

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

5 *The manuscript presents and discusses results from a long-term study of the PM_{2.5} 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.*
10 *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.*

15 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_{wb} and *m/z* 60),
20 component ratios and day-night variability, we believe that the factor is adequately characterized. However, the reviewer is right to indicate a possible uncertainty and this is now reported in the revised manuscript.

25 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.

30 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
35 of 3.5% (0-12.4%) in explained variances for the source components. The mean difference in the factor contributions to PM_{2.5} 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 nighttime average contributions. The mean difference in the fractional contribution to PM_{2.5} is +3.4%.

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

5

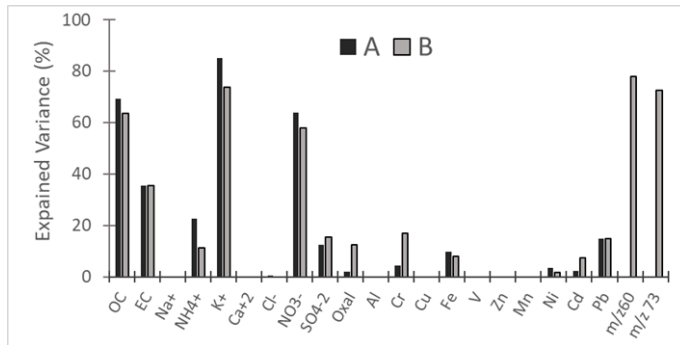


Figure S2: Explained variances for PM_{2.5} components by the biomass-burning factor in the original solution (A) and in the solution including ACSM fragments for the winter 2015-2016 (B).

10

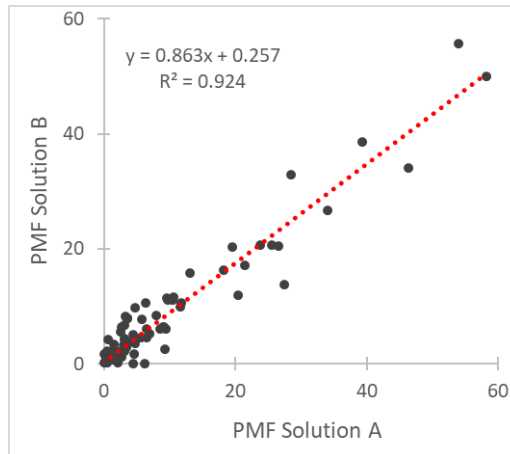


Figure S3: Comparison of calculated contributions (µg m⁻³) of the biomass burning factors, in the original solution (A) and in the solution including ACSM fragments for the winter of 2015-2016 (B).

15

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

Specific comments:

- 5 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?*
10 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.*
15 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.
20
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.*
25 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.
- 30 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.*
35 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_{2.5} mass was derived from the 24-h samples or from the day and night samples.*
40 As winter samples consist of 12h samples the PM_{2.5} 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.

5 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_{wb} obtained? Some info and/or literature references on this are needed in Section 2.

10 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.

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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".

20 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.

25 14. Page 10, lines 10-13: I do not understand the reasoning. If the molar ratio of NH₄/nssSO₄ is smaller than unity, would one not expect a mixture of H₂SO₄ and NH₄HSO₄?

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

30 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, 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.

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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)?

40 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 technical and minor corrections mentioned below 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".
- 5 - 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".
- 10 - 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".
- 15 - 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".
- 20 - 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".
- 25 - 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".
- 30 - 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".
- 35 - 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".
- 40 - 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".
- 5 - 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".
- 10 - 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".
- 15 - 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 12, 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".
- 20 - 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".
- 25 - 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".
- 30 - 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".
- 35 - 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".
- 40 - 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.
- 5 - 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:

- 10 *Page 2: It is unclear what "CPF probability" indicates. In the Main text CBPF is mentioned. We have clarified this. We have also updated these graphs using wind direction data in degrees instead of sectors.*
- Page 3, line 1: Replace "wind speed and speed" by "wind direction and speed in m s⁻¹".*
- Page 4: The Table heading should be above the Table instead of below.*

15 **References**

- 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.
- 20 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.

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 #3

Received and published: 7 May 2018

5

A long data series of PM_{2.5} speciation (more than 800 samples) obtained at an urban background site in Athens during a two-year period is presented. Description is focused on the winter period in order to quantify the impact of heating emissions and to define effective mitigation actions. A Positive Matrix Factorization was applied, identifying six sources for PM. The importance of domestic heating in winter is highlighted, and authors suggested a significant contribution of biomass burning (BB). However, this contribution can be overestimated (see below). Results obtained with an aethalometer are used for the interpretation of the BB contribution. However, these measurements are not properly described. The text is long and redundant. An effort must be made to reduce the length of the text. Some minor clarifications are needed before publication in ACP.

15 We would like to thank the reviewer for his/her comments. We made an effort to decrease the length of the text omitting redundant and repetitive sentences, we removed figure 4 and moved some details on the PMF methodology to the supplement. Below we list our responses to his/her comments (in italics) and the corresponding changes in the manuscript.

20 *Page 3, section 2.2. Please, clarify the analysis performed for the 24h and the 12h samples. Were the 24h and 12h filters collected simultaneously during winter? Did you analyze total K, Mg and Na by ICP? Only the soluble fraction of these elements is presented, However, the contribution of the insoluble fraction of these elements can be important during dust events.*

25 During winter only 12h samples were collected. As it was not clear enough, a change in the manuscript has been made to clarify this. Total elements were also measured by ICP but we decided not to include them in an effort to keep the length of the manuscript to a minimum as requested by the reviewers.

Section 2.3: did you consider both, 24h and 12h filters for the PMF? Why did you perform the PMF analysis for the winter samples only? A higher number of cases may favor the identification of factors.

30 Emphasis was given as the title indicates in wintertime. As said before during wintertime mainly 12h samples have been collected leading to a sufficient number of samples to allow for a robust PMF analysis. The reviewer is right that it is possible for additional factors to be extracted with more data. However, we have run models for the combined winter-summer dataset and did not identify further viable factors of significant contribution – at least for this site. Moreover, inclusion of summertime PMF would further increase the length of the manuscript.

Section 3.1 and 3.2. There are more recent papers on PM_{2.5} levels and composition and source apportionment in Europe. See Amato et al., Atmos. Chem. Phys., 16, 3289-3309, 2016

We thank we reviewer for pointing it out and they have been included in the manuscript.

40

Section 3.2.1. Please, use ranges from <DL (specify for each component) to the maximum value; avoid referring to 0 concentrations.

As pointed out by the reviewer reference to 0 concentrations has been avoided and replaced by <DL.

Page 7; line 12. *These elements (Mn, Cr, Ni, V, As: : :) may also be associated to mineral dust. I would say “: : of major anthropogenic origin: : ”*

5 The reviewer is correct and the appropriate change has been performed in the manuscript.

Section 3.3; page 7, line 31. *How did you estimate the sea salt fraction of these PM components? Please, add references.*

10 As requested by the reviewer, information and the appropriate references have been included in Section 3.3.

Page 8, section 3.4.1. *The combined effect of meteorology (less developed boundary layer, low wind speed: :) and the increase of the domestic emissions result in a poor air quality in winter. Thus, page 8 – line 28-30; the increase of PM2.5 concentrations during the night in winter may be related to the lower development of the boundary layer during the night and not only to the increase of the emissions of domestic heating.*

15 Based on boundary layer measurements and model estimates above Athens, Kassomenos et al. (1995) reported a decrease of BL during night-time during all seasons and in fact, the day-night BL height difference is more pronounced during the summer. Thus, the night-time accumulation of the pollutants during winter compared to summer clearly highlights the impact of additional emission sources related to heating.

25 *More information on the aethalometer measurements and model is needed. The description of the BC measurements should be included in the section 3.4.2 on carbonaceous components. Does the daily evolution of BC_{wb} differ from that of BC_{ff}?*

30 Information on the aethalometer measurements and the model used was added to the manuscript in the section 3.4.2 as requested by the reviewer. The daily evolution of the two components BC_{wb} and BC_{ff} is indeed quite different as it was already described in Fourtziou et al. (2017) and Gratsea et al. (2017) and these two references were added now to the manuscript. No additional info was added as i) it is out of the scope of the work and ii) to avoid further increasing the length of the manuscript.

Page 10. Lines 28-32. *The insoluble fraction of Mg, K and Na is usually associated to the dust fraction.*

We agree with the reviewer but here we refer to the soluble part not to the insoluble one.

35 *Page 11, lines 10 to 15. Mineral K is usually associated to clay minerals more than to carbonates. Could you check the correlation between K⁺ and Al for dust events and for non-biomass periods?*

40 As it is correctly stated by the reviewer, mineral K is indeed associated with Al, given its crustal origin. Here K⁺ refers to the soluble fraction whereas Al to the total (soluble and insoluble fraction). Despite this fact, K⁺ correlates with both Al and nss-Ca²⁺ during dust events and outside wood burning periods. However, as the regression with nss-Ca²⁺ has a better coefficient (most probably because both refer to the soluble fraction) we prefer to use nss-Ca²⁺ to estimate the wood burning fraction of K⁺.

Page 11, line 25. Please, replace : : :2011)” by : : :2011).”

Indeed, the full stop was missing. Thank you for noticing.

Page 14. Section 3.5.2 Line10. Please, add a figure or a reference for BB vs BCwb correlation.

5 As stated before, the variability of BC and BCwb during winter-time was already discussed in Fourtziou et al., 2017 and Gratsea et al., 2017 and these two references were now added to the manuscript.

Line 11. Please, specify the period for the ACSM measurements carried out by Bougiatioti et al., 2014. The PMF profile for BB is characterized by a high contribution of nitrates. This correlation can be due to covariation induced by meteorological factors Authors explained the association of nitrates with the BB factor by high emission of NO_x by biomass burning and by the lower acidity. However, as explained later NO_x better correlated with the vehicular emission factor. May a fraction of nitrates be derived from fuel oil emissions? Then, the contribution of BB may be overestimated.

10
15 First, we clarify that the reference to the work of 2014 was included to indicate the ACSM methodology and referred to measurements performed in Crete. We have updated the text to mention the ACSM measurements in Athens which cover the full period 2016-2017 as well as the winters in 2014-2015 and 2015-2016 and are presented in Stavroulas et al. (2018).

20 We agree with the reviewer pointing out the relevance of meteorological conditions for the observed variability, especially for the present analysis which is conducted in a sub-daily basis. As already stated in the manuscript, this variability is of importance for the atmospheric chemistry processes. The presence of NO₃⁻ in the BB factor can be explained by increased night-time local emissions of NO_x from biomass burning and by the lower acidity occurring during BB events, which as shown in Bougiatioti et al. (2014) favours the partitioning of NO₃⁻ in the particulate phase. It should be mentioned that except NO_x, biomass burning should also comprise a significant local source of ammonia emissions (Zhou et al., 2015), which otherwise in the area of Athens are very limited (Fameli and Assimakopoulos, 2016). These are important for the rapid ammonium nitrate formation especially at low temperatures (Paulot et al., 2017) encountered in our site during the night in winter.

25
30 We have clarified in the text that NO_x concentrations were used as measured at a nearby roadside traffic site, merely as a proxy of traffic variability in the area (Grivas et al., 2018), in order to validate the vehicular factor. At the urban-background site location, direct NO_x emissions from road fuel combustion are of less importance.

35 Numerous efforts to extract a separate secondary nitrate factor were conducted, however this was not possible, while in every case nitrate was principally associated with the BB factor. Solutions with more than six factors also did not perform adequately in terms of rotational uncertainty, having an increased number of incorrectly assigned factors and numerous swaps in the BS-DISP procedure.

40 According also to the suggestion of Reviewer #1, the 6-factor PMF solution was validated using additional biomass-burning tracers. Since measurements of levoglucosan were not performed in this work, PMF was again run adding data for the *m/z* 60 and *m/z* 73 fragments from ACSM measurements concurrently conducted at the site during the winter of 2015-2016. At their study performed during wintertime in Athens using various wood burning tracers, Fourtziou et al. (2017) have reported significant correlations between, nss-K⁺, levoglucosan, and ACSM-derived *m/z* 60, the last being considered as a

fingerprint of levoglucosan. The results of the repeat analysis did not differ significantly from those reported in the original manuscript and NO_3^- was again associated with the BB source.

Our experience and other source apportionment studies for $\text{PM}_{2.5}$ in Athens (Paraskevopoulou et al., 2015; Diapouli et al., 2017) indicate that an independent nitrate factor is difficult to isolate, due to the widespread presence of direct sources in the area, its fast chemical conversion from precursor emissions and the dependence of its partitioning on atmospheric conditions.

