

**Interactive comment on “Multiyear chemical composition of the fine aerosol fraction in Athens, Greece, with emphasis on winter-time residential heating” by Christina Theodosi et al.**

**Anonymous Referee #2**

*Received and published: 1 May 2018*

*The manuscript presents and discusses results from a long-term study of the PM<sub>2.5</sub> aerosol composition for Athens, Greece. Emphasis is given to the impact of residential heating during winter. The manuscript is definitely of interest to aerosol researchers who are involved in related work. The study would have benefited from measuring the wood-burning marker levoglucosan during the winter campaigns, though. Since no pure wood burning marker was included in the analysis, the assessment by PMF of the contribution from wood burning has likely a substantial associated uncertainty. There is no information given about this uncertainty in the manuscript, but there should be. Furthermore, as indicated below, the current manuscript is on several occasions unclear, there are problems with the references, and the manuscript also suffers from many other (mostly technical) shortcomings. Consequently, substantial revision is needed before it can be published in ACP.*

We would like to thank the reviewer for his/her comments. We agree that a specific biomass burning tracer other than soluble K would have strengthened the characterization of the relevant factor. However, due to the large number of filters in the study it was not possible to perform levoglucosan measurements as well. Given the correlations of the factor with the biomass burning tracers (BC<sub>wb</sub> and  $m/z$  60), component ratios and day-night variability, we believe that the factor is adequately characterized. However, the reviewer is right to indicate a likely uncertainty and this is now reported in the revised manuscript.

Furthermore, in order to provide an indication of such an uncertainty, we have repeated the PMF analysis including data on the  $m/z$  60 and  $m/z$  73 fragments, from collocated ACSM measurements, for the winter of 2015-2016, when such data were available. From previous work conducted at the present site (Fourtziou et al., 2017) these have been validated as important BB tracers and are considered fingerprint fragments of levoglucosan, displaying strong correlations.

The  $m/z$  60 and 73 values in  $\mu\text{g m}^{-3}$  were averaged for the respective filter sampling intervals. The number of available cases was 109, still adequate to perform the analysis. We note that combining data from chemical analysis and aerosol mass spectrometry in the same receptor model, while not frequent, has been attempted in past studies (Li et al., 2004; Dall'Osto et al., 2014).

A similar 6-factor solution was again obtained. We compared the resulting BB source profile and the time-series of BB contributions to those of the original dataset without the additional tracers. The results reveal that differences are minor. The source profiles closely agree and there is a mean absolute difference of 3.5% (0-12.4%) in explained variances for the source components. The mean difference in the factor contributions to PM<sub>2.5</sub> for the winter of 2015-2016 was +0.68  $\mu\text{g/m}^3$  (higher in the original solution). The latter is analyzed in +0.59  $\mu\text{g/m}^3$  in day-time and +0.82  $\mu\text{g/m}^3$  in night-time average contributions. The mean difference in the fractional contribution to PM<sub>2.5</sub> is +3.4%.

The results regarding the uncertainty are summarized in the following figures and will be added as supplementary material.

