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Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* "The contribution of wood burning and other pollution sources to wintertime organic aerosol levels in two Greek cities" *by* Kalliopi Florou et al.

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*General comments:*

**(1)** *Florou et al. describe aerosol measurements from two Greek cities. Using PMF, the authors resolve factors for BBOA, HOA, COA, and OOA. The authors find that biomass burning is a significant contributor to organic aerosol in both cities. In Patras, the authors resolve two biomass burning factors (BBOA-I and BBOA-II). The time profile and mass spectra of these two factors are quite different. These two factors may result from differences in (a) the degree of atmospheric aging, (b) the composition of the fuel, (c) the burning conditions, or (c) a combination of these processes. The influence of biomass burning emissions on regional air quality is important to assess. This*



*study is particularly interesting because it is focused in a region that has seen large increases in wood stove usage, which may be a result of the recent Greek economic crisis (Paraskevopoulou et al., 2014). Given its relevance, this work will be of general interest to the atmospheric community. Overall, the methods the authors employ are good. I especially commend the authors for the extensive amount of detail they provide to justify the PMF results and the comparisons they make with previous published BBOA factors.*

We appreciate the constructive comments and suggestions by the referee.

**(2)** *I have one major comment pertaining to the resolution of the two biomass burning factors in Patras (see below). I believe addressing this comment will significantly strengthen the paper. Also, some of the sentences can be improved to help with the overall flow of the paper. Editorial comments are provided at the end of this review. The authors identify two biomass burning factors associated with the Patras data set. The resolution of these two factors is interesting, and I believe the authors may be able to draw more conclusions from these results. The authors hypothesize that the differences between these two factors arise from either (a) different degrees of aging (b) different types of combustion or fuel, or (c) some combination of these mechanisms. The authors seem to emphasize that the differences between BBOA-I and BBOA-II could result from aging. Can the authors elaborate more about the impact of different fuels?*

We have followed the reviewer's suggestion (see also Comments 2 and 13 of the first reviewer's suggestion) and added some discussion and analysis of the various hypotheses. In principle, the two factors could correspond to different fuel types. However, the corresponding emissions should have either a different temporal or a spatial profile in order to be separated by PMF. Given that residential biomass burning in a city like Patras is due to tens of thousands of individual sources (fireplaces, wood stoves, etc.) spread all over the city following a similar burning schedule on average it is difficult to see how PMF would be able to separate the BBOA from different fuel types. The null hypothesis is that the BBOA factor represents an average of the emissions of all fuel types. However, there are other potential explanations (e.g., different areas of the city using different fuel types and the emissions arriving at the site at different types) that could involve the use of different fuel types. We have added the above discussion to the revised paper.

**(3)** *The authors note similarities between BBOA-II and AMS spectra of burned olive tree branches. Do people in Patras use multiple types of fuels, whereas those in Athens typically use one? It would be helpful for the reader to know what types of fuels are typically burned for home heating.*

In general people in Greece use multiple fuel types that can vary from region to region due to the availability of the corresponding type of biomass. For example, in Patras citizens use either softwood (pine, fir, etc.) or hardwood (oak, beech, olive tree). In Athens, people use mainly pine and fir. This information has been added to the paper.

**(4)** *I find it striking that nitrate in Patras is so strongly associated with organic aerosol (Fig S7). As the authors note, BBOA is the dominant organic component; therefore, I wonder if BBOA in Patras is also the dominant source of ON. The authors mention that ON was not strongly associated with BBOA plumes in Athens, but do not make a similar statement for Patras (lines 275-279); therefore, I'm assuming the evening nitrate in Patras is indeed affected by ON.*

In Patras, ON was 44 percent of the total nitrate for the period from 16:00 until 24:00 LST (for the whole dataset) that is during the BBOA high concentration periods. This has been added to the paper.

**(5)** *Furthermore, the correlation with evening nitrate enhancements seems to be better for BBOA-I than for BBOA-II (line 359). Could this imply that BBOA-I was a significant*



*source of ON in Patras?*

The $R^2$ between the BBOA-I and the AMS nitrate was 0.55, while that between the BBOA-II and nitrate was 0.09. BBOA-I also correlated better ($R^2$=0.31) with ON in Patras than BBOA-II ($R^2$=0.09). So the reviewer's hypothesis is correct, most of the ON in Patras was associated with BBOA-I and not with BBOA-II. This is now clarified in the revised manuscript.