The chance that an overestimation could be due to nitrates is now mentioned in the revised manuscript, according to the reviewer's suggestion. We believe that the BS-DISP error margins of Figure 8, can provide an indication of the uncertainty related to nitrate apportionment. As an upper limit of overestimation, we considered the total nitrate assigned to the BB factor (as NH_4NO_3). In this case, the overestimation during day-time and night-time would be 0.58 and 1.18 $\mu\text{g m}^{-3}$, respectively. The respective contributions of the factor to $\text{PM}_{2.5}$ would be 16% and 35% during the two periods of the day (3% and 4% less than the reported solution, respectively). For comparison, Amato et al. (2016) have reported an annual secondary nitrate contribution of 0.7 $\mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ in suburban Athens.

As a further check, the original solution was constrained (Amato and Hopke, 2012) for the presence of nitrate in the biomass burning factor. In the absence of definitive a priori information on the nitrate participation in the source profile, due to the secondary nature of the component and the composite mixture of softwood and hardwood burned in the area (Fourtziou et al., 2017), nitrate contributions were pulled down, for a maximum dQ increment of 5%. Although there is not an absolute criterion for the acceptable increase in the object function, it was observed that performing harder pulls affected the solution as a whole, altering the characterization of factors. For the selected constrain, the average contribution of BB to nitrate was limited to 29% and its mass fraction in the source profile to 0.004 (from 0.01) $\mu\text{g } \mu\text{g}^{-1}$. The mean contribution of the factor to $\text{PM}_{2.5}$ was 1.5% (0.4 $\mu\text{g m}^{-3}$) lower than in the original solution

The overall contribution of the factor to $\text{PM}_{2.5}$ mass taking into account the estimated overestimations would be then 28-30% (from 32%), which is still a considerably large value. Indicatively, Diapouli et al. (2017) have reported annual mean contributions of BB at sites in Athens in the range of 23-46% of $\text{PM}_{2.5}$.

Page 15. The vehicular source is characterized by a relatively higher contribution during night in the winter period. Can be this diurnal trend related to a significant contribution of fuel oil domestic heating? The vehicular source highly correlated with BCff; does the diurnal trend of BCff reproduce the trend of vehicular traffic? Is there other source of BCff during night in winter?

It is true that some involvement from heating fuel combustion in the vehicular emission factor can't be overruled but it is very difficult to account for, quantitatively. Especially in Greece, due to large tax hikes in heating oil, it has been reported that occasionally road transport diesel is used instead, for residential heating. There have also been issues with road diesel fuel adulteration by heating fuel oil (Kalligeros et al., 2003).

However, the relative contribution of space heating from oil to aerosol emissions in central Athens, has always been considered of secondary importance (Economopoulos, 1997). Even more so, in the years of the recession in Greece, the use of oil for space heating has reached a low-point. Faneli and Assimakopoulos (2016) have recently estimated that the share of heating oil is less than 2% in the total PM_{10} emissions from domestic heating in Greece, the rest emanating from fire-places and wood stoves.

The diurnal variation of road traffic in Athens (Grivas et al., 2012; Fameli and Assimakopoulos, 2015) can reproduce the variability of BCff at the Thissio site (Fourtziou et al., 2017), if the diurnal variability of meteorological factors is taken into account (BL height changes and increased wind speeds in the afternoon). The typically bimodal circadian variation of BCff generally coincides with those of traffic-related gaseous pollutants and of PM₁₀ at traffic stations in Athens (Grivas et al., 2008).

It is noted that, in the center of Athens, where the site is located, due to increased commercial and recreational activity, late-afternoon and evening traffic is not negligible. In addition, there are traffic restrictions for passenger vehicles in the center of Athens during daytime (7:00-20:00, based on odd-even plates system). Data from traffic sensors on roads inside the restricted circulation zone, during December-January, show that night-time/daytime traffic volumes are comparable (ratio of 0.96). This, combined to the formation of the stable nighttime boundary layer at low heights can lead to an increase of the net contribution.

Overall, as stated in the manuscript, the night-time contributions of the vehicular source are slightly higher (by a factor of 1.5) compared to day-time, a difference not assessed as statistically significant at the 0.05 level, while the contribution of this source to PM_{2.5} is similar during night and day (19%). However, since a minor influence of domestic heating can't be excluded, we specifically mention it in the revised text.

Page 15, Line 20. V/Ni derived from fuel oil combustion sources is usually associated to SO42-; however, SO42- is not significantly associated in this factor

We agree with the reviewer that in some cases stronger associations between fuel-oil combustion and sulfate have been reported. However, we note that sulfate is present in the oil combustion source profile (we have selected a different marker in the corresponding Figure to make this clearer).

Due to the identification of additional sources closely associated with sulfate and to the small overall contribution of the oil combustion factor to PM_{2.5} mass, its explained variance by the factor is relatively small (4%). This value is in line with Amato et al. (2016) which have attributed fine particulate S to fuel oil combustion at rates of 2%-13%, at a suburban background site in Athens and at an urban background site in Barcelona, respectively. Also, Reche et al. (2012), have displayed an explained variability circa 5% for fine particulate S in the fuel oil combustion factor for Barcelona. Pandolfi et al. (2011), at the heavy-oil emission hotspot of Gibraltar, have reported that the explained variance of the relevant factor for sulfate is around 10%.

The mass fraction of sulphate in the source profile (0.07 µg/µg) is comparable to results from Grivas et al. (2018) that calculated for the fuel oil combustion profile in PM_{2.5} values of 0.08 and 0.15 µg/µg at urban background and traffic sites in the center of Athens, respectively. Additionally, the source profile reported by Kocak et al. (2011) in Istanbul contains sulfate at approximately 0.05 µg/µg. Therefore, we considered the sulfate association in the oil-combustion factor to be within the range reported by past studies in Athens and other cities in the Mediterranean.

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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 #1

5 Received and published: 22 May 2018

10 *The paper by Theodosi et al. reports about the large observational study monitoring particulate matter sources in central Athens emphasizing contribution of biomass burning, especially during winter and in particular during the night. The study presents no new knowledge, nor scientific advancement, although it provides very detail account of sources and is methodologically correct. The paper is often buried in details and often repetitive and better focus on the main idea is necessary. At the moment the paper looks more like a report than scientific paper. Better focus and summary at the end of sections is necessary and perhaps separating results from discussion. The paper ends abruptly with conclusions as an extensive summary. Quite an improvement (including the English) is needed before the paper can be accepted for*
15 *publication.*

We would like to thank the reviewer for his/her comments. We disagree that no new knowledge is provided. Similar works on long-term aerosol chemical characterization are very scarce in Europe. Especially in Greece, this is the first time that daily and 12-h filter samples have been analysed for ions, OC/EC and trace metals to provide a complete chemical characterisation in the largest urban centre for more than two years.

20 Although not easy, as the reviewers have asked for additional details, we tried to decrease the length of the manuscript by removing repetitive and redundant sentences and moving one figure to the supplementary material.

25 The conclusion section was reworked thoroughly and now includes the key findings and some remarks of interest for a wider scientific audience.

Below we list our detailed response to his/her comments (in italics) and the corresponding changes in the manuscript.

30 *Comments:*

I guess the authors are overstressing when repeatedly refer to the Greater Athens Area, because a single station in the city centre can hardly described the entire Greater Athens area. Clearly more stations are necessary to monitor greater agglomerate area due to different population/build up density, anthropogenic activities and traffic. Therefore, a better reasoning is required to refer to GAA if possible at all. Very often the authors go into unnecessary simplification and repetition, e.g. regarding temperature inversions and limited mixing. Every specialist is aware of the phenomenon and mentioning it once in detail is enough.

40 It is clear that several stations are required to obtain a complete picture for a large agglomeration such as GAA but on the other hand it is understandable that it would be very difficult to perform such a chemical analysis in-depth for several stations. As a reminder, in the present work more than 800 filters have been collected and analysed for main ions, OC/EC and metals with emphasis (twice daily) on the winter period. As shown in Gratsea et al. (2017), by comparing Thissio data with several (5) stations of the National Air

Pollution Monitoring Network, our station captures quite well the temporal variability of primary pollutants like CO within the GAA. In addition Thissio station is not directly impacted by sources and its position on a hill at the center of Athens allows it to be considered representative of the background in the wider area. For that reason we consider the station as representative as possible for the GAA, at least for its central part. It is also worth noticing that during the sampling period, this was the sole urban background station monitoring PM concentrations in the densely-populated central Athens (gathering 1.03 million people, almost a third of the GAA population), and its results can be considered relevant for the exposure of a large part of GAA inhabitants.

“The high correlation between the five NAPMN sites and Thissio, as well as the relative difference in absolute levels, support the characterisation of Thissio as an urban background site, non-intensively affected by local traffic; From Gratsea et al., 2017).

However as suggested by the reviewer the term GAA is now not mentioned in the manuscript. Also atmospheric conditions are now mentioned only once in the manuscript.

Minor comments:

Page 2, line 6. *through emission reduction measures.*

Line 9. : : *toxic and carcinogenic components.*

Line 12. *Trace metals are also related to chronic and acute...*

Line 18. : : *such as traffic and industrial activities.*

Line 19. *since the winter 2011-2012.*

Line 21. *the great impact.*

Line 25. *Linking them to the presence*

Line 33. : : *has been undertaken in Southern Europe, offering challenging conditions (what is challenging there by the way?)*

Page 3, line 2. *the current work was focused on winter period.*

Line 4. *The aerosol sources during the night are not new. Rephrase to "... highlight the impact of night time PM sources".*

Line 10. *It is still representative of central Athens, especially during high pollution events during stagnant meteorological conditions. A single site cannot represent the whole GAA as suburban areas were not monitored. It is methodologically wrong to assume that a single site can serve as a reliable average of the entire GAA.*

Line 13. *why this word of caution when the next sentence explains everything?*

Line 17. *On a yearly basis, air masses of Northern origin from central and eastern Europe account for almost two thirds of the time.*

Line 20. *Ventilation is a poor term. You should be stating about stagnant conditions during which most severe pollution events have been occurred persisted for X % of time.*

Line 28. *Unclear. Were the 447 samples in addition to 848 samples or a fraction of them?*

Line 30. *Controlled RH=%?? conditions. Please specify.*

Page 4, line 17. : : *in detail by Theodosi: : :*

Line 26. *Not contrast, but patterns, as no one can know in advance if they will contrast.*

Line 27. *trivial repetitive sentence.*

Page 5, line 9. unclear - combined OR night-day?

Line 27. Was it really lower limit at 0.3ug/m³ which is inconceivably low for urban PM_{2.5} concentration. Was it realistic and how did it compare to chemical mass?

Page 6, line 8. zero OC or EC cannot be observed anywhere on Earth (even in Antarctica there is observable BC of 1ng/m³). Refer to below DL of Xug/m³.

Line 10. To be mathematically correct one should only present the arithmetic average if data are normally distributed in which case arithmetic average and median are closely similar number. We don't see that therefore data are lognormally distributed in which case the range and the median should be presented only. It has to be consistently presented either median alone or ALWAYS with the median, rather than selectively presenting median.

All the aforementioned suggestions have been performed.

Line 26. Excellent agreement should not be necessarily expected, "results were in close agreement". Close agreement suggests long-range transport as the main source.

Page 7, line 17. remained within the same order of magnitude between studies with only slight differences in between. Chemical mass closure. Given that all major and minor particulate matter species were measured, the chemical mass closure has been attempted. However, given the large uncertainty in OM/OC ratio and no data for the current study, how useful the chemical closure exercise was?

An OM/OC ratio equal to 1.8 determined from Aerosol Chemical Speciation Monitor (ACSM) measurements at the same location, within the study period (Stavroulas et al., 2018) was used to perform a more accurate mass closure.

Page 8, lin 19. Could further limit dispersion of pollutants.

Line 31. 289 days with smog conditions ...

Page 9, line 29. No statistically significant seasonality can be seen in SO₄ time series considering error bars. Note the lowest concentrations in November-December 2014. Rewrite as the text is not reflecting the Figure.

The text was rewritten as "SO₄²⁻ concentration in the PM_{2.5} fraction presented no statistical significant seasonality with the lowest values in winter"

Page 10, line 4. What is the anthropogenic source of SO₄ during summer if long-range transport is blamed? Is it not biogenic (Mediterranean DMS) instead?

Page 11, line 3. : : suggesting insignificant influence from wood burning. Is it impossible that fraction of Na increase is due to higher primary in winter?

Yes it could be possible but as both Cl and Mg are decreasing during night and Na is not, this could be an indication of a small contribution from heating and especially biomass burning, as previously reported by Fourtziou et al. (2017).