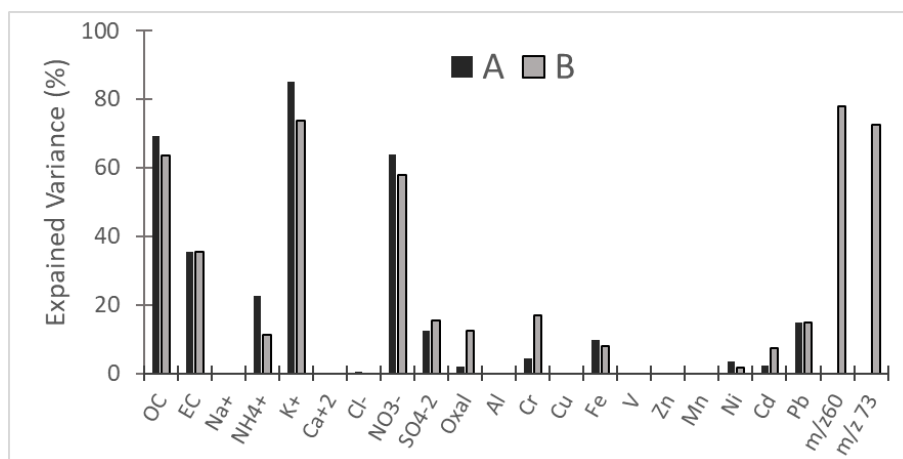


Figure S2: Explained variances of PMF-components by the biomass-burning factor in the original solution (A) and in the solution including ACSM fragments for the winter 2015-2016 (B).

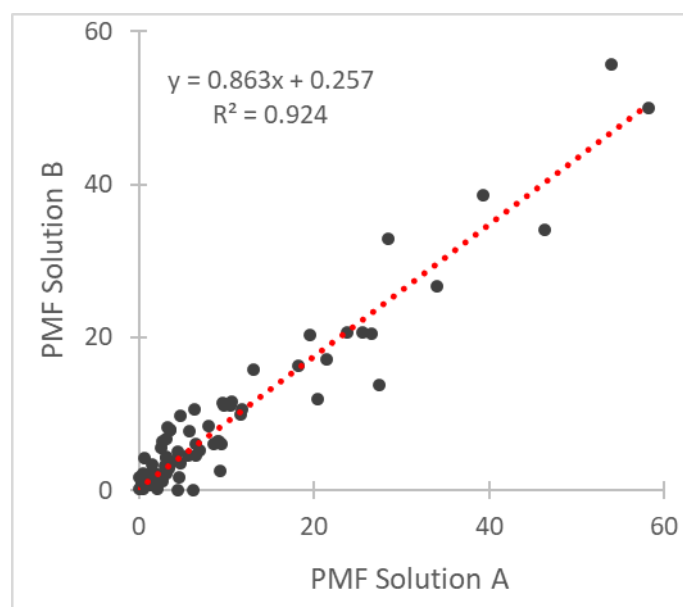


Figure S3: Comparison of calculated contributions ( $\mu\text{g m}^{-3}$ ) of the biomass burning factors, in the original solution (A) and in the solution including ACSM fragments for the winter of 2015-2016 (B).

Below we list our response to the reviewer's specific comments (in italics) and the corresponding changes in the manuscript.

*Specific comments:*

1. Page 2, line 24: *It seems that there is something missing after "between winter 2012".*  
We thank the reviewer for noticing and the missing word "winter 2013" was added.

2. Page 2, line 12: *Is there something missing after "the city center and" or should the "and" just be deleted?*

The reviewer is right the word "and" has been deleted.

3. Page 3, lines 25-29, and further within the text: *It seems that during winter separate day and night samples were collected in addition to the regular 24-h samples. However, later in the manuscript (e.g., in Figure 4(a) and Figure 5), it is not clear whether the winter data were derived from the regular 24-h samples or from the day and night samples.*

As mentioned in section 2.2 “During the three occurring winter periods (from December to February), two-month intensive campaigns (sampling frequency of 12h; n=447) were conducted”. Thus, in winter mainly 12h samples were collected and the results at figures 4a and 5 reporting results during winter originate from these 12-h samples.

4. Page 4, line 26: *Abbreviations and acronyms (here PMF) should be defined (written full-out) when used for the first time within the body of the manuscript.*

5. Page 7, line 23: *Abbreviations and acronyms (here IM and SS) should be defined (written full-out) when used for the first time within the body of the manuscript.*

Most abbreviations and acronyms used throughout the manuscript have been defined when they were used for the first time within the body of the manuscript. For instance PMF/IM/SS have been defined in the abstract, Page 1, line 12. However, we thank the reviewer for helping us improve the manuscript and carefully checked for additional omissions.

6. Page 8, lines 1-2: *There are no sulphate and ammonium data in Figure 3.*

The reviewer is correct and this sentence has been corrected accordingly to represent exactly what the Figure illustrates.

