Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-356-RC1, 2018

Response to Anonymous Referee #3 comments

The manuscript "Sources and processes that control the submicron organic aerosol in an urban Mediterranean environment (Athens) using high temporal resolution chemical composition measurements" presents the submicron aerosol chemical composition in Athens, Greece. In addition to study the seasonal variation of the main chemical species, organics, sulfate, nitrate, ammonium, chloride and black carbon, the sources of organics were assessed by statistical methods using Positive Matrix Factorization (PMF). The results of PMF showed that in winter there were five factors for organic aerosol (OA); fossil fuel combustion (HOA), biomass burning (BBOA), cooking (COA) and two different oxidized organic aerosols (SV-OOA and LV-OOA), of which primary sources were pronounced. In summertime, most of the OA was associated with oxidized factors representing secondary organic aerosol.

This paper exploits an extensive data set (more than a year of data) and the instruments used are present-day. However, the results of this study follow very closely to those presented previously for urban areas in winter and summer not revealing any novel sources of aerosols or phenomena in urban area.

My main concern is though the PMF/ME2 analysis. Authors found biomass burning and cooking factor by constraining them with reference mass spectra. My feeling is that any factor can be constrained and a mass fraction of _10% is obtained for that factor even though there is no clear evidence of the existence of that factor. A standardized methodology to perform source apportionment on AMS data using the ME2 is given in Crippa at al. (2014) but since the authors do not show the results (residues) without constraining factors, or constraining only HOA, I can't be sure that the given methodology has been followed. My fear is that authors discovered factors that do not exist (especially COA). As it is discussed Mohr et al. (2012) the actual differentiation between AMS aerosol spectra from cooking and traffic (or BBOA) is difficult for unit mass resolution spectra (ACSM data), and it is mostly based on the relative abundances of signals at m/z 55 and 57. Authors need to provide the evidence of COA more carefully. According to Crippa et al. (2014) the presence of the meal hour peaks is necessary to support COA at least in urban areas. In the paper of Stavroulas et al. it is stated that COA exhibits a slight hump during lunchtime but this hump is very difficult to see from the figures. COA as well as all the other PMF factors, except LV-OOA, had largest concentrations in nighttime. If meteorology (boundary layer height) affects that much on concentrations, PMF analysis can be very tricky and it may not be possible to distinguish all the sources, and that needs to be acknowledged in the paper.

I think that the data presented in this paper in worth publishing. However, major changes need to be done before this paper merits publication in ACP. I recommend that authors redo PMF analysis according to Crippa et al. (2014) and consider the validity of BBOA and COA in every step (and show results from every step in supplement). Additionally, I suggest authors to concentrate on novel results that interest the whole scientific community not just Athens area, and state it clearly what are the new findings presented in this paper.

Response: *We thank the anonymous referee for the review and we try to incorporate his/her suggestions and comments in the revised version of the manuscript. Authors have taken into consideration the referee's concerns, especially concerning the PMF analysis and the COA factor and have addressed the raised issues respectively. The revised manuscript includes a clearer approach in presenting the different PMF runs, reporting all the steps of the strategy and the evaluation of the results in a systematic way. A sensitivity analysis of the alpha values used is also presented, depicting the validity of the derived factors (e.g. replicating the methodology of Mohr et al. (2012)).*

Major comments

1. Page 2-3, Introduction; Introduction section concentrates too much on Athens area and do not give general introduction to the research questions and issues related. I suggest taking more global point of view to the topic in introduction.

Response: *The revised version the Introduction is more focused on the novel results that interest the wider scientific community and not only on wintertime emissions and biomass burning.*

2. Page 11; "3.3. Source apportionment of organic aerosol" section is too long. Because the methods (PMF/ME2) are quite commonly used nowadays, and described in the literature, this section needs to be shorten or moved to experimental or supplement leaving only clear results to "Results and Discussion" section. Authors used ME2 traditional way so there are no scientifically new results in this section regarding the use of ME2.