Page 12. 3.4.4a Crustal elements

Line 26. Present in tailpipe emissions, not included.

Page 14. Lines 31-34. Reword – confusion with mean annual contributions and “such large wintertime contributions” – Corrected.

Page 15, line 13. What is the reason for heavy duty vehicles in central Athens?

Karageorgos and Rapsomanikis (2010) have also mentioned the presence of heavy vehicles in central Athens, as a factor for particle emissions. The main reason is bus circulation, most probably of tourist buses, whose traffic is relatively dense in the area of the site, where various attractions are located.

Line 23. westerly advections, not flows - Corrected.

5 *Line 28. there is no information whether particles were internally or externally mixed. And even if known there is no sulphate particle in existence* - Corrected.

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

10

Multiyear chemical composition of the fine aerosol fraction in Athens, Greece, with emphasis on winter-time residential heating

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Abstract. In an attempt to take effective action towards mitigating pollution episodes in Athens, precise knowledge of PM_{2.5} composition and their sources is a prerequisite. Thus, a two year chemical composition data set from aerosol samples collected in an urban-background site of central Athens, from December 2013 till March 2016, has been obtained and Positive Matrix Factorization (PMF) was applied in order to identify and apportion fine aerosols to their sources. A total of 850 aerosol samples, were collected on a 12 to 24h basis and analyzed for major ions, trace elements, organic and elemental carbon, allowing us to further assess the impact of residential heating as a source of air pollution over Athens.

The ionic and carbonaceous components were found to constitute the major fraction of the PM_{2.5} aerosol mass. The annual contribution of the Ion Mass (IM), Particulate Organic Mass (POM), dust, Elemental Carbon (EC) and Sea Salt (SS) were calculated at 31%, 38%, 18%, 8% and 3%, respectively and exhibited considerable seasonal variation. In winter, the share of IM was estimated down to 23%, with POM + EC being the dominant component accounting for 52% of the PM_{2.5} mass, while in summer IM (42%) and carbonaceous aerosols (41%) contributed almost equally.

Results from samples collected on a 12h basis (day and night) during the 3 intensive winter campaigns indicated the impact of heating on the levels of a series of compounds. Indeed PM_{2.5}, EC, POM, NO₃⁻, C₂O₄²⁻, nssK⁺ and selected trace metals including Cd and Pb were increased by almost a factor of 4 during night compared to day, highlighting the importance of heating on air quality in Athens. Furthermore, in order to better characterize winter-time aerosol sources and quantify the impact of biomass burning on PM_{2.5} levels, source apportionment was performed. The data can be interpreted on the basis of six sources namely biomass burning (32%), vehicular emissions (19%), heavy oil combustion (7%), regional secondary (20%), marine aerosol (9%) and dust particles (8%). Regarding night to day patterns their contributions shifted from 19, 19, 8, 30, 11 and 9% of the PM_{2.5} mass during day to 39, 19, 6, 14, 7 and 6% during night, underlining the significance of biomass burning as the main contributor to fine particle levels during night-time in winter.

1 Introduction

The scientific interest in aerosols has widely increased during the last decades due to their impact on air quality, human health and climate change (e.g., Seinfeld and Pandis, 1998). Legislation regarding atmospheric particulate matter is gradually

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becoming more stringent, as a result of the frequent episodes encountered on regional or even continental scales, associated also with synoptic and mesoscale meteorological conditions (Querol et al., 2009). Hence, significant efforts are targeted towards improving air quality through emission reduction measures (Daskalakis et al., 2016).

Particles with diameter of 2.5 µm or less are of particular interest due to the fact that they contribute significantly to detrimental health effects (Dockery and Pope, 1994; Ostro et al., 2006), penetrating more efficiently the cell membranes (Salma et al., 2002; Li et al., 2003; Bell et al., 2009) and acting as carriers of toxic and carcinogenic components (Beddows et al., 2004). Recent epidemiological studies have highlighted the risk of exposure to enhanced levels of carbonaceous aerosols, revealing notable associations with cardiovascular mortality and morbidity (Ostro et al., 2010; Lipsett et al., 2011; Krall et al., 2013). Trace metals are also related to chronic and acute health problems due to their toxicity (Pope et al., 2002; Stiebet et al., 2002).

In Greece, air quality has improved since the advent of the global economic recession in 2008, due to the abrupt cut down of anthropogenic sources such as traffic and industrial activities (Vrekoussis et al., 2013; Gratsia et al., 2017). However, since the winter 2011-2012 the extensive use of wood as fuel for residential heating appears to have changed this decreasing trend, at least for the winter period (e.g., Gratsia et al., 2017). Burning wood in residential stoves (and fireplaces) is an important source of directly emitted fine particulate matter (PM_{2.5}), EC and polycyclic aromatic hydrocarbons (PAH), with great impact on air quality (EEA, 2013; 2014). Paraskevopoulou et al. (2015) have shown that at a suburban site (Penteli) in the Greater Athens Area, the contribution of Particulate Organic Matter (POM) to the additional local aerosol mass, increased by 30% between winter 2012 and winter 2013. Fourtziou et al. (2017) have reported on several wood burning tracers monitored during winter 2013-2014, linking them to the presence of severe smog events due to wood combustion for residential heating.

Informed decision making towards improving air quality, demands precise knowledge of PM chemical speciation and source attribution. Based on the effect of finer particles on health and their association with urban sources, in contrast to natural aerosols, it is even more important to focus such analyses on fine aerosol fractions. In this study, PM_{2.5} was chemically characterized for inorganic species, such as trace elements and water-soluble ions, as well as for carbonaceous components, such as organic and elemental carbon. To our knowledge, this is the first time that such a long-term, uninterrupted estimation of the chemical composition of PM_{2.5}, a chemical mass closure exercise and source identification of particulate matter, took place in parallel, at an environment in Southeastern Europe offering challenging conditions in terms of pollution contributors and timing (recession period). Given the intensive use of wood as fuel for residential heating since winter 2012 in Athens, the current work was focused on winter periods. In order to highlight the impact of night-time winter PM sources air quality of urban Athens, aerosol sampling was intensified from routine 24h time resolution to 12h resolution during the three consecutive winters (2013-2014 to 2015-2016).

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2 Experimental

2.1 Sampling site

Aerosol sampling was conducted at the central premises of the National Observatory of Athens situated on a small hill (110m a.s.l.), in downtown Athens (Thissio, 38° 0.00' N, 23° 43.48' E). This urban background site is not directly impacted by local human activities as it is surrounded mostly by a pedestrian zone and moderately-populated neighbourhoods. Therefore, the site could be considered as representative of the exposure of the majority of population in the Greek capital, as demonstrated by Gratsea et al. (2017).

2.2 Sampling and chemical analyses

PM_{2.5} aerosol was collected on Quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47mm, Pall) with a Dichotomous Partisol Sampler 2025 (Rupprecht & Patashnick, 16.7 L min⁻¹), on a daily basis during a period of more than two years (December 2013 - March 2016). During the three winter periods (from December to February), the sampling frequency was changed to 12h in an attempt to study in depth the characteristics of emissions from heating activities, resulting in a collection of 447 filters out of the total of 848. The PM_{2.5} aerosol mass was gravimetrically determined (samples were conditioned pre- and post sampling at 20 ± 3 °C and 45 ± 5% RH for 48h) using a microbalance (Fourtziou et al. 2017; Paraskevopoulou et al. 2014), and filters were stored until the chemical analysis. Filter blanks and blank field samples were also prepared and analyzed. All PM_{2.5} samples were analyzed for organic (OC) and elemental carbon (EC), water-soluble ions (Cl⁻, Br⁻, NO₃⁻, HPO₄²⁻, SO₄²⁻, C₂O₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺), elements of crustal origin (Al, Fe, Ca) and trace elements (Zn, Pb, Cu, Ni, V, Cr, Mn, Cd, As). All reported concentrations were corrected for blanks. The chemical speciation data were utilized to perform a chemical mass closure exercise and chemometric receptor modelling for source apportionment.

Filters were analyzed for the carbonaceous components, with the Thermal-Optical Transmission (TOT) technique (Birch and Cary, 1996), using a Sunset Laboratory OC/EC Analyzer, as described in detail by Theodosi et al. (2010a) and Paraskevopoulou et al. (2014), applying the EUSAAR-2 protocol (Cavalli et al., 2010).

Filter parts were analyzed by ion chromatography (IC) for the determination of the main ionic species mentioned above, as described by Paraskevopoulou et al. (2014).

An acid microwave digestion procedure, followed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Electron ICAP 6000 Series), was applied for the determination of major and trace metal concentrations during this long-term sampling period (n=848) following the procedure described in detail by Theodosi et al. (2010b). All 12 elements, were also determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer, NexION 300X) for all winter (December-February) and summer (June-August) samples (n=592). Results reported hereafter for Al, Ca, Mn, Fe, V, Cr, Ni, Cu, Zn correspond to ICP-OES analysis, while for Cd, As and Pb to ICP-MS.

Hourly meteorological data on horizontal wind velocity and direction from NOA's station at Thissio were additionally retrieved.

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2.3 Source apportionment

In order to identify major winter-time sources of PM_{2.5} and their day-night patterns, Positive Matrix Factorization (PMF) receptor modelling was performed on the 12-h winter chemical composition data.

In the PMF factor analytic model, speciated sample data are decomposed into matrices of factor contributions and factor profiles. The matrix elements are obtained through the minimization of weighted decomposition residuals (object function - Q) in an iterative process. Uncertainties associated with the analysis of individual species are used for weighting. In the present case, the multilinear engine (ME-2) program was used for solving the PMF problem in the setting of the EPA PMF5.0 software. Uncertainties per species and sample were calculated (Reff et al., 2007) based on the error fraction of the measurement and the method detection limit for each component.

Values equal to 5/6th of the detection limit were assigned as uncertainty to samples below detection limits (BDL). Missing data points were substituted by the geometric mean of the respective species concentrations and given four times this value as uncertainty. PM_{2.5} was set as a total variable and had its uncertainty tripled so that it would not overly influence solutions. The PMF analysis was performed on the day/night dataset to obtain the source profiles and the day and night contributions to PM_{2.5} were calculated separately (Bernardoni et al., 2011; Canha et al., 2014).

Solutions involving 4-10 sources were examined and the ratios of actual (robust) to expected values of Q (Q_R/Q_{EXP}) were recorded. The selected solution, which was obtained for six factors, was physically interpretable, and the reduction of the Q_R/Q_{EXP} for solutions with a greater number of factors was small, indicating that new factors were not introducing additional information (Brown et al., 2015). The impact of small-medium scale atmospheric circulation has also been taken into account, by examining associations between source contributions and wind direction and velocity. Bivariate conditional probability function (CBPF) calculations and graphical interpolation in polar coordinates have been performed according to the methodology developed by Uria-Tellaitxe and Carslaw (2014). The stability of the obtained solution against random sampling errors and rotational ambiguity was assessed using the BS-DISP procedure of the EPA PMF 5.0 (Paatero et al., 2014). More details on PMF model parameters and BS-DISP results are reported in the supplementary material.

3 Results and discussion

3.1 PM_{2.5} levels

The daily PM_{2.5} mass concentration at the urban background site of Thissio, from all 12-h and 24-h samples, varied significantly from 1 to 144 $\mu\text{g m}^{-3}$, with higher concentrations occurring in the winter (mean: 27.4±8.7 $\mu\text{g m}^{-3}$; median: 27.5 $\mu\text{g m}^{-3}$) and lower in the summer (mean: 14.7±1.2 $\mu\text{g m}^{-3}$; median: 15.0 $\mu\text{g m}^{-3}$) (Figure 1).

The annual mean PM_{2.5} concentrations of the two complete years of the study period (2014 and 2015), based on daily values, were equal to 22.7±16.4 (median: 18.0 $\mu\text{g m}^{-3}$) and 19.3±16.1 $\mu\text{g m}^{-3}$ (median: 15.2 $\mu\text{g m}^{-3}$), respectively, both being lower than the annual PM_{2.5} limit imposed by the EU Ambient Air Quality Directive (2008/50/EC), which is set at 25 $\mu\text{g m}^{-3}$.

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$Unc. = \sqrt{(error\ fraction \times concentration)^2 + MDL^2}$. [1]

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The PM_{2.5} values reported here are in good agreement with those reported in other urban environment studies, for Athens (18-26 µg m⁻³, Theodosi et al., 2011; Mantas et al., 2014, Paraskevopoulou et al., 2015) or other European cities (15-30 µg m⁻³, Putaud et al., 2010; Amato et al., 2016).