7. Page 8, line 8: *It is unclear whether the number of samples (780) includes only 24-h samples or also day and/or night samples.*

Since it was not clear, a comment has been included to specify that all samples both 12h and 24h have been considered.

8. Page 8, line 15: *It is unclear whether the winter PM<sub>2.5</sub> mass was derived from the 24-h samples or from the day and night samples.*

As winter samples consist of 12h samples the PM<sub>2.5</sub> winter value derived from these samples. The reviewer is right and as it was not clear a comment has been included in the manuscript.

9. Page 8, line 16, and further in the manuscript: *Reference is made here to Figures 5a,b and later to subfigures for Figure 7, but the different subfigures of Figures 5 and 7 are not labeled with a, b, c, and so on.*

Indeed the reviewer is correct and figures have been labelled as suggested.

10. Page 8, lines 22-23: *There is no info on the aethalometer in Section 2. What size fraction was measured with it? And how was BC<sub>wb</sub> obtained? Some info and/or literature references on this are needed in Section 2.*

As instructed by the reviewer additional information are provided in the manuscript (Section 3.4.2), along with the appropriate reference.

11. Page 9, line 16: *The use of the word "between" is incorrect here. Could it be replaced by "of"?*

Done.

12. Page 9, line 17: *Why is the word "morning" used here? How were "morning" data obtained? Should it not be "day"?*

The word “morning” has been replaced by “day”.

13. Page 9, line 27: Why is there only one correlation coefficient given for the winter? Or were the same correlations obtained for OC and EC?

Indeed, they both had the same correlation coefficient and a sentence was added in the manuscript on that direction.

14. Page 10, lines 10-13: I do not understand the reasoning. If the molar ratio of  $\text{NH}_4/\text{nssSO}_4$  is smaller than unity, would one not expect a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ ?

The reviewer is right and we meant equivalent ratio not molar ratio. It has been appropriately changed in the manuscript.

15. Page 11, line 17: It is unclear what is meant by "increase by about 57%". Increase of what relative to what?

As it is presented in table 2,  $\text{nssK}^+$  presents a day to night increase equal to 54% once all winter samples are included, while equal to 57% if only SP events are included. That is the reason we refer to an "increase by about 57%". As requested by the reviewer an explanation was added.

16. Page 13, lines 11-13: I cannot follow the reasoning. Would the correlations between the three elements during winter not suggest that wood burning is an important source, considering that this was also observed in the study of Maenhaut et al. (2016)?

We fully agree with the reviewer and we do understand his/her point. Correlations of As, Cd and Pb during winter suggests emissions from wood burning as mentioned in Page 13, line 4-7. Furthermore, the fact that As and Cd, Pb have been associated with coal combustion further supports that hypothesis. The reference Maenhaut et al., 2016 was also added to indicate that other studies reach the same conclusion too.

17. Page 16, line 9: Abbreviations and acronyms (here EF) should be defined (written full-out) when used for the first time within the manuscript.

Done.

18. Page 17, line 12: It is unclear what is meant by "fuel" here.

It refers to fossil fuel use, and it was corrected accordingly in the manuscript.

19. Pages 18-26, Reference list: There are several problems. For authors with more than 1 initial, there should be a space between the initials; each initial should be followed by a full stop (.); for references with at least 3 authors, there should be ", and" before the last author (note that for references with only 2 authors, there should not be ", and" but "and" instead; the publication year should be at the end of the reference and not after the authors; "Kawamura and Iskushima, 1993" (on page 21, lines 13-14) should be moved down to before "Kawamura et al., 1996"; "Uria-Tellaexte and Carslaw, 2014" (on page 25, lines 9-10) should be moved down to before "Valaoras et al., 1998".

We thank the reviewer for raising these issues and we would like to apologise for our mistakes. All changes proposed have been performed

20. Further problems with the references: The following references are in the text, but not in the Reference list: - page 14, lines 22 and 32: Amato et al., 2016.