Response: *The approach on presenting the PMF analysis has been updated in the revised version, since most reviewers suggested clarifications in the apportionment strategy followed and the presentation of the results. However, following the reviewer's request, it was moved in the supplementary material. The section features now less discussion on the PMF method and focuses in a more efficient way to the results.*

3. Page 11, line 323; unconstrained runs, the results from unconstrained runs need to be presented in supplement. It is very difficult for the reader to trust the results (especially BBOA and COA factors) if unconstrained results are not shown. The technical guidelines for constraining are given in Crippa et al. (2014) and the results for each step needs should be presented.

Response: *The results from the unconstrained runs, together with runs with only one factor constrained with a reference HOA spectra, and additional runs with two factors constrained with HOA and BBOA reference spectra have been added to the supplement. It is, in our opinion, evident that in the unconstrained runs the HOA-like factor is present. When constraining the HOA factor and observing the spectra in the 4 and 5 solution runs, factors clearly resembling to COA and BBOA emerge.*

4. Page 12; affinity between spectra by the theta angle approach, why did you use this approach here and Pearson correlation (with R2 earlier)? It is very confusing for readers that are not familiar with this angle approach. I suggest to use Pearson correlations (R2) throughout the manuscript.

Response: *We used the theta angle approach for further justification of the selected solutions. As stated in the manuscript (L348) spectra with angles larger than 30 degrees correspond to correlation coefficients <0.86, which can still be considered as a strong correlation, even though as a theta angle it is considered that the spectra exhibit significant differences. As the confusion for readers that are not familiar with this approach has also been pointed out by some other reviewers, squared Pearson correlations (R^2) are now used in the revised version of the manuscript.*

5. Meteorological parameters; meteorological parameters are not given in the paper. Please provide at least temperature, radiation and boundary layer height that are important regarding the concentrations and the sources of aerosol.

Response: *Meteorological parameters of ambient temperature, relative humidity, solar radiation and wind speed are now incorporated in the revised supplementary material. Unfortunately, measurements of PBL height were not available during the reported periods. The discussion regarding PBL height has been updated though and is going in to more detail, given the fact that long term observations of PBL height in Athens have been recently published (Alexiou et al., 2018).*

Minor comments

6. Page 1-2, Abstract; line 30-31; "These results highlight the rising importance of biomass burning in urban environments during wintertime." The contribution of biomass burning to organics was 10% in wintertime. It's quite a small contribution. This sentence needs an evidence or to be modified.

Response: *It is true that the contribution of the primary biomass burning OA factor is around 10% of organic aerosols. Nevertheless, the SV-OOA factor identified for the winter period contributes another 31% and is strongly linked to biomass burning as indicated by its correlation with tracers such as BC_{wb} (R^2=0.85) and nss-K^+ (R^2=0.61) elevating the biomass burning related factors contribution to 41% of OA.*

7. Page 3, line 82; "non-refractory part"; you also measured BC, why it is not included in main objectives (BC is refractory component)?

Response: *The term non-refractory part is now omitted.*

8. Page 4, line 101-102; “s/n 140-139” not needed here

Response: *The instrument’s serial number has been removed from the revised manuscript*

9. Page 4, line 102; Aerodyne Research Inc.

Response: *Amended*

10. Page 4, lines 112-120; “The instrument has participated in an intercomparison study:” This information is not relevant. Please remove this intercomparison section or move it to supplement.

Response: *Information related to the instruments participation to ACMCC’s intercomparison study has now been moved to the supplement.*

11. Page 4, line 118-120; give RIE values

Response: *IE for NO3 and RIEs for NH4 and SO4 are now stated in the revised supplement.*

12. Page 5, line 122-123; default collection efficiency of 0.5, please use equation of Middlebrook et al., (2012) to calculate composition dependent collection efficiency.

Response: *The issue of using a constant collection efficiency of 0.5 has also been raised by Anonymous Referee #2. Chemical composition dependent CE has now been applied to the dataset according to Middlebrook et al. (2012). All concentrations have been updated accordingly.*

13. Page 5, line 138-139; more information is needed on SMPS measurements; size range, how number size distribution was converted to mass concentration (density)?

Response: *The details regarding the SMPS size range as well as the reference to the method used to convert Volume concentration obtained by the SMPS to mass concentration were given in the original manuscript in lines 210 – 217 in §3.1. This piece of information has now been moved to the more appropriate “Instruments and Methods” section.*

14. Page 5, line 140-144; give more details of selected absorption exponents, are they default values or did you calculate them specifically from this data set/ for this location?