3.2 PM_{2.5} chemical composition

5 3.2.1 Carbonaceous components

Figure 2a represents the time series of the daily concentration levels of OC, which ranged from below DL to 49.5 µg m⁻³ (mean: 4.0±2.0 µg m⁻³; median: 3.1 µg m⁻³; Table 1), and of EC, from below DL to 19.3 µg m⁻³ (mean: 1.5±1.0 µg m⁻³; median: 1.1 µg m⁻³). Both carbonaceous components, exhibited a distinct seasonal variability, with lower mean concentrations during summer, in the order of 2.9±0.1 µg m⁻³ (median: 2.9 µg m⁻³) and 0.7±0.1 µg m⁻³ (median: 0.8 µg m⁻³) for OC and EC, respectively. Mean winter values were higher and equal to 6.3±2.9 µg m⁻³ (median: 5.8 µg m⁻³) and 2.8±1.2 µg m⁻³ (median: 2.6 µg m⁻³), respectively.

OC and EC concentrations fall within the range reported for background urban sites across Europe (Barcelona, Florence, Milan; Amato et al., 2016, OC=2.4-6.5 µg m⁻³ and EC=0.9-1.8 µg m⁻³). Their levels are higher than those reported for a remote background site in Crete, Greece (Koulouri et al., 2008; OC=1.8±1.4 µg m⁻³ and EC=0.27±0.18 µg m⁻³) and a suburban site in Athens (Remoundaki et al., 2013; OC=2.4 µg m⁻³ and EC=1.0 µg m⁻³), while significantly lower than those previously reported for megacities such as Istanbul (Theodosi et al., 2010a; OC=6.6 µg m⁻³ and EC=2.9 µg m⁻³).

3.2.2 Ionic Composition

SO₄²⁻ was the main ion contributor to the fine aerosol mass accounting for 16% (mean: 3.0±0.8 µg m⁻³; median: 2.9 µg m⁻³), while NH₄⁺ and NO₃⁻ followed with contributions of 7% (mean: 1.4±0.7 µg m⁻³; median: 1.1 µg m⁻³) and 2% (mean: 0.5±0.4 µg m⁻³; median: 0.3 µg m⁻³), respectively. Figure 2b represents the daily variation of SO₄²⁻ and NO₃⁻, while Table 1 provides the annual levels of all the examined ions.

The mean SO₄²⁻ concentration is in close agreement with the value (3.1±0.8 µg m⁻³) reported for the suburban station of Penteli by Paraskevopoulou et al. (2015) and also with other recent studies performed in Athens (e.g. Mantas et al., 2014). Notably, a substantial decrease is apparent in comparison to the levels recorded during the previous decade in the area (Karageorgos and Rapsomanikis, 2010; Theodosi et al., 2011). The annual measured levels of NO₃⁻ at Thissio are significantly higher from those reported for suburban and background locations in Greece, while for NH₄⁺ they are comparable (e.g. Mantas et al., 2014; Paraskevopoulou et al., 2015), highlighting the respective roles of local (NO₃⁻) and regional (NH₄⁺; see below) contributing sources.

Several other water-soluble ions were also identified such as Cl⁻, Br⁻, HPO₄²⁻, C₂O₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺. Annual means (Table 1) ranged between 19.4 ng m⁻³ for Br⁻ (median: 14.2 ng m⁻³) to 307±196 ng m⁻³ for Na⁺ (median: 369 ng m⁻³). All

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annual mean concentrations of these ions are in the same range as those reported for PM_{2.5} in Athens (Theodosi et al., 2011; Pateraki et al., 2012; Remoundaki et al., 2013; Paraskevopoulou et al., 2015).

3.2.3 Trace metals

Table 1 summarizes the mean annual concentrations of elements and trace metals during the sampling period and Figures 2c-f represent the daily variation of several representative metals. The mean annual concentrations of elements of crustal origin such as Al, and elements of mixed origin, still with a significant crustal component, such as Fe and Ca, vary from 0.26 to 0.75 $\mu\text{g m}^{-3}$ (Table 1). The mean annual values for elements of major anthropogenic origin (Mn, V, Cr, Cd, Ni, Cu, As, Pb) are generally very low, varying from 1.7 to 27.1 ng m^{-3} . On a monthly basis, the concentrations of toxic metals originating from human activities, such as As, Cd, and Ni, which are mainly confined in the PM_{2.5} fraction (Koulouri et al., 2008), do not exceed a few ng m^{-3} .

Compared to values reported in earlier studies for other locations in Athens during approximately the last decade, the trace element concentrations have remained within the same order of magnitude (Karanasiou et al., 2009; Theodosi et al., 2011; Pateraki et al., 2012; Mantas et al., 2014; Paraskevopoulou et al., 2015). As expected, the values are higher than those reported for several other rural background locations around Europe and Greece (Salvador et al., 2007; Koulouri et al., 2008; Viana et al., 2008; Pey et al., 2009; Alastuey et al., 2016).

3.3 Chemical mass closure

From the aerosol chemical components measured here -Ion Mass (IM), Particulate Organic Mass (POM), dust, EC and Sea Salt (SS)- the mass closure of the PM_{2.5} aerosol samples can be undertaken. IM was calculated as the sum of the non sea salt (nss) constituents (NH_4^+ , NO_3^- , K^+ , SO_4^{2-} , Br^- , HPO_4^{2-} and $\text{C}_2\text{O}_3^{2-}$), estimated for the compounds having a sea-salt component by using Na^+ as a reference and the equation described by Sciare et al. (2005).

Dust was estimated using Al (Ho et al., 2006) assuming an upper crust concentration of 7.1% (Wedepohl, 1995). POM was estimated by multiplying the measured OC with a conversion factor (CF) of 1.8, derived from ACSM measurements in Athens (Stavroulas et al., 2018) aimed at the characterization of submicron organic aerosol sources. SS originating species were calculated from the sum of the measured ions: Na^+ , Cl^- , Mg^{2+} , ssK^+ , ssCa^{2+} and ssSO_4^{2-} (Sciare et al., 2005; Pio et al., 2007).

The results of the mass closure exercise on a mean monthly basis are shown in Figure 3 (results on a mean seasonal basis are reported in the supplementary material - Figure S1).

The corresponding chemical mass closure can explain about 99% of the measured fine aerosol mass, leaving out a considerably low proportion of the unaccounted mass, which is usually water (Ohta and Okita, 1990). By comparing the PM_{2.5} mass (determined from the filter weighting of all 12 and 24h samples) and the sum of individual chemical aerosol components, a significant correlation is revealed, with a slope equal to 0.98 ($r=0.88$, $n=780$; not shown).

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On an annual basis, POM contributes 38% to the total PM_{2.5} mass, while EC comprises the 8%. IM accounts also for a significant part of the PM_{2.5} mass (31%), with SO₄²⁻ (16%) and NH₄⁺ (7%) being the dominant ions. The annual contribution of dust and SS is 18% and 3%, respectively.

POM and IM present considerable seasonal variation. In winter, IM is reduced (down to 23%), the dominant component being POM (42%), and the rest is shared by dust (18%), EC (10%) and SS (4%). In summer, IM is the main component (42%), followed by POM (36%), dust (24%), EC (5%) and SS (4%).

3.4 Temporal variability of winter mass and aerosol chemical composition: the role of residential heating

3.4.1 PM_{2.5} mass

The significant increase in fine aerosol mass in Athens during winter compared to summer points towards an important additional PM source (Figures 4a, b). During winter-time, residential heating using fossil fuel, wood and coal are important sources of directly emitted PM_{2.5} (EEA, 2013; 2014). The winter stable atmospheric conditions in conjunction with the seasonal decrease of the boundary-layer height (low wind speeds, temperature inversions and low-intensity solar radiation) could further limit dispersion of pollutants. High levels of PM mass during winter due to wood burning have also been observed in prior studies in the two largest urban metropolitan cities in Greece. Athens and Thessaloniki (e.g. Saffari et al., 2013; Florou et al., 2017; Gratsea et al., 2017).

It is noteworthy that during winter, PM_{2.5} concentrations during night-time (mean 32.9 µg m⁻³; median 30.5 µg m⁻³) are almost twice as high (80% increase; Table 2) as during day-time (mean 19.1 µg m⁻³; median 19.2 µg m⁻³), which constitutes additional evidence for the role of domestic heating. Using the approach introduced by Fourtziou et al. (2017), i.e., by selecting periods with wind speed lower than 3 m s⁻¹ and an absence of precipitation, 289 days with smog conditions (hereafter named SP; Smog Period) associated with increased levels of air pollutants (NO, CO, BC) have been identified during the 3 examined winters. By further studying the PM_{2.5} concentrations during these smog events, a 96% increase during night-time compared to day-time was observed (Table 2, statistically significant at 99.9% level; p<0.001).

3.4.2 Carbonaceous components

Primary OC and EC from residential heating can explain the net seasonal trend with higher values during winter as presented in Figures 4c-f. Indeed their levels during winter-time are higher by 55% for OC and 74% for EC, emphasizing the intensity and the sporadic nature of the residential heating source.

This is further evidenced by the seasonal variation of Black Carbon (BC) and its wood burning fraction (BC_{wb}), obtained with the use of an aethalometer (AE33) during the period 2015-2016 (Figure 5). BC measurements on total particulate matter (no cut-off inlet) were conducted by means of the new generation seven wavelength Magee Scientific AE33 aethalometer, at one-minute resolution. The wood burning and fossil fuel fractions (BC_{wb} and BC_{ff}, respectively) were derived by the on-line application of the two-component model in combination with the dual-spot compensation technology provided by the

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instrument (Drinovec et al., 2015). Further details on the daily evolution of BC_{wb} and BC_{fr} fractions at the present site can be found at Gratsea et al., (2017) and Fourtziou et al., (2017).

To highlight the impact of heating on carbonaceous levels, Figures 6b and c present their day and night-time variability in winter. The average OC and EC concentrations increased 3 and 2 times during night compared to day, respectively (Table 2).

A similar tendency is observed during smog events (SP, Table 2). More specifically, the average OC and EC concentrations during the night for all three winter campaigns are equal to $9.4 \mu\text{g m}^{-3}$ and $3.8 \mu\text{g m}^{-3}$ ($12.6 \mu\text{g m}^{-3}$ and $5.1 \mu\text{g m}^{-3}$ for SP), respectively, with corresponding mean day-time values of $2.7 \mu\text{g m}^{-3}$ and $1.6 \mu\text{g m}^{-3}$ ($3.4 \mu\text{g m}^{-3}$ and $2.0 \mu\text{g m}^{-3}$ for SP). Consequently, the contribution of POM to the total mass of $PM_{2.5}$ in winter is higher during the night ($52 \pm 4\%$, median 50%) than in the day ($27 \pm 10\%$, median 23% ; Figure 6b, c). Similarly, for EC, in winter, a smaller but yet evident average increase was also observed during night ($12 \pm 1\%$, median 12%) compared to day ($8 \pm 3\%$, median 9%).

The significant correlation between OC and EC in Athens during winter (slope=2.36; $r=0.94$; $n=472$), more enhanced during night-time (slope=2.49; $r=0.96$; $n=226$) compared to day-time (1.62; $r=0.85$; $n=221$), indicates that they originate from the same sources. Notably, the higher OC to EC ratio during summer (3.21; $r=-0.59$; $n=114$), as well as their negative correlation, could be explained by the enhanced photochemical organic aerosol formation in the atmosphere, from low-volatility compounds produced by the oxidation of gas-phase anthropogenic and biogenic precursors (Paraskevopoulou et al., 2014).

3.4.3 Ionic composition

SO_4^{2-} concentration in the $PM_{2.5}$ fraction of aerosol didn't present a pronounced seasonality, with a slightly increasing trend from spring to summer (Figure 2b). During the dry season (spring and summer), the absence of precipitation, and the increased photochemistry lead to secondary aerosol formation and increased lifetime in the area (Mihalopoulos et al., 1997), resulting in the appearance of higher concentrations. In winter, SO_4^{2-} accounts for 8% of the $PM_{2.5}$ mass, while in summer for 26%. During winter, SO_4^{2-} did not show any significant day to night variability (about 11% increase during SP; Table 2), indicating that heating is not the major source of SO_4^{2-} . In addition, the summer maximum suggests that the majority of SO_4^{2-} originates from long-range transport and thus it can be considered as an indicator of regional sources (Mihalopoulos et al., 1997; Theodosi et al., 2011).