- page 16, line 18: Dall'Osto et al., 2012; there is Dall'Osto et al., 2013 in the Reference list to which not is referred within the text.

We thank the reviewer for helping us to improve the manuscript. All references have been checked.

21. Page 31, caption of Figure 5: This caption should be extended. What does the line inside each box indicate? And what do the whiskers mean? Why do some whiskers end on a dash and other not?

The reviewer is correct and in order to provide more information to the reader additional information have been included in the figure caption. The fact that some whiskers end on dash and other do not is due to the fact that in the latter we intentionally changed the maximum bound of the y axis in order to emphasize on the values presented.

22. Technical and other (mostly minor) corrections:

We would like to thank the reviewer for his/her time and all below mentioned technical and minor corrections have been considered.

- page 2, line 2: replace "interest on" by "interest in".
- page 2, lines 3 and 20; page 8, line 24; page 11, line 32: replace "e.g." by "e.g.,".
- page 2, line 13, and on several occasions further in the manuscript: for references within parentheses there should be a comma before the publication year.
- page 2, line 30; page 4, line 2; page 7, line 3: replace "water soluble" by "watersoluble".
- page 2, line 33: replace "in the" by "in".
- page 3, line 8: replace "Athens," by "Athens".
- page 3, line 16; page 10, line 4: replace "long range" by "long-range".
- page 3, line 17: replace "Northern sector" by "northern sector".
- page 3, line 19: replace "Southern sector" by "southern sector".
- page 3, line 21: replace "Athens" by "Athens".
- page 3, line 22: replace "are provided" by "is provided".
- page 3, line 27: replace "to the" by "in the".
- page 4, line 11: replace "species concentrations" by "species".
- page 4, line 13: replace "in ultrasonic bath and" by "in an ultrasonic bath and the extracts were" and replace "0.45\_m" by "0.45 \_m".
- page 4, line 17: replace "in details" by "in detail".
- page 4, line 20: replace "while" by "while for".
- page 4, line 27: replace "on 12-h" by "on the 12-h".
- page 4, line 31: replace "with analysis" by "with the analysis".
- page 5, line 10: replace "their contributions" by "the day and night contributions".
- page 5, lines 17-18: replace "probability (CBPF) function" by "probability function (CBPF)".
- page 5, line 29: replace "concentration of" by "concentrations of".
- page 6, line 8: replace "represents time" by "represents the time".
- page 6, line 22: replace "concentration of" by "concentrations of".
- page 7, line 14: replace "confined in" by "confined in the" and replace "they do not" by "do not".
- page 7, line 15: replace "exceed few" by "exceed a few".
- page 7, line 17: replace "trace element" by "the trace element".
- page 7, line 23: replace "Mass Closure" by "mass closure".
- page 7, line 27: replace "relative ratio" by "concentration".
- page 8, line 19: replace "low winds" by "low wind speeds".
- page 8, line 24: replace "in GAA" by "in the GAA".
- page 8, line 30: replace "i.e" by "i.e.,".