Response: *The absorption exponents used for the BC source apportionment are the default values used by the AE-33 software,* $a_{ff} = 1$ *and* $a_{bb} = 2$. *No fine tuning of the apportionment model was conducted in this* *study. We feel that a sensitivity analysis of Angstrom exponents used, does not lie within the scope of this manuscript and will certainly be addressed in future work.*

15. Page 5, line 144; remove "Necessary"
Response: *Amended.*

16. Page 5, line 145; remove "historic"
Response: *Amended.*

17. Page 6, line 160; on the organic mass spectra obtained
Response: *Amended.*

18. Page 7, line 185; "following section"; give the number of sections
Response: *Amended.*

19. Page 7, line 194-196; describe PM2.5 filter collection and thermal-optical method in experimental section

Response: *Details on the filter sampling procedure and thermal-optical protocol used are now given in the revised version of the manuscript.*

20. Page 8, line 223; add time base for averages e.g. 1-hour average
Response: *Amended.*

21. Page 8, line 244, change "to the levels" to "on the levels"
Response: *Amended.*

22. Page 8-9, line 244-247; "These observations are in accordance:" this sentence is unclear and needs to be modified

Response: *This sentence has now been modified accordingly. It is now clear that the levels of maximum concentrations measured by Florou et al., 2017, during a campaign from 10/01/2013 until 09/02/2013 for organics, BC and nitrate are similar to the ones measured for all three winter measurement periods reported in this study.*

23. Page 9, line 261-262; "additional primary emissions from heating play a role", based on what? Explain how you see this addition in results.

Response: *The stated addition refers to the largely elevated concentration levels of organics and BC which during winter are also emitted from central heating systems and fireplaces. Necessary clarifications have been made in the revised text.*

24. Page 9, line 273; what are increased local sources for nitrate in winter?

Response: As seen in our study, but also in the study of Florou et al. (2017), nitrate concentrations follow a similar trend with the organic aerosol, as well as with BC. Therefore, the combination of the low temperatures during nighttime along with the increased local combustion sources which lead to reduced acidity, result at the favorable partitioning of nitrate in the aerosol phase. This is clarified in the revised text.

25. Page 11, line 309-312; "higher organics concentration during early night could possibly be due to biogenic/vegetation sources that produce volatile components that condenses on particulate phase during night." This assumption needs evidence, maybe reference or can you see this in mass spectra of organics?

Response: *This assumption is backed when taking into account the PMF analysis of section §3.3. It is clear in Figure 5 that more than one third of the night time peak is attributed to the SV-OOA factor. SV-OOA exhibits good correlation with reference mass spectra obtained for SOA linked to the oxidation of biogenic precursors. An* $R^2=0.90$ *was found when correlating to IEPOX-OA from Budisulistiorini et al. (2013), while correlation with SOA formed by the oxidation of b-pinene (Bahreini et al., 2005) yielded an* $R^2=0.89$*. A reference to this discussion in section 3.3 has now been added to the sentence.*

26. Page 12, line 354-356; if HOA; COA; SV-OOA and LV-OOA are mentioned here for the first time the long names should be given. Please double-check when abbreviations are given for the first time.

Response:
Indeed, the factor abbreviations are given here for the first time in the manuscript. In the revised text their whole names will be given with the abbreviations in parenthesis, to be used throughout the text.

27. Page 13, line 383-385; "OA precursors are maximum during night similar to SVOOA". Please give reference or results.

Response: *Biogenic SOA precursors such as a- and b- pinene and limonene are known to exhibit maximum concentrations during nighttime (e.g Harrison et al., 2001 for measurements performed in a forest area of Greece). Measurements of biogenic SOA precursors performed in Athens during winter and summer time (Kaltsonoudis et al., 2017) also show an increase during nighttime. Furthermore, based on the recent field study of Li et al. (2018), isoprene-derived SOA tracers, such as Methyltetrahydrofuran-diols and C5-alkene triols, mainly formed by reactive uptake of IEPOX, exhibit a clear diurnal variability with maximum values* *during nighttime and minimum during day. Similarly, organosulfates derived from isoprene have been found to exhibit their higher concentrations during night, in biogenically influenced urban regions Hatch et al. (2011). All these references are now added in the text.*

28. Page 13, line 385-387; “SV-OOA shares some similarities with SOA from diesel exhaust”. This is too vague. Give correlation coefficient or remove sentence. How much diesel vehicles there are in Athens?