The concentration of NH_4^+ presents a less pronounced seasonal trend, with a similar monthly distribution pattern as that of SO_4^{2-} , in agreement to previous observations, in Athens (Mantas et al., 2014; Paraskevopoulou et al., 2015). As in the case of SO_4^{2-} , NH_4^+ did not present a day to night increase (less than 10% during SP; Table 2). NH_4^+ vs SO_4^{2-} and consequently nss SO_4^{2-} , were significantly correlated ($r=0.64$) for the entire sampling period (December 2013-March 2016), with a slope on an equivalent basis ($NH_4^+/nssSO_4^{2-}$) smaller than unity (0.62), indicating partial neutralisation of nss SO_4^{2-} by NH_4^+ . This suggests that a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$ is formed in the area. Previous studies in Athens and the Eastern Mediterranean have reached the same conclusion (Siskos et al., 2001; Bardouki et al., 2003; Koulouri et al., 2008). NH_4^+ is significantly correlated to NO_3^- only in winter ($r=0.73$; $p<0.001$), indicative of NH_4NO_3 formation, as previously suggested for the Greater Athens Area (GAA) (Karageorgos and Rapsomanikis, 2007; Remoundaki et al., 2013; Paraskevopoulou et al., 2015).

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NO₃⁻ levels present higher concentrations in the winter (Figures 2b, 4g). This pattern is related to the formation of NH₄NO₃ stabilized under the low temperatures prevailing during winter (Park et al., 2005; Mariani and de Mello, 2007). NO₃⁻ could originate from local pollution sources, such as vehicular traffic and combustion for heating purposes. NO₃⁻ levels are considerably reduced in summer (Figure 4h), due to the thermal instability and volatilization of the NH₄NO₃ (Harrison and Pio, 1983, Querol et al., 2004). A similar seasonal pattern for NO₃⁻ has been reported previously in Athens (Sillanpää et al., 2006; Paraskevopoulou et al., 2015). During winter months, NO₃⁻ levels were found to be significantly higher by 53% (53% also if SP is considered; p<0.001 in both cases) during night-time compared to day, indicating important contribution from heating (Figure 6d, Table 2). A significant correlation of NO₃⁻ with OC, EC and PM_{2.5} was also observed during winter (r=0.58, 0.60 and 0.56 respectively; p<0.001), further supporting their common origin. In summer no statistical significant correlation between these compounds was found.

For the rest of the ions analyzed, their seasonal distribution depends on their main sources which can be classified into marine, mineral or mixed. Cl⁻, Na⁺ and Mg²⁺ controlled by sea spray emissions are expected to have the same seasonal variability, which is related to the prevailing wind speed and direction. However, the temporal variation of Mg²⁺ in Athens revealed higher levels during the warm season (spring-summer), most probably from local dust resuspension and/or regional dust transport, while Cl⁻ and Na⁺ present high levels during winter, most probably due to stronger southern winds prevailing during this period. Cl⁻ and Mg²⁺ didn't present an increase (even recording a slight decrease) during night compared to day. On the other hand, Na⁺ increased by about 21% (Table 2) indicating a small contribution from heating and especially biomass burning, as previously reported by Fourtziou et al. (2017).

nssCa⁺², considered as an effective tracer of crustal sources in the area (Sciare et al., 2005), is distinctly higher in the warm season due to dust transport from the Sahara and/or regional dust resuspension, the latter due to the absence of precipitation. Regarding nssK⁺ a bimodal distribution is observed with peaks in spring and winter. The first peak is associated with Saharan dust outbreaks and the second as a result of biomass burning emissions. The latter corroborates previous reports for online fine mode K⁺ measured at the same site (Fourtziou et al., 2017). In order to discriminate between the influences of Saharan dust and biomass burning on nssK⁺ levels, we have used Ca²⁺ as a tracer of crustal origin. During the period from March to October, with limited emissions from local biomass burning sources, nssK⁺ and Ca²⁺ exhibit a significant correlation (r=0.83), confirming their crustal origin. Thus, by using the nssK⁺/Ca²⁺ slope from their linear regression (y=0.82x+0.08), the nssK⁺ of crustal origin (K⁺_{dust}) can be identified allowing to further estimate nssK⁺ of biomass origin (K⁺_{bb}) from the following equation:

$$K_{bb}^{+} = nssK^{+} - K_{dust}^{+}$$

K⁺_{bb} levels during the winter period account for 70% of the total nssK⁺ levels and present a well-defined day-night contrast. Mean night-time K⁺_{bb} concentrations of 0.5 µg m⁻³ are by 57% increased relative to day-time (Figure 6e; Table 2; p<0.001), highlighting the role of nssK⁺ as a tracer of wood burning in agreement with Fourtziou et al. (2017). During all three winter campaigns (n>400), the estimated K⁺_{bb} correlates significantly with OC, EC and NO₃⁻, especially during night-time (r=0.58, 0.57 and 0.46, respectively) compared to day-time (r=0.15 to 0.23).

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C₂O₄²⁻ exhibits peaks during winter due to biomass burning emissions (Kawamura et al., 1996; Kawamura and Ikushima, 1993) and during summer linked to enhanced photochemistry, along with increased emissions of biogenic volatile organic compounds (Theodosi et al., 2011). C₂O₄²⁻ presents strong correlations with OC and EC during summer (r=0.42-0.63) due to common emission processes such as photochemical and/or heterogeneous reactions (Myriokefalitakis et al., 2011). SO₄²⁻ presents a significant correlation with C₂O₄²⁻ independent of season (r>0.54; p<0.001). Such correlations have generally been observed in many different sampling locations around the world (Pakkanen et al., 2001; Yao et al., 2003), and can be attributed to heterogeneous reactions during both seasons as proposed by Myriokefalitakis et al. (2011). During winter, from the compounds impacted by heating sources and examined so far, C₂O₄²⁻ correlates significantly only with NO₃⁻ (r=0.41). In addition, higher concentrations during night (about 30%) compared to day (Table 2) have been also observed, indicating local biomass-burning emissions as possible contributors of C₂O₄²⁻. However, the significant correlations with both SO₄²⁻ and tracers of biomass burning clearly indicate that C₂O₄²⁻ have mixed sources of both local and regional origin and significant precaution is required when C₂O₄²⁻ is used as exclusive tracer of biomass burning.

3.4.4 Trace metals

3.4.4a Crustal – related elements

Al is typically associated with soil dust resuspension and thus mainly linked to natural sources. It presents higher concentrations and larger variations during the transitional (spring and autumn) periods when the air mass trajectories originate predominantly from North Africa and are often associated with intense sporadic peaks of mineral dust (Figure 2c). Mn and Fe, which are affected by diverse natural and anthropogenic sources, present the same seasonal variation (Figures 2c, f), and especially Mn reveals a statistically significant correlation with Al (r=0.59). However, the moderate correlation of Al with Fe (r=0.44), suggests the existence of additional sources for Fe most probably anthropogenic.

Regarding the diurnal pattern of Al, it is higher by about 30% during day-time compared to night (Table 2), most probably due to traffic related dust resuspension. A different behavior was observed for the other two “crustal” elements, with Mn presenting no difference between day and night-time (Table 2), whereas for Fe slightly higher levels were observed during night compared to day by about 10% (Table 2). The above described diurnal variation corroborates our hypothesis for mixed sources, natural and anthropogenic for both Mn and Fe, most probably from combustion emissions, in addition to dust (local or regional).

3.4.4b Elements of anthropogenic origin

The measured trace metals originating from human activities (V, Cr, Cd, Ni, Cu, Cd and Pb) relate to a variety of sources. As presented in Figures 2d-f, the elements of anthropogenic origin exhibit well defined seasonal trends with peak values during winter, as a result of additional sources, especially heating, but also of meteorology. When their diurnal distribution was examined during winter-time, only Cd and Pb presented a significant increase (at 95% confidence level) during night-time compared to day, in the range of 11 to 16% (up to about 40% when SP periods are considered; 99.9% confidence level). The

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above tendency indicates emissions from heating and especially wood burning, in agreement with Maenhaut et al. (2016). The other elements either present an insignificant increase in their levels during night (case of V, Ni) or even a decrease compared to day (case of [traffic-related Cu](#)).

Significant correlations of As with Pb and Cd ($r=0.39$ and 0.66 , respectively) were observed [during the whole period](#). When considering the three intensive winter campaigns, higher correlations were obtained between As and Cd ($r=0.74$) and moderate for Pb ($r=0.38$), suggesting that heating using coal [and wood](#) could be a source of the aforementioned heavy metals (Nava et al., 2015; [Maenhaut et al. 2016](#)). [In fact, As has been associated with wood combustion, where copper chrome arsenate \(CCA\) treated timber is being used for residential heating purposes \(Fine et al., 2002; Khalil and Rasmussen, 2003; Alastuey et al., 2016\)](#). Strong correlations of Pb with $PM_{2.5}$, OC, EC, $nssK^+$, NO_3^- during winter further reinforce the link with wood combustion sources [at our site](#). Indeed, [winter-time Pb concentrations](#) present a significant correlation with $PM_{2.5}$ mass during night-time ($r=0.84$), as compared to day-time ($r=0.14$). [On the contrary, during summer, Pb significantly correlates](#) with Cd ($r=0.68$), indicating [the prevalence of regional sources for both elements during the non-heating season](#). Finally, As, Pb and Cd present no pronounced [overall or season-specific associations to elements such as Cu and Zn, which are considered as effective brake and tire wear tracers, generally \(Weckwerth, 2001; Amato et al., 2009\) and in the area \(Manalis et al., 2005; Grivas et al., 2018\)](#).

During summer relatively high correlation coefficients were calculated between [SO₂²⁻ and the typical heavy oil combustion tracers V and Ni](#), ($r=0.69$ and 0.60), [respectively](#). This indicates common emission patterns and source types such as shipping. The V/Ni ratio during that period was equal to 1.2, slightly lower than the range of 2 to 4 reported by Viana et al. (2008) to identify shipping emissions, pointing to additional fuel combustion sources. During winter the poorer correlation of V with Ni ($r=0.16$) can be explained by a decrease in shipping activities and thus Ni could be related to petrochemical and metallurgical activities (see below).

3.5 Winter-time $PM_{2.5}$ source apportionment

3.5.1 PMF modeling

The model identified six unique factors, characterized as biomass burning, vehicular emissions, regional secondary, heavy oil combustion, dust particles and sea salt. Factor contributions to modelled concentrations of species and source profiles are presented in Figure 7. [Average contributions of factors to \$PM_{2.5}\$ concentrations, separately for day-time and night-time sampling periods are shown in Table 3](#). $PM_{2.5}$ concentrations were adequately reproduced by the model with high correlation coefficient and slope in modeled vs. observed values regression ($r = 0.92$; slope=0.94; intercept: [not significantly different from 0](#)). Results of the BS-DISP error estimation process, with over 95% accurate bootstrap mapping, small change of the Q value and minimal factor swaps [indicated the stability of the solution](#). Details are provided in Table S1 according to recommendations of Brown et al. (2015).

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3.5.2 Source profiles and contributions

- Biomass burning (BB)

The factor is identified by the strong presence of K^+ and elevated OC/EC ratios (3.6 on average), suggestive of non-fossil fuel primary emissions. Small amounts of Cl^- , $C_2O_4^{2-}$, Fe and Pb were also included (Maenhaut et al., 2016), once again indicating wood-burning associations which have been suggested in section 3.4.4b (Table 2). Ratios of SO_4^{2-} to K^+ below unity likely indicate relatively fresh biomass-burning emissions (Viana et al., 2013). Source contributions correlated highly to α ethalometer-determined BC_{wb} ($r=0.88$). Strong correlations ($r=0.92$) were also observed for the winter of 2015-2016 with the mass fragment of m/z 60, quantified by an aerosol chemical speciation monitor (ACSM) concurrently operating at the same site (Stavroulas et al., 2018). The m/z 60 fragment is considered a good tracer for biomass burning emissions (Alfarra et al., 2007) and its levels are closely associated with levoglucosan concentrations. Approximately 35% of EC concentrations are attributed to biomass burning, close to the average winter-time BC_{wb} fraction, which is equal to 32% for the winter period 2015-2016 (Figure 5) and 44% during 2013-2014 (Fourtziou et al., 2017). Similarly, for OC, the PMF estimated BB contribution of $2.7 \mu g m^{-3}$ to fine OC is comparable to the $2.3 \mu g m^{-3}$ of biomass-burning organic aerosol estimated to be present in submicron non-refractory OM in Thissio, during the winter of 2013 (Florou et al., 2017).

