tracers such as sulfate, levoglucosan etc, it is not as informative to report R^2 values of individual m/z and the factor itself. This information should be moved to the supplementary info and preferably with a table format.*

We modified the text, providing less information about the correlation R^2 between the factors and individual m/z. All the above correlations are now summarized in Table S2.

c. *Page 7263. There are three large spikes in HOA on Nov 26, Dec 12 and 14. What are the sources? The authors should at least comment on this.*

The three large HOA spikes on November 28 and December 12 and 14 are probably due to the Institute diesel back-up power generator, which was activated during the power outages in the area. We added this comment to the caption of Figure 10.

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d. I do not agree with the authors reasoning in choosing an $f_{\text{peak}}=-0.2$. In PMF analysis, it is advised that one should explore the rotational freedom of the solution (using f_{peak} parameter) after the approximate best number of factors is determined (Ulbricht et al., 2009). However, in this case, the authors actually used f_{peak} to determine the number of factors to start with. Their reason for choosing $f_{\text{peak}}=-0.2$ was solely based on minimizing the angle between otBB-OA chamber spectrum and their otBB-OA factor from ambient data. Given that there is also variation in the chamber otBB-OA spectrum (Table S1, largest angle = 13.2) and that the angle between the otBB-OA chamber spectrum and otBB-OA factor does not vary that much for f_{peak} values between -2 and 0, I do not see any strong reason why they needed to use a f_{peak} value other than zero.

In our PMF analysis we first selected the number of factors (see answer below) and secondly the f_{peak} . First we investigated the correlation between the times series of the three factors (i.e. OOA, HOA and otBB-OA) with other compounds like sulfate, ammonium, potassium and chloride (Figure S11a). In the range of f_{peaks} -2 to 2 the R^2 between OOA and sulfate was 0.57-0.59, the R^2 between OOA and ammonium was 0.71-0.73, the R^2 between otBB-OA and potassium 0.32-0.36 and the R^2 between otBB-OA and chloride was 0.53-0.54. The small sensitivity of the above R^2 values to the f_{peak} value, makes the selection of an appropriate f_{peak} difficult. We then checked the correlation of the time series of each factor with the rest (Figure S11b). All the R^2 values were below 0.1. However the R^2 between the times series of HOA and otBB-OA had a discontinuity at $f_{\text{peak}}=0$ and 0.2, with lower correlation for the negative f_{peak} (approximately half of that of the positive f_{peak}). This is a first indication that we should select a negative f_{peak} .

Since we have measured the otBB-OA mass spectrum another criterion would be the comparison the source otBB-OA mass spectrum (average of 4 experiments) to the PMF otBB-OA mass spectrum, as shown in Figure S11c. The 2 mass spectra became very similar in the negative f_{peak} region. Any of these f_{peak} values (-2 to 0) are candidates for the final solution. The smallest angle is for $f_{\text{peak}}=-0.2$ ($\theta=10.5$ degrees)

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while for $f_{\text{peak}} = -0.6, -0.4$ and 0 the angle is 10.5 . The differences are extremely small and our results are independent of the selection of f_{peak} in this region. We prefer not to choose an $f_{\text{peak}} = 0$ because there is a discontinuity between $f_{\text{peak}} = 0$ and 0.2 and these f_{peak} are the limits of two different solutions. It makes sense to avoid selecting a solution at the limit but a solution next to it. In any case, between $f_{\text{peak}} = -0.6$ and 0 there is no change in the mass spectra ($R^2 = 0.999$) and the corresponding time series between the same factors each other for the f_{peak} above). We made the corresponding additions in the supplementary information.

e. Based on the discussion provided in the supplementary information, I think that a 4 factor solution would be more appropriate (i.e., there is a COA factor). From Figure S5, it is obvious that an additional factor is needed to describe their data. The authors cannot simply pick and choose to discard certain part of their data (Fat Thursday) and perform PMF analysis on the remaining data. In Figure S8, the COA spectrum is distinctively different from other factors. The authors argued that by creating a COA factor it “destroys” the otBB-OA, I do not agree with this. The authors stated that with the COA factor, the correlation between the chamber otBB-OA spectrum and otBBOA factor got worse. However, from Figure S6 the angle between these two is only between 15-20 for $f_{\text{peak}} = 0$, which is not too off from the variation in chamber otBBOA itself (Table S1, largest angle = 13.2). Further, the authors suggested that the correlation of otBB-OA factor and the fourth factor (OOA) increases with increasing f_{peak} from -0.4 to 2 . Looking at Figure S9, even with a $f_{\text{peak}} = 0$, the R^2 between the otBB-OA factor and OOA factor is < 0.2 . Together with the fact that the otBB-OA spectrum and OOA spectrum are distinctly different, I think it's suffice to say that the COA factor is a real factor and should be included in the solution.

In order to investigate the utility of including a COA factor in our solution, we evaluated the effect of the Fat Thursday (which is actually 12 hours out of a total of 20 days of data) in our data analysis performing the PFM analysis including and excluding these data. As mentioned in the SI, section 6, paragraph 2, excluding the Fat Thursday

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data the 3 factor solution does not practically change compared to the 3 factor solution including the Fat Thursday inputs. Moreover moving to a 4 factor solution (excluding the Fat Thursday data) the OOA spectrum is split into 2 identical spectra for $f_{\text{peak}} = -2$ to 2 (Figure S9). This implies that there is no COA factor in our data except for the day of the Fat Thursday and that the 12 hours of cooking aerosol emissions introduces artifacts, probably due to their small contribution to the whole data set (2.5

The angle theta comparison between the chamber otBB-OA and PMF otBB-OA spectra of the 4 factor solution (including the Fat Thursday data) is shown in Figure S5, in order to investigate the behavior of the otBB-OA spectrum for different f_{peak} . For f_{peak} less or equal than -0.6 the 2 mass spectra have a lower angle (less than 10 degrees) but the “COA” mass spectrum is actually an OOA mass spectrum (Figure S6). For f_{peak} greater or equal than -0.4 the 2 mass spectra differ 15-28 degrees (which is higher than the variation in chamber otBB-OA itself (largest angle = 13.2, Table S1). However, the correlation of the otBB-OA and the COA (not the OOA) time series increases with increasing f_{peak} from -0.4 to 2 (Figure S8). The fourth factor is not the OOA but the COA. This indicates that in the f_{peak} range -0.6 to 2 the PMF mixes the otBB-OA and COA factors which are both primary sources. Thus we concluded that the 3 factor solution is the best way to represent our data.

We made the corresponding additions and modifications in the supplementary information discussing our selection.

f. *Overall, I would suggest the authors to re-evaluate their PMF solutions. Based on all the info provided in the manuscript, I would guess that a 4 factor solution with $f_{\text{peak}}=0$ would be appropriate. The authors of course should evaluate this carefully and provide justifications in the revised manuscript.*

Our results are robust as far as the selection of f_{peak} is concerned (the -0.2 used here produces the same results as 0). We present both the 3-factor and 4-factor solutions in the supplementary information. We prefer to focus on the 3-factor solution in the main

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paper because it appears to be more robust than the 4-factor solution. Having a major source that dominates the OA composition for a few hours and does not appear during the other 20 hours of the study appears to create problems to the PMF algorithm and to reduce the quality of the solution.

g. *Figures S5 and S6. It is nice that the authors showed these residues in details. I suggest the authors to also include a plot of Q/Q_{exp} in the revised manuscript.*

Done.

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