Response: *A correlation coefficient for the comparison with the mass spectra obtained by Sage et al. (2008) has been added to the revised version of the manuscript.*
A concrete number for the diesel vehicles in Athens is not available. According to local authorities, the number of new diesel passenger vehicles sold in Greece since the lift of the long-standing ban in the two major cities exceeds 300,000. The larger part of these vehicles are expected to circulate in the area of Athens.

29. Page 13, line 3963-397; “COA shown moderate correlation with nitrate”. Explain why.

Response: *COA is not expected to be a semi-volatile component, therefore a correlation with nitrate is not to be expected. Probably this moderate correlation is due to the similar diurnal variability of the two components, characterized by pronounced nighttime peaks.*

30. Page 14, line 403; Is figure number here really 8? Double-check figure numbers.

Response: *Yes, the Figure number here is stated correctly. Figure 8 shows the results of the back-trajectory cluster analysis carried out.*

31. Page 14, line 410; “COA exhibits a slight hump during lunch hours.” I really can’t see this hump in Figure 5. There is similar lump between 4 and 9 am. How do you explain this morning lump? Please add negative standard deviations to Figure 5 (and all the other figures as well) because it’s confusing (and maybe misleading) when only positive deviations are shown. Add also zero-lines to Figure 5 and Figure 6.

Response: *Performing a similar exercise as for the inorganic components diurnal variability, where we calculated the diurnal variability normalized to the mean value, it is evident that during early morning, namely at 05:00 and 06:00 the COA factor concentration is 47% and 49% of the mean daily value respectively. On the contrary during early afternoon at13:00, 14:00 and 15:00 concentration rises to 64%, 62% and 63% of the mean value respectively.*

32. Page 14, line 417; “moderate hump for SV-OOA during mid-day”. I can’t see this hump in Figure 5. If you think this “hump” is true show it with numbers e.g. how much SV-OOA increased during mid-day compared to e.g. morning.

Response: *Following a constant decline of the, normalized to the daily mean, concentration of the SV-OOA factor, from roughly 137% of the mean to 80% starting from 00:00 until 10:00, a plateau is observed with almost constant normalized values around 80% from 10:00 to 14:00. Another decline follows until the minimum (60% of the mean) at 18:00 before the rise until midnight. Peak values of the normalized LV-OOA concentrations occur within this 10:00 to 14:00, namely 107% and 106% of the mean at 13:00 and 14:00 respectively.*

33. Page 16, line 463; How did you calculate Nss-K?

Response: *nss-K^+ concentrations are derived from fine mode potassium measured by PILS (sampling through a PM_1 cyclone) corrected for seawater influence, using Na^+ concentrations (also measured by PILS) and the Na/K ratio in seawater as reference (Seinfeld and Pandis, 1998; Sciare et al., 2005). A clarification is now added in the revised version of the manuscript.*

34. Page 16, line 467-471; “SV-OOA mass spectra includes also fingerprint fragments of biomass burning m/z 60 and 73”; what fraction of these mass fragments were associate with BBOA and SV-OOA (and other factors)?

Response: *For the fragment m/z=60, 41.4% is attributed to the BBOA factor, 46.7% is attributed to the SV-OOA factor and 3.4%, 8.5% to HOA and COA respectively. For fragment m/z=73 the fractions are 26.6% for BBOA, 48.3% for SV-OOA, 7.1% for HOA, 12.9% for COA and 5.1% for LV-OOA.*

35. Page 16, line 477-478; why COA correlates with potassium and chloride?

Response: *As seen from the comparison with external mass spectra, COA is very similar (R^2=0.93) to the meat charbroiling spectra found in the chamber study by Kaltsonoudis et al. (2017), therefore it is expected to exhibit a good correlation with potassium, a tracer for biomass burning from restaurants/rotisseries. Similarly, chloride is also emitted during biomass burning (Akagi et al., 2011). This reference is added to the revised text.*

36. Page 16, line 484-490; “SV-OOA in cold period is linked to the fast oxidation of primary combustion sources (BBOA and HOA) which is also reflected on its diurnal variability.” This sentence needs explanation and proof.