The average contribution of the BB factor in $PM_{2.5}$ during night-time is estimated at 3.4 times the day-time value, double the respective increase (1.7 times) in fine aerosol mass (Table 2). Overall, biomass burning was found to be the source with the largest input to winter-time $PM_{2.5}$ concentrations in the urban-background setting of central Athens. Biomass burning has been recognized as an important contributor to fine particle levels in post-recession Athens, with mean annual contributions varying between 7-10% (Paraskevopoulou et al., 2015; Amato et al., 2016). In the present case, for the confined winter-time period, the average share of the BB factor was found to be much higher (32%). Such large winter-time contributions are increasingly being reported for urban background locations in Southern Europe (Nava et al., 2016; Squizzato et al., 2016; Diapouli et al., 2017; Cesari et al., 2018). Florou et al (2017) have attributed 25% of winter-time (2013) non-refractory submicron aerosol to biomass burning organics at the same site, a result compatible with the presently estimated contribution.

Due to the fact that only water-soluble K^+ was included as a tracer for biomass burning in the PMF analysis, it is possible that some uncertainty is associated with estimated contributions (Pachon et al., 2013). In order to provide an indication of such an uncertainty, and in the absence of levoglucosan measurements, we have repeated the PMF analysis, for the winter of 2015-2016, adding data on the m/z 60 and m/z 73 mass fragments, from collocated ACSM measurements. These have been validated as important BB tracers at the present site, displaying strong correlations with levoglucosan, as detailed in Fourtziou et al. (2017). Combination of data from chemical analysis and aerosol mass spectrometry in the same receptor model has been occasionally reported in the literature (Li et al., 2004; Dall'Osto et al., 2014).

A similar 6-factor solution was again obtained and -based on the comparison of resulting BB explained variances and contributions with those of the original dataset (supplementary Figures S2 and S3)- differences were found to be small. The source profiles closely agree and a mean absolute difference of 3.5% (0-12.4%) was calculated for explained variances of

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species. The average difference in the factor contribution to PM_{2.5} for the winter of 2015-2016 was +0.68 µg m⁻³ (higher in the original solution). The latter is analysed in +0.59 µg m⁻³ in day-time and +0.82 µg m⁻³ in night-time average contributions. The mean difference of the fractional contribution to PM_{2.5} is 3.4%.

NO₃⁻ was predominantly classified in the biomass burning factor. NO₃⁻ in central Athens is formed as a product of fast chemical processes involving fresh NO_x emissions at a local level (Theodosi et al., 2011). In cold-weather conditions, nitrate condensation of semi-volatile ammonium nitrate in the particle phase is enhanced. Especially during the night, when temperatures drop significantly and fresh wood-burning NO_x is abundant, nitrate concentrations rise significantly (53%; section 3.4.3), establishing a pattern of temporal covariance with biomass burning indicators (Xie et al., 2008; Amato et al., 2016). Moreover, associations between biomass burning aerosols and nitrate that are observed in Southern Greece (Bougiatioti et al., 2014), have been attributed to reduced acidity, which facilitates NO₃⁻ partitioning in the particle phase (Guo et al., 2016). Higher night-time pH values are anticipated both due to the ionic content of wood-burning emissions and because of increased water content during the nocturnal hours (Bougiatioti et al., 2016), especially in humid conditions favourable for the occurrence of winter-time smog events.

While a separate secondary nitrate factor has been occasionally identified in PMF studies in Athens (Amato et al., 2016), in this winter fine particle dataset, it was not possible to obtain a stable solution with more than six factors. The absence of a nitrate factor in PMF results for PM in Athens has also been reported by Paraskevopoulou et al. (2015) and Diapouli et al. (2017). The latter, at two urban and suburban background sites in Athens, presented a nitrate mass fraction in the BB factor similar to the one presently reported (around 0.1 µg µg⁻¹), with the factor being the main contributor to fine nitrate. Since the possibility that the secondary nitrate included in the BB factor might be inflating its contribution can't be completely ruled out, the total nitrate attributed to the factor (as NH₄NO₃) has been considered as an upper bound of overestimation. In this case, the overestimation during day-time and night-time would be 0.58 and 1.18 µg m⁻³, respectively. The contributions of the factor to the PM_{2.5} would still be 16% and 35% during the two day periods (3% and 4% less than calculated). For comparison, Amato et al. (2016) have reported an annual secondary nitrate contribution of 0.7 µg m⁻³ for PM_{2.5} in suburban Athens.

25 - Fossil fuel sources (VEH and OIL)

The vehicular emissions factor (VEH) is characterized by an abundance in EC, OC, Cu and to a lesser extent Zn and Pb. Factor contributions correlate well with the fossil fuel fraction of BC (BC_{ff}, r=0.86). The factor also correlates much better than the biomass burning factor with NO_x (r=0.93) and CO (r=0.90) concentrations, measured at a nearby roadside traffic site (0.9 km to the NE) and used as indicators of local traffic variability (respective correlations with BB factor: r-NO_x=0.64, r-CO=0.63). Moreover, the factor is significantly anti-correlated with the CO/NO_x concentration ratio (r = -0.60), which has been used to discern between traffic and BB emissions, since the latter contain more CO in comparison with combustion in engines where, due to higher temperatures, a larger amount of NO_x is produced (Sandradewi et al., 2008). The EC/OC ratio in the factor equals 0.65, suggestive of vehicular exhaust emissions (Pio et al., 2011). The overall contribution of 19% to PM_{2.5} is reasonable for urban background locations in Europe (Belis et al., 2013) and comparable to previous results in Athens (Paraskevopoulou et

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al., 2015). While an interference of fuel emissions from domestic heating in the factor can't be completely excluded, it is believed that it wouldn't be significant, given the low share of heating oil combustion to total PM emissions from domestic heating in Greece (Fameli and Assimakopoulos, 2016). Average night-time contributions are slightly higher (by a factor of 1.5); however the difference was not statistically significant at the 0.05 level.

5 The oil combustion factor (OIL) is dominated by the presence of V and Ni, at ratios indicative of residual oil combustion (V/Ni: 1.8). Sulfate is present at the source profile with a contribution of $0.07 \mu\text{g } \mu\text{g}^{-1}$ and an explained variance of 4%, values that are relatively small, but within the range of those reported for oil combustion factors in other cities in the Mediterranean (Amato et al., 2016; Kocak et al., 2011; Reche et al., 2012). The observed V/Ni ratio appears to fall short from the typical values reported for shipping emissions (Pandolfi et al., 2011). In Athens, a major part of shipping emissions that affect the
10 inner parts of the basin derive from passenger and cruise ship activity, which during the winter months diminishes. Karageorgos and Rapsomanikis (2010) have reported winter-time V/Ni ratios of 1.5-1.9 for sites in central Athens for fine particles deriving from mixed harbour and industrial emissions in the S-SW part of Athens. As it can be seen in Figures S4a, b, moderately high contributions are associated with westerly advectations from the industrialized Thriassion plain, while exceedances of the 75th percentile are more probable with winds from the harbour zone to the south. No pronounced day-night contrasts were observed,
15 indicating that oil combustion for residential heating should not influence the source profile. The average contribution of the factor in $\text{PM}_{2.5}$ (7%, $1.5 \mu\text{g } \text{m}^{-3}$) is within the range reported for Mediterranean areas affected by harbour emissions (Perez et al., 2016).

- Secondary sources (SEC)

20 The factor is characterized mainly by the presence of sulfate. The observed $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio in the source profile (2.2) is close to the stoichiometric, modified by the presence of NH_4NO_3 . $\text{C}_2\text{O}_4^{2-}$ is predominantly associated with this factor, its close correlation to SO_4^{2-} having been attributed to common in-cloud processing mechanisms (Yu et al, 2005), in agreement with the results in section 3.4.3. The OC/EC ratio exceeds the value of two (2.3). In comparison to year-round observations, reduced OC/EC ratios (Grivas et al., 2012) and regional contributions (Paraskevopoulou et al., 2015) have been documented in the area
25 during winter months, due to limited formation of secondary organics from photo-oxidation processes. Higher contributions were observed during day-time, most probably due to increased photochemical activity. Grivas et al. (2018), estimated $5.5 \mu\text{g } \text{m}^{-3}$ of secondary regional contribution for the cold period of 2011-2012 (extending from mid-October to mid-April), at an urban background location in Central Athens, consistent with values presently reported.

30 - Natural sources (DUST and SS)

The factor identified as dust is characterized by the presence of Al, Fe, Ca^{2+} and Mn. The observed ratio of Fe/Al (2.1) is higher than the values reported for local top-soil (Argyrazi and Kelepertzis, 2014) or for Saharan dust (Formenti et al., 2003). It appears that road dust -rich in trace elements deriving from mechanical wear or vehicles- is incorporated in the dust factor as indicated above in section 3.4.4a. A further indication of the participation of road dust is the abundance of Cr in the factor,

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which is largely enriched (enrichment factor $EF > 100$, using Al as the reference element), with respect to the upper crust composition (Wedepohl, 1995). Dust contributions do not present significant day-night variability and overall they account for 8% of the $PM_{2.5}$ concentrations, in line with contributions to $PM_{2.5}$ reported for the urban background of central Athens during 2011-2012 (Grivas et al., 2018).

- 5 High contributions to Cl^- and Na^+ are characteristic for the marine aerosol factor, which records higher-than-median contributions (Figure S4c) mainly during moderate flows from the sea, five km to the S of the site (Figure S4c). Ca^{2+} ions participate at a fraction of Cl^- representative of the composition of seawater. Cl^- depletion is limited during the winter months, allowing for a more realistic quantification of the input of marine aerosols to the fine particle fraction. A relatively higher contribution of the factor to particle mass (9%), in comparison to past studies in Athens is noted (Paraskevopoulou et al., 10 2015), probably related to the closer vicinity of the site to the sea.

4 Conclusions

This study reports detailed measurements of $PM_{2.5}$ chemical composition at central Athens, from December 2013 to March 2016, including 3 intensive winter campaigns. Approximately 850 daily $PM_{2.5}$ samples were collected and analysed for the main ions, trace metals, OC and EC, quantifying a range of useful tracers for monitoring the contribution of the different 15 sources to the aerosol load in Athens.

From the results, it appears that in spite of reductions in anthropogenic emissions during the past years, mean annual $PM_{2.5}$ levels persist in the vicinity of $20 \mu g m^{-3}$, a value of relevance for increased population exposure in urban background areas, as evidenced by its selection in the EU Average Exposure Indicator of the 2008/50/EC directive.

- 20 Levels of both POM and EC considerably increased during winter (POM $11.6 \mu g m^{-3}$; EC, $2.8 \mu g m^{-3}$) compared to summer (POM $5.2 \mu g m^{-3}$; EC $0.7 \mu g m^{-3}$), underlining the major role of heating-related emissions during winter in Athens. It is noteworthy that winter EC levels exceed mean winter EC concentration measured in PM_{10} at a roadside location in central Athens, 10 years prior to this study (Grivas et al., 2012), indicating the recent intensification of winter-time emissions of carbonaceous compounds.

- Ionic concentrations exhibit a summer maximum, with SO_4^{2-} and NH_4^+ concentrations up to 3.8 and $1.7 \mu g m^{-3}$, respectively. 25 This is related to the significant contribution from photochemistry during that period, combined with less precipitation and higher regional transport as both compounds are related to regional rather than local sources. Overall, the long-term sulfate measurements indicate that levels in the area have progressively declined during the last two decades, reflecting the reductions of regional emissions of sulfur oxides from energy production in Greece.

- The importance of residential heating was highlighted by examining the diurnal variation of measured species during winter- 30 time. During the heating period, from November to February, $PM_{2.5}$, POM, EC, NO_3^- , $nssK^+$ and $C_2O_4^{2-}$ significantly increased during night compared to day-time, due to the intensive use of fossil fuel and wood for heating purposes. Heavy metals such as As, Cd and Pb were also found to be associated to heating activities in winter. However, the present results from long-term

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measurements, indicate that violations of the EU target values for As, Cd, Ni, as defined in the 2004/107/EC directive, are unlikely at urban background locations in the area.

In order to further quantify the importance of residential heating during winter in the city centre of Athens, PMF source apportionment was performed with specific emphasis on day-night patterns. Biomass burning was found to be the source with the largest input to winter-time PM_{2.5} concentrations (32%) in the urban-background site of central Athens, with a higher night-time contribution (39%) to the PM_{2.5} compared to day-time (19%). The vehicular emissions and oil combustion factors contributed almost equally between night and day (19% and 7% for the two factors, respectively). The factors representing natural emissions (crustal and marine) presented slightly higher contributions during day-time (9% dust and 11% SS) compared to night-time (6% dust and 7% SS). Regional secondary sources were found to be the source with the largest input to winter day-time PM_{2.5} concentrations equal to 30%, higher by a factor of almost 2 compared to night-time contributions.