- page 8, line 32: replace "have been" by "has been".
- page 9, line 8: replace "winter POM" by "winter, POM".
- page 9, line 12: replace "on carbonaceous" by "on the carbonaceous".
- page 9, line 13: replace "Similar" by "A similar".
- page 9, line 19: replace "on fine" by "on the fine".
- page 9, line 26: replace "correlation with" by "correlation with the".
- page 9, line 28: replace "Composition" by "composition".
- page 10, line 1: replace "low winds" by "low wind speeds".
- page 10, line 21: replace "considerably reduce" by "are considerably reduced".
- page 10, line 22: replace "Similar" by "A similar".
- page 10, line 34: replace "concentrations in" by "in".
- page 11, line 6: replace "from Sahara" by "from the Sahara".
- page 11, line 7: replace "Regarding, nssK+" by "Regarding nssK+, ".
- page 11, line 9: replace "from on line" by "from online".
- page 11, line 12: replace "present" by "exhibit a".
- page 11, line 17: replace "i.e." by "i.e.,".
- page 11, line 22: replace "exhibit" by "exhibits".
- page 11, line 23: delete ", respectively".
- page 11, line 25: replace "2011)" by "2011).".
- page 11, line 32: replace "e.g wood" by "e.g., wood".
- page 12, line 5: replace "as it is linked" by "and thus mainly linked".
- page 12, line 7: replace "maxima also" by "maxima are also".
- page 12, line 8: replace "road re-suspended" by "resuspended road".
- page 12, line 14: replace "Different" by "A different".
- page 12, line 16: replace "trends, corroborates" by "trends corroborate".
- page 12, line 18: replace "Anthropogenic" by "anthropogenic".
- page 12, line 19: replace "The analyzed" by "The measured".
- page 12, line 22: replace "they related" by "are related".
- page 12, line 26: replace "it is included" by "is included".
- page 12, line 29: replace "amongst other" by "and non-ferrous metals production amongst others".
- page 13, line 14: replace "in our site" by "at our site" and replace "significant" by "a significant".
- page 13, line 18: replace "seasonally basis" by "seasonal basis".
- page 13, line 28: replace "Factors" by "Factor".
- page 13, line 30: replace "PM2.5" by "The PM2.5".
- page 13, line 31: replace "n.s." by "not significantly different from 0".
- page 13, line 32: replace "indicating" by "indicated" and place "indicated the stability of the solution" at the end of the sentence on page 14, line 1.
- page 14, line 5: replace "Burning" by "burning".
- page 14, line 13: replace "or EC" by "of EC".
- page 14, line 16: replace "to 2.3" by "to the 2.3".
- page 14, line 21: replace "are abundant" by "is abundant".
- page 15, line 14: replace ", however" by "; however, ".
- page 16, line 4: replace "Sources" by "sources".
- page 16, line 9: replace "to upper" by "to the upper".
- page 16, line 10: replace "8% of" by "8% of the".
- page 16, line 28: replace "to aerosol" by "to the aerosol".
- page 17, line 2: the parentheses around the percentages should be removed.
- page 17, line 4: replace "Ionic" by "The ionic".

- page 17, line 8: replace "significant" by "a significant".
- page 17, line 13: replace "lesser extend" by "lesser extent".
- page 17, line 19: replace "with higher" by "with a higher".
- page 17, line 21: replace "respectively" by "respectively,".
- page 17, line 31, and page 18, line 1: replace "acknowledges" by "acknowledge".
- page 23, line 7: replace "Nair, and" by "and Nair,".
- page 25, line 27: replace "Waenhaut" by "Maenhaut".
- page 30, line 1: replace "aerosol species" by "aerosol component or species".
- page 35, line 1: replace "to component" by "to the component".
- pages 36, 37 and 38: the Table headings should be above the Tables instead of below.
- page 36: the information on the Sampling, Location and Reference should be at the top of Table 1 instead of at the bottom.
- page 37, line 3: replace "The annual" by "Annual".
- page 37, line 27: replace "elements during" by "elements and species during".

*Comments for the Supplement:*

*Page 2: It is unclear what "CPF probability" indicates. In the Main text CBPF is mentioned.*

*Page 3, line 1: Replace "wind speed and speed" by "wind direction and speed in m s<sup>-1</sup>".*

*Page 4: The Table heading should be above the Table instead of below.*

Dall'Osto, M., Hellebust, S., Healy, R. M., Connor, I. P., Kourtchev, I., Sodeau, J. R., Ovadnevaite, J., Ceburnis, D., O'Dowd, C. D., and Wenger, J. C.: Apportionment of urban aerosol sources in Cork (Ireland) by synergistic measurement techniques, *Sci. Total Environ.*, 493, 197-208, 2014.

Li, Z., Hopke, P. K., Husain, L., Qureshi, S., Dutkiewicz, V. A., Schwab, J. J., Drewnick, F., and Demerjian, K. L.: Sources of fine particle composition in New York city, *Atmos. Environ.*, 38, 6521-6529, 2004.