Response: *In Figure 7(b) the strong correlation of the SV-OOA factor with BCwb (R^2=0.85) nss-K^+ (R^2=0.61) and CO (R^2=0.63) proposes a clear link of the semi volatile compound to primary combustion sources and especially wood burning. As this factor also correlates moderately with BCff (R^2=0.40) and* *given that CO is also emitted by all combustion sources, a contribution from HOA oxidation cannot totally ruled out.*

37. Page 17, line 494-495; “moderately hump for COA during lunchtime”. This cannot be seen in Figure 6.

Response: *Close attention is paid in the used terminology in the revised version of the manuscript.*

38. Page 17, line 499-500 ”A moderate peak during the morning traffic hour (partly masked by the high night values) for SV-OOA,” This peak is very difficult to see in Figure 6 (concentrations) and it does not exist in contributions figure. Please, re-consider how you define peaks/humps etc. in the paper.

Response: *As mentioned in the previous comment, we agree with the reviewer concerning the nomenclature used in the text and in the revised version we will pay attention to the terminology used.*

39. Page 17, line 510-513, “SV-OOA comes from the rapid oxidation of freshly emitted BBOA”, this needs more explanation. What is the oxidation process, what are the oxidants in wintertime? In general, it said that SV-OOA is linked to quick atmospheric processing of VOCs within few hours. This needs to be explained in more detail (with results).

Response: *As also pointed out to anonymous referee #2, the fast oxidation of fresh biomass burning in plumes within just a few hours after emission is not new in the literature (Lathem et al., 2013; Cubison et al., 2011), and is correlated both with external time series such as* BC_{wb}*, nss-*K^{+}*, and CO, as well as with mass spectra from oxidized biomass burning, therefore we do not feel that our assessments are unjustified. Although an exact mechanism is not yet established in the area, field observations suggest nighttime heterogeneous reactions and also involvement of nitrate radicals (Bougiatioti et al., 2014).*

40. Page 18, line 533-534; “organics, BC and nitrate double their concentrations during night-time as a results of additional primary combustion for heating purposes.” Do you suggest that nitrate and BC are mostly from heating? I think that the increase in winter in nighttime is mostly due to boundary layer change.

Response: *Organics and BC are indeed mostly from heating. If the increase would mostly be due to the boundary layer, similar concentrations would also be seen during the warm season, as well, as the boundary layer height is not that different between warm and cold season (Alexiou et al., 2018). The significant enhancement of winter-time fine PM levels due to heating emissions has been well-documented for Athens, even prior to the advent of the economic recession (Chaloulakou et al., 2005).*

On the other hand, nitrate is not directly emitted, but the higher concentrations are due to the combined effect of temperature and reduced acidity to the partitioning in the aerosol phase, as it has already been mentioned. These are further clarified in the revised text.

41. Page 19, line 557-559; "HOA being affected by combustion from central heating", The impact of central heating was not discussed in Results section. If the authors think that this is the source of HOA it should be discussed and (justified) earlier.

Response: *HOA is the factor that represents fossil fuel combustion, which is portrayed by both vehicular traffic, as well as heating oil combustion in central heating units However, based on emission inventories for Greece, primary non-methane hydrocarbon and aerosol emissions from central heating are much smaller compared to traffic (Fameli and Assimakopoulos, 2016). These points are clarified in the revised text.*

42. Figure 1; Add "1-hour averaged" mass concentrations
Response: *Amended.*

43. Figure 4; in upper figure you use "organic aerosol" but in lower figure "Organics". Please be consistent with the names.
Response: *Amended.*

44. Figure 6; why did you plot COA and nss-K to the same figure? Based on the time series they correlate quite well. Do you suggest that they originate from the same source?

Response: *The selected pairs in Figure 6 have been rearranged in order to be in accordance with those presented in figure 5.*

45. Table 1; please give the name of the month clearer way e.g. using Jan, Feb etc.
Response: *Amended.*

Technical comments:
46. Page 6, line 163; time series
Response: *Amended.*

Rerefences

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