Based on these source apportionment results, one can infer that biomass burning, can account for a large part of the observed increase in PM_{2.5} levels in winter night-time. Moreover, the smog events are likely to inflate the number of exceedances of the 24-h limit value for PM₁₀ samples at the station. It is noteworthy that the contribution of the biomass burning factor was estimated over 10 µg m⁻³ on 32% of the analysed days. An important effect of winter-time biomass burning emissions is the reversal of the long-established seasonal pattern of PM concentrations at urban background sites in Athens. Whereas, prior to the recession, the monthly variation of PM₁₀ and PM_{2.5} concentrations at urban and suburban background sites produced an enhancement during the summer period, attributed to secondary particles (Kassomenos et al., 2014), the results from this long-term study indicated that winter-time levels at the urban background of Athens are now significantly higher during winter.

It has been demonstrated that the contribution of the BB factor triples during the evening and night hours in winter-time. Such an increase is notable, even though its direct impact for population exposure might be moderated by the fact that the majority of the population stays mostly indoors during this time frame. On the other hand, this specific source type, has been also linked to significant indoor exposure from fireplaces and wood-stoves, so its effects are adding up.

Given the apparent importance of biomass burning as a major pollution source in Athens -escalating since the winter of 2012- chemical composition measurements should continue in order to track its year-to-year variability. Additionally, estimation of the biomass burning-related sources using other approaches such as high resolution measurements of the organic submicron fraction (i.e the work by Stavroulas et al., 2018), should be helpful to elucidate not only the potential impacts of this environmental issue, but also the related dynamic processes in the atmospheric chemistry of urban areas.

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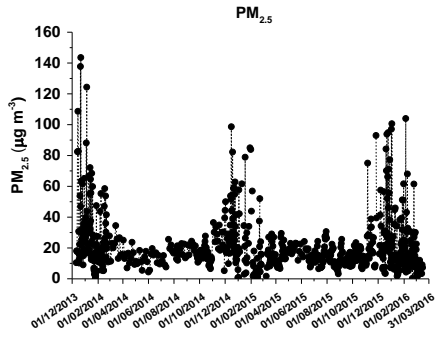
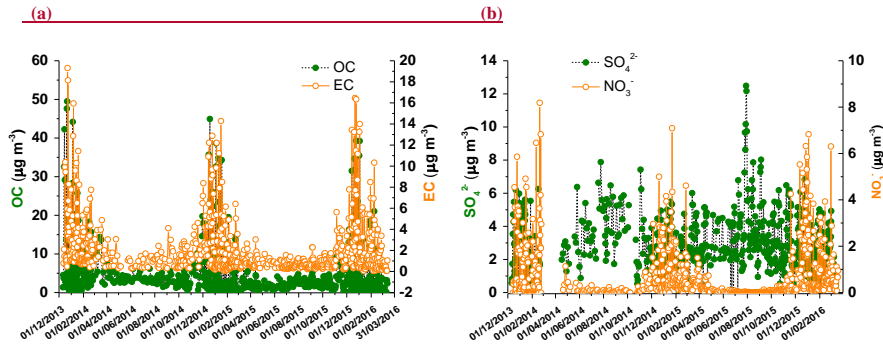


Figure 1: Daily $PM_{2.5}$ mass concentrations ($\mu g m^{-3}$) at Thissio station for the studied period December 2013 to March 2016.

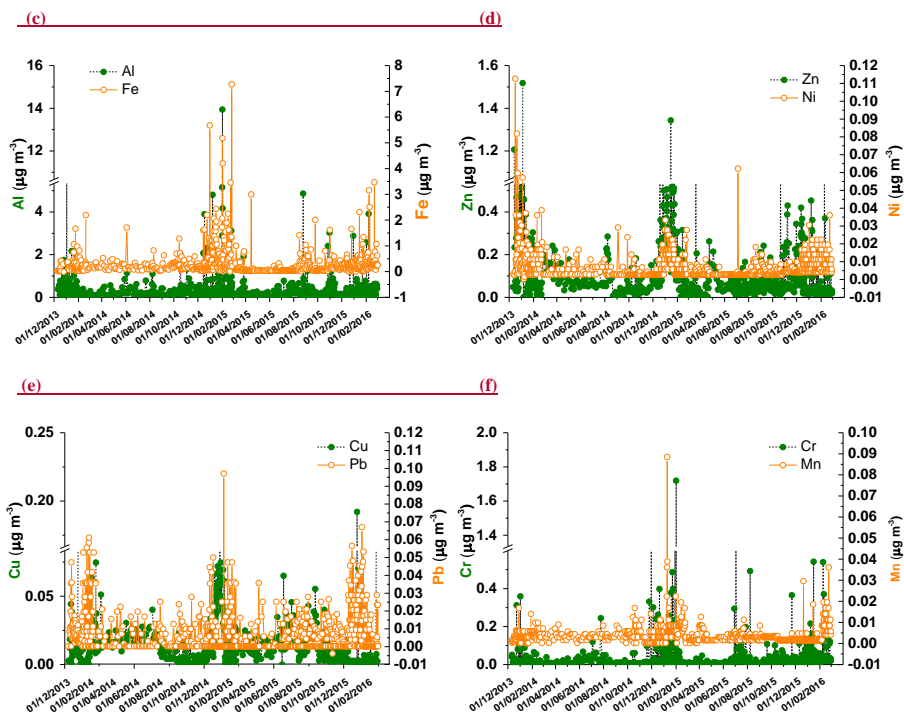


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5 Figure 2: Daily variation of (a) OC, EC, (b) SO_4^{2-} , NO_3^- , (c) Al, Fe, (d) Zn, Ni, (e) Cu, Pb and (f) Cr, Mn for PM_{2.5} samples collected at Thissio for the sampling period December 2013–March 2016.

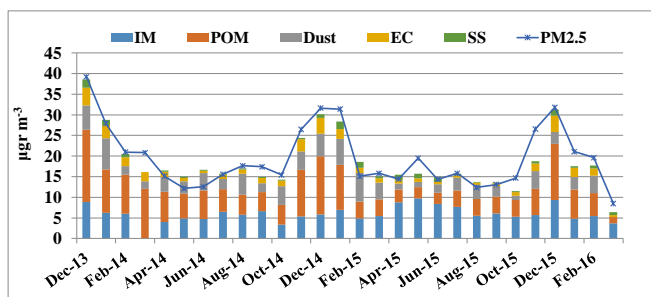
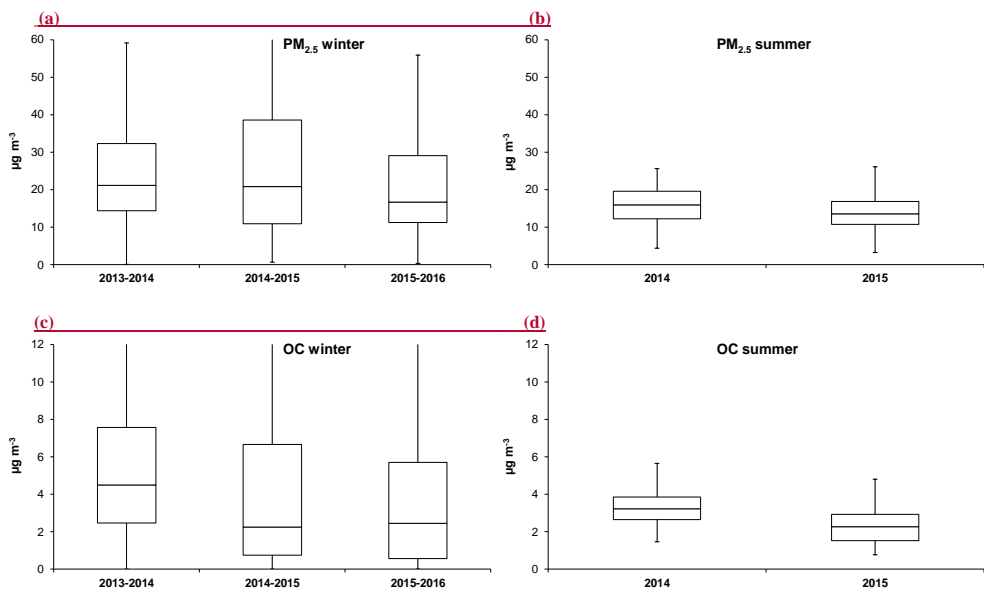
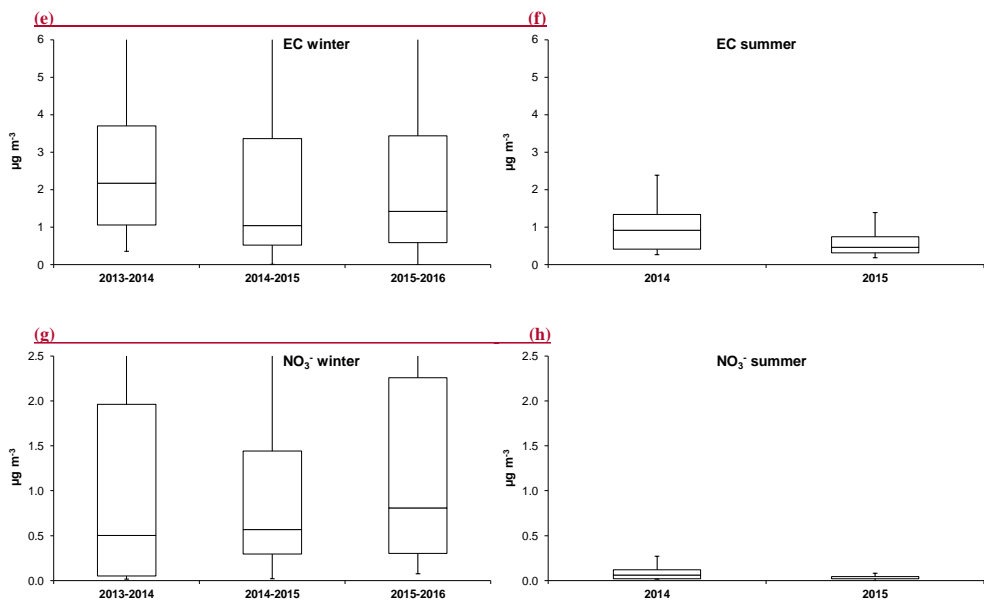
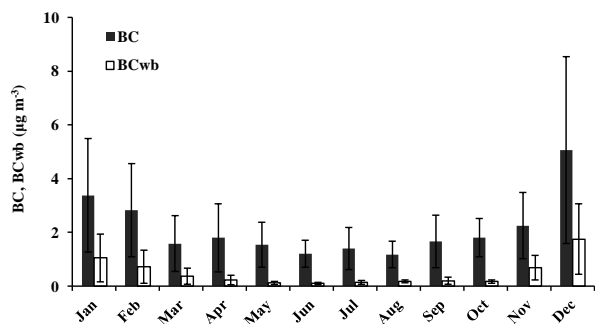


Figure 3: Annual seasonal chemical mass closure of each aerosol species for PM_{2.5} samples collected at Thissio for the studied period.