**(6)** *ON (as well as nitrate) is typically the result of secondary processes; however, the nitrate trace appears to be better correlated with the "fresh" biomass burning factor (BBOA-I) rather than the "aged" biomass burning factor (BBOA-II). This, along with the nearly identical diurnal patterns (I would expect the "aged" factor to have a broader diurnal pattern), leads me to question whether the differences between BBOA-I and BBOA-II are truly due to chemistry. Therefore, could differences in fuel composition explain these observations? I ask about composition because recent work has shown that the emissions of nitrogen containing organic compounds (such as acetonitrile) strongly depend on the composition of the fuel (Coggon et al. 2016). Fuels containing low amounts of nitrogen (e.g. wood) emit lower amounts of N-organics than fuels containing large amounts of nitrogen (e.g. grasses, the boughs of trees). The same behavior has been observed for inorganic nitrogen gasses, such as NH4 and NOx (e.g. Burling et al., 2010). Consequently, if different fuels were burned, then different amounts of ON could be formed due to differences in the amount of NOx emitted or, perhaps, differences in emissions of primary organic nitrogen. If this were the case, then it would (1) be very interesting and (2) be an explanation for the different factor profiles for BBOA-I and BBOA-II.*

These are good points and have been added to the revised paper together with the corresponding references. We have extended the discussion of the potential explanations of the nature of the two BBOA factors in Patras stressing the possibility that they may due to different fuel types (see also our response to Comment 2 above). For the case of Athens, during nights (from 20:00 until 3:00 LST) in enhanced OA plumes exceeding 15 $\mu$g m-3, the ON fraction of nitrate was approximately 20 percent. In Patras, ON was 44 percent of the total nitrate for the period 16:00 until 24:00 LST (for the whole dataset) and 37 percent for the case of OA plumes exceeding 30 $\mu$g m-3 (16:00 until 24:00 LST).

**(7)** *Already, it appears that there may indeed be differences due to composition, as the two biomass burning factors appear to have different correlations with acetonitrile (Table S2). Note: The authors seem to mix up notation, as well as the city to which they are referencing (please be consistent with notation.). Is Table S2 for Patras (see caption)? Likewise, does BBOA-fr refer to BBOA-I and BBOA-ox refer to BBOA-II? If so, the BBOA factor with the higher correlation to acetonitrile (BBOA-fr) could be an indication that this factor originated from a source composed of higher nitrogen.*

We agree that these different correlations do support the hypothesis of two different types of fuels. This argument has been added to the paper. Table S2 has been renamed to Table S1. This table refers to Athens. BBOA-fr and BBOA-ox are the new resolved BBOA factors, by extending the solution from a 4 to a 5 factor solution. BBOA-fr is the BBOA-I from section SI.7b and BBOA-ox is the BBOA-II from the same section. The notation in the table has been changed.

**(8)** *To tease out differences between composition vs. chemistry, I suggest that the authors do a more thorough comparison of the BBOA factors with the gas-phase compounds measured by PTR-MS. Do the authors also have NOx measurements? If so, this may also help in the interpretation of these data. One way that the authors could tackle this question is by repeating PMF with the inclusion of some gas-phase species. Acetonitrile will likely vary depending on fuel composition, but other biomass burning markers (e.g. 2-furfuraldehyde (m/z 97)) may not show similar dependencies.*

This is an excellent suggestion for future work. Unfortunately, there was not a PTR-



MS monitoring during the Patras measurements. We will make this a priority in future campaigns in the area.

**(9)** *Alternatively, to avoid doing tedious PMF analyses, the authors can do a "plume" analysis to pick out differences in PTR-MS measurements when enhancements of biomass burning is dominated by BBOA-I vs. those when BBOA-II is dominant. Regardless of the outcome, I do believe that the authors need to provide a more complete discussion about the differences between BBOA-I and BBOA-II. As mentioned above, the aging explanation is questionable; therefore, the authors should consider discussing, in detail, other possible mechanisms.*

We agree with the aging explanation is weak and that the potential existence of two different sources deserves at least equal discussion. We have added this to the revised paper in response to the comments and suggestions of the two reviewers. Unfortunately, there was not a PTR-MS available during the Patras measurements.

*Other Comments:*

**(10)** *Line 122. Please define VOCs.*

The definition has been added.

**(11)** *Line 135. What do you mean by "main ions." Are you referring to nitrate, sulfate, and ammonium?*

Yes we are referring to the above ions. A clarification has been added.

**(12)** *Line 167 – 168. This sentence is unclear. Do you mean that differences in m/z 18, 28, and 39 were the reasons for higher theta values between the BBOA and COA spectra resolved by PMF and those from the HR spectral database? How would this change if you were to remove these ions from the analysis?*

Yes. The theta angle is higher because of the differences in these three m/z. If one excludes these specific m/z values, the theta angle decreases. We have rephrased the corresponding sentence to avoid confusion.

**(13)** *Lines 223-230. Here, the authors discuss the correlation between OA, acetonitrile, m/z 79, and m/z 69. It should be noted that furan (m/z 69) and benzene have large contributions from biomass burning (Gilman et al., 2015; Hatch et al., 2015; Stockwell et al., 2015); therefore, these masses may be affected by other sources than just petrol.*

This point has been added in the revised paper together with a reference to Kaltsonoudis et al. (2016) who have analyzed the wintertime Athens VOC data set in great detail.

**(14)** *Line 246. Please add "the" between "in" and "Patras".*

Done.

**(15)** *Line 275-277. This sentence is confusing. Do the authors mean that ON fraction at night is high, except during peak OA enhancements? If so, it may be clearer to indicate that ON is high at nights, but not in enhanced OA plumes.*

It was clarified in the text. ON was higher (38 percent) on average during nighttime (17:00 until 3:00 LST for the whole dataset) compared to periods of enhanced OA levels exceeding 15 $\mu$g m-$3$ (19 percent) which were all associated with high BBOA concentrations.

