Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-721-RC2, 2016

Atmospheric Chemistry and Physics
Discussions
Open Access

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.

Anonymous Referee #2

Received and published: 21 September 2016

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.

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.

Major Comment:

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? 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.

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. 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? 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 depends 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 NH_4 and NO_X (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 NO_X 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. 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.

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 NO_X 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. 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.

Other Comments

Line 122. Please define VOCs.

Line 135. What do you mean by “main ions.” Are you referring to NO_3^-, SO_4^{2-}, NH_4^+ ?

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?

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, Stockwell et al. 2015, Hatch et al. 2015); therefore, these masses may be affected by other sources than just petrol.

Line 246. Please add “the” between “in” and “Patras”

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 exceeding 15 μg m^{-3}.

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.

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

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

Line 358 and Line 363. Both factors correlate similarly to BC ($R^2 \sim 0.26$), so I would not say that CO correlates modestly with BBOA-I (line 358) and poorly with BBOA-II (line 363).

Fig 6. I believe that the BBOA traces are mislabeled. Is this correct?

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

Editorial comments

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.

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.

1)Please use commas around interrupters. For example, at line 221, the sentence would read more clearly as "The nitrate was, on average, 0.48 μg m^{-3} ..." Similar examples can be found at line 240 and 564.

2)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.

3)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.

References

Burling, I. R., et al. (2010). 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.

Coggon, M. M., et al. (2016), Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers, Geophys. Res. Lett., 43.

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