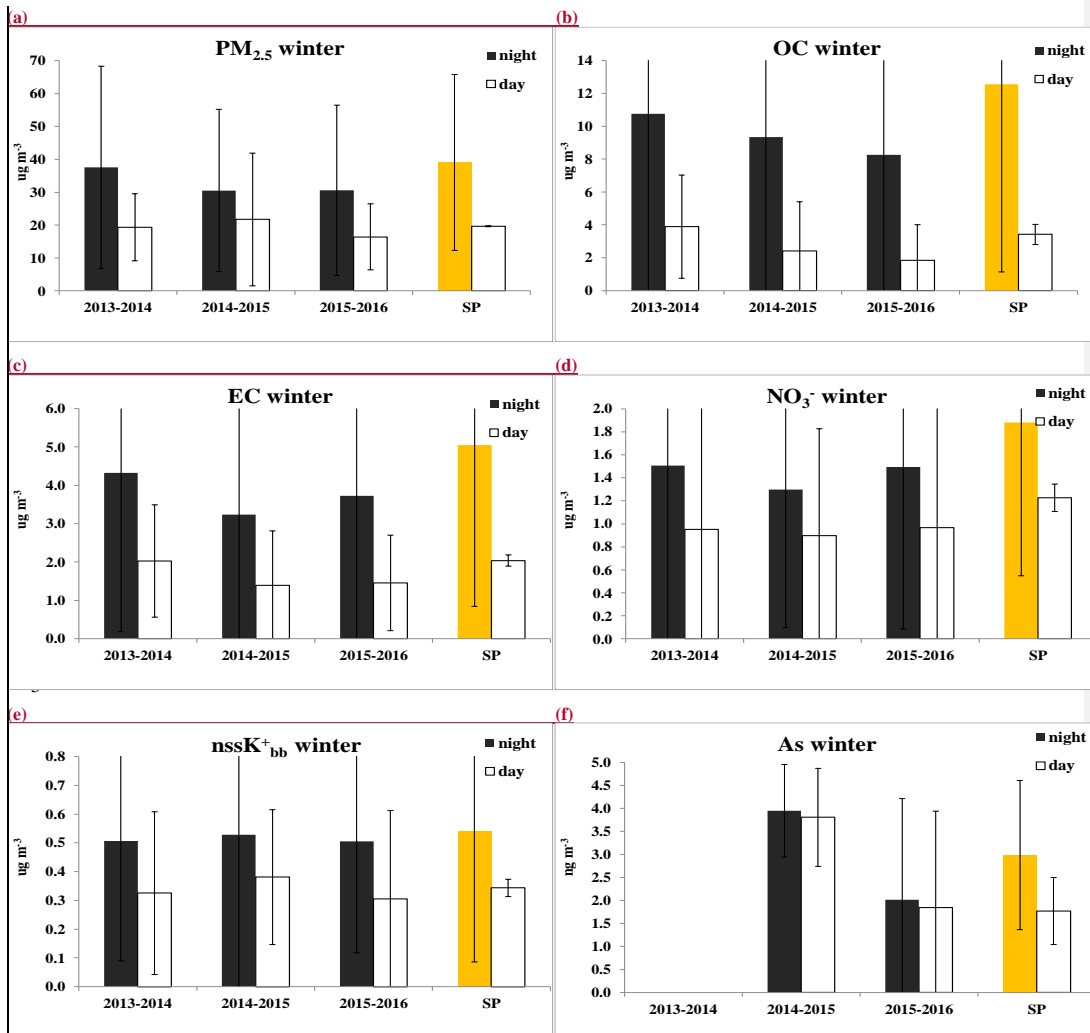


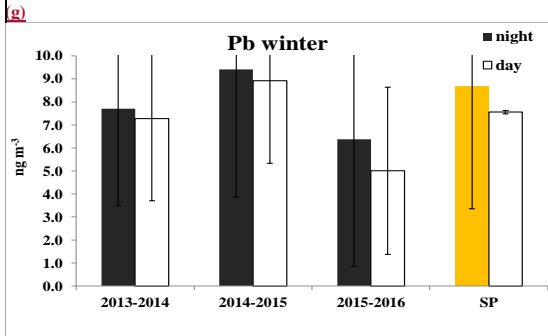
5 **Figure 4:** Winter and summer interquartile range ($\mu\text{g m}^{-3}$) for $\text{PM}_{2.5}$ mass, OC, EC and NO_3^- concentrations in the urban site of Thissio for the studied period December 2013 to March 2016. **The ends of the whisker are set at $1.5 \cdot \text{IQR}$ above the third quartile (Q3) and $1.5 \cdot \text{IQR}$ below the first quartile (Q1).**



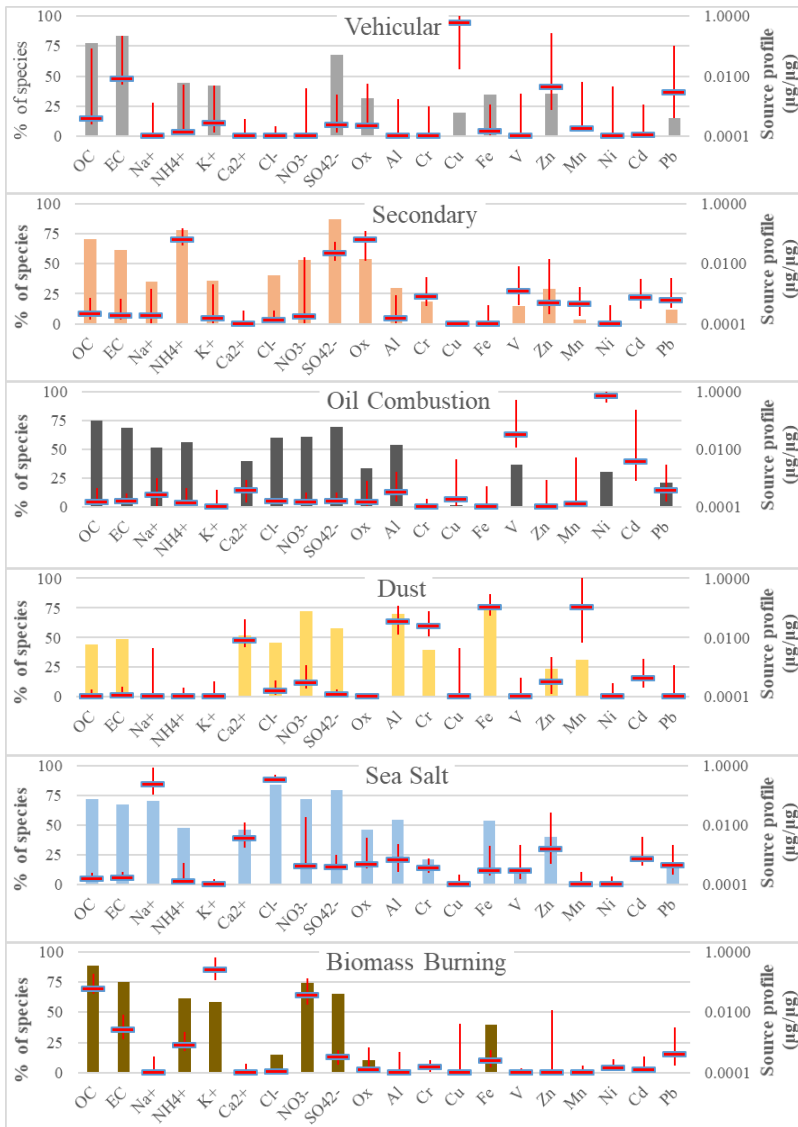
10 **Figure 5:** Seasonal variation of BC and BC_{wb} at Thissio during May 2015-May 2016. **The November point corresponds to black carbon measurements during fall of 2016. Posterior data are used in order to depict a non interrupted annual pattern.**

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5 Figure 6: Winter PM_{2.5} mass, OC, EC, NO₃, nssK⁺_{bb}, As and Pb values (µg m⁻³) divided into day-time and night-time samples. SP refers to concentrations when only smog events occurred.



5

Figure 7: Average contributions to the component mass (% , red [markers](#)) and source profiles ($\mu\text{g mg}^{-1}$, colored [vertical bars](#)) of PMF-resolved sources. Error bars providing the interquartile range from bootstrap resamples.

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Table 1: Mean, standard deviation, median and range of measured concentrations for PM_{2.5} aerosol samples, collected at Thissio and other urban sites in Athens. Values for PM_{2.5}, OC and EC are in $\mu\text{g m}^{-3}$, whereas for the rest of the species in ng m^{-3} .

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ng m ⁻³	PM _{2.5}		PM _{2.5}		PM _{2.5}	PM _{2.5}	PM _{2.5}
	Mean	Median	Mean	range	Summer/Winter Mean	Mean±stdev	Mean±stdev
Sampling	Dec 2013-March 2016 (n=850)		Summer 1987 (n=27)		Summer 1982 /winter 1982-1983 (n=29)	Sep 2005- Aug 2006 (n=109)	4 short- term seasonal campaigns Jun 2011-Feb 2013 (n=211)
Location	Athens urban		Athens urban		Athens urban	Athens urban	Athens urban
Reference	This study		Scheff and Valiozis, 1990		Valaoras et al. (1988)	Theodosi et al. (2011)	Paraskevopoulou et al. (2015)
PM _{2.5}	19.1±7.1	15.5	80.7	27-127		29.4±10.3	33±12
OC	4.0±2.0	3.12	16.9	5.7-43.4	25.7/16.1	-	5.55±2.01
EC	1.5±1.0	1.12	4.2	1.2-18.6	8.20/11.0	-	2.06±0.78
Cl ⁻	272±197	155	350	0-1300	75/440	490	182±80.2
Br ⁻	19.4±10.7	14.2	130	0-589	140/380	-	-
NO ₃ ⁻	476±377	278	2000	500-5100	-	1090	896±634
HPO ₄ ²⁻	54.3±37.4	46.4	-	-	-	-	72.9±73.6
SO ₄ ²⁻	3033±835	2933	10400	4100- 23700	-	5790	3293±1473
C ₂ O ₄ ²⁻	143±56	123	-	-	-	320	203±50.4
Na ⁺	307±196	369	369	0-1890	-	830	255±78.7
NH ₄ ⁺	1422±685	1112	-	-	-	920	843±433
K ⁺	273±109	268	428	24.2-833	160/380**	460	150±76.7
Mg ²⁺	64.0±31.6	60.7	132	0-653	-	50	8.84±10.9
Ca ²⁺	160±127	113	-	-	-	320	219±246
Al	293±106	263	408	-	130/850	-	494±95.3
As	1.9±0.2	1.83	-	-	34/13	-	4.35±5.56
Ca	745±522	501	2610	776-4970	-	-	898±254
Cd	1.7±0.7	1.75	220	0-1141	-	-	1.16±0.60
Cr	27.1±20.4	19.6	-	-	-	-	18.8±6.29
Cu	14.8±5.2	16.2	50.6	0-143	35/260	-	17.4±5.75
Fe	264±125	234	1100	293-1990	490/300	-	304±110
V	6.9±2.4	6.61	-	-	-6.60	-	7.79±3.86
Zn	93.0±50.1	73.1	273	46.8-615	130/210	-	94.9±34.8
Mn	4.6±1.4	5.06	21.6	0-70.3	-/14.0	-	5.68±1.23
Ni	6.0±2.6	4.86	11.6	0-37.4	21.0/8.60	-	5.16±2.41
Pb	4.1±3.4	3.68	699	162-2273	610/1100	-	12.5±2.46

Table 2: % increase in the diurnal distribution of all studied elements and species during night-time compared to day in winter for all winter samples (n=447) and smog pollution events (SP, n=289).

	%	Full winter period			Only SP		
		mean	stdev	median	mean	stdev	median
5	PM_{2.5}	80%****	120%	55%	96%****	158%	80%
	OC	254%****	278%	200%	278%****	285%	232%
	EC	134%****	189%	113%	148%****	207%	115%
	Cl⁻	-6%	2%	-6%	-1%	11%	-10%
10	NO₃⁻	53%****	32%	90%	53%****	17%	111%
	SO₄²⁻	9%	15%	3%	11%****	14%	7%
	C₂O₄²⁻	29%***	18%	33%	28%*	22%	35%
	Na⁺	36%	219%	6%	21%	46%	13%
	NH₄⁺	13%****	7%	13%	9%****	5%	12%
	nssK⁺_{nb}	54%****	68%	34%	57%***	53%	39%
	Mg²⁺	-11%	16%	0%	0%	13%	0%
15	Ca²⁺	-57%	65%	0%	-70%	90%	0%
	Al	-26%	53%	-19%	-11%	40%	-19%
	As	11%	2%	26%	22%	4%	70%
	Cd	16%*	6%	0%	37%****	12%	0%
	Cr	-2%	20%	-13%	21%	15%	33%
	Cu	-24%	66%	-50%	-23%	70%	-50%
	Fe	9%	10%	13%	31%*	5%	29%
20	V	1%	3%	0%	5%	4%	17%
	Zn	18%	34%	9%	9%	4%	30%
	Mn	-5%	27%	0%	1%	14%	0%
	Ni	-3%	17%	0%	5%	7%	33%
	Pb	12%*	35%	10%	20%****	34%	19%

25 ****p<0.001 (99.9%) *** p<0.01 (99%), ** p<0.025 (97.5%), * p<0.05 (95%)

Table 3: Average day/night contributions of identified sources to PM_{2.5} (µg m⁻³). Respective percentages in parentheses. Statistical significance (p) refers to differences for day-night pairwise comparison assessed with Wilcoxon signed-rank non-parametric tests.

Source	Day	Night	Significance (p)
Biomass Burning	3.4 (19)	11.4 (39)	0.00*
Vehicular	3.4 (19)	5.4 (19)	0.11
Secondary	5.3 (30)	4.1 (14)	0.00*
Oil Combustion	1.4 (8)	1.6 (6)	0.52
Dust	1.6 (9)	1.8 (6)	0.57
Sea Salt	2.1 (11)	2.1 (7)	0.18
<i>Unaccounted</i>	0.4 (2)	2.6 (9)	

*significant at the 0.05 level