**(16)** *Lines 300 – 306. How should the reader interpret the diurnal patterns in O:C, H:C, and OSC? Do the enhancements of H:C during high OA reflect that these periods were affected mostly by primary emissions? The variability of O:C seems to be the inverse of H:C, suggesting that the composition of background OA dominates the observed*



*O:C ratio during "off hours" (e.g. 4:00, 11:00, and 15:00), which is consistent with PMF results. The authors should provide additional discussion describing the cause in O:C, H:C, and OSc variability.*

The explanations of the patterns by the reviewer are correct. The primary emissions mainly from traffic lead to reductions of the average O:C and increases in H:C during the corresponding peak periods. We have added the corresponding discussion in the revised paper.

**(17)** *Line 322. I believe it's better to state that the COA factor was resolved, rather than "added".*

We agree and we have made the corresponding change.

**(18)** *Line 331. Here, I would state that the PMF model "resolved" four factors rather than "identified" four factors.*

We have followed the suggestion of the reviewer.

**(19)** *Line 358 and Line 363. Both factors correlate similarly to BC, so I would not say that CO correlates modestly with BBOA-I (line 358) and poorly with BBOA-II (line 363).*

We have made the suggested change.

**(20)** *Fig 6. I believe that the BBOA traces are mislabeled. Is this correct?*

We have corrected the typographic error.

**(21)** *Table S2. Do these correlations correspond to the Patras data set? Also, what is BBOA-fr and BBOA-ox?*

These correspond to the Athens dataset for the case of 5 factors. We have added this information together with the definition of the two BBOA factors (BBOA-1 and BBOA-2) that are resolved by PMF in this case.

*Editorial comments*

**(22)** *Section Formatting: The authors delineate sub-sub sections with bold text (e.g. line 86). I recommend numbering sub-sub sections (e.g. 4.1.1 Patras, 4.1.2 Athens, etc). This makes it easier to reference sections in the main text.*

We have made the recommended change.

**(23)** *Grammar: There are sentences scattered throughout the manuscript that are difficult to follow. Most of these sentences would improve with better formatting. Below are a few observations of grammatical errors. Addressing these comments will help the manuscript read more fluently. Please use commas around interrupters. For example, at line 221, the sentence would read more clearly as "The nitrate was, on average, 0.48 . . ." Similar examples can be found at line 240 and 564.*

We have followed the suggestions of the two reviewers to make the corresponding sentences easier to follow.

**(24)** *These authors are inconsistent with the use of commas after introductory elements. For example, at line 179, the authors use a comma to separate the introductory element (During the Athens campaign, ...); however, a comma is not included after the introductory element at lines 176 – 177 (During February 26-27 and March 5 the air masses. . .). Similar examples can be found at lines 145, 217, 236. Please be consistent and use commas.*

We have made the corresponding changes making consistent use of the commas after introductory elements.



**(25)** *The authors write some sentences with multiple dependent clauses. At times, it is difficult to understand what the authors are trying to convey. For example, at lines 70-72, the authors write "The PMF source apportionment algorithm, used unconstrained, was applied to the corresponding datasets, estimating the contributions of the different OA sources, without assuming any a priori knowledge of their origin." Here, several clauses are combined into one long, hard-to-read sentence. I recommend splitting up the sentence to clearly state each clause. Other examples include sentences at lines 127- 129, 236 – 238, and 241-243.*

We have simplified the suggested sentences splitting them up in simpler sentences.

**References**

Burling, I. R., Yokelson, R. J., Griffith, D. W. T., Johnson, T. J., Veres, P., Roberts, J. M., Warneke, C., Urbanski, S. P., Reardon, J., Weise, D. R., Hao, W. M. and De Gouw, J.: Laboratory measurements of trace gas emissions from biomass burning of fuel types from the southeastern and southwestern United States, Atmos. Chem. Phys., 10, 11115–11130, doi:10.5194/acp-10-11115-2010, 2010.

Gilman, J. B., Lerner, B. M., Kuster, W. C., Goldan, P. D., Warneke, C., Veres, P. R., Roberts, J. M., de Gouw, J. A., Burling, I. R. and Yokelson, R. J.: Biomass burning emissions and potential air quality impacts of volatile organic compounds and other trace gases from fuels common in the US, Atmos. Chem. Phys., 15, 13915–13938, doi:10.5194/acp-15-13915-2015, 2015.

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E. and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography–time-of-flight mass spectrometry, Atmos. Chem. Phys., 15, 1865–1899, doi:10.5194/acp-15-1865-2015, 2015.

Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E., Theodosi, C. and Mihalopoulos, N.: Long-term characterization of organic and elemental carbon in the PM2.5 fraction:

the case of Athens, Greece, Atmos. Chem. Phys., 14, 13313–13325, doi:10.5194/acp-14-13313-2014, 2014.

Stockwell, C. E., Veres, P. R., Williams, J. and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Chem. Phys., 15, 845–865, doi:10.5194/acp-15-845-2015, 2015.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-721, 2016.