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

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A long data series of PM2.5 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.

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

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.

During winter only 12h samples were collected. As it was not clear enough, a change in the manuscript has been performed 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.

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 PM2.5 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.

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: : :"
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.
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.
Based on boundary layer measurements and model estimates above Athens (e.g. 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.

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 BCwb differ from that of BCff?
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. On the other hand the daily evolution of the two components BCwb and BCff 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 in 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.

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?
As 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 K^+ correlate with both Al and nss-Ca^{2+} during dust events and out of wood burning periods. However as regression with nss-Ca^{2+} has a better coefficient (most probably because both refer to the soluble fraction) we prefer to use nss-Ca^{2+} to derive 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.
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 NOx by biomass burning and by the lower acidity. However, as explained later NOx 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.
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).
We agree with the reviewer pointing 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 NO_3^- 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 NO_3^- in the particulate phase. It should be mentioned that except NO_x, biomass burning is also 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 factors for rapid ammonium nitrate formation especially at low temperatures (Paulot et al., 2017) encountered in our site during the night in winter.
We have clarified in the text that NO_x concentrations were used as measured at a nearby kerbside 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 emissions from road fuel combustion are of minor importance.
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.
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 studies with source apportionment for $PM_{2.5}$ 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, the fast chemical conversion from 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 determination. As an upper limit of overestimation due to nitrate, 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 μg m^{-3}, respectively. The respective contributions of the factor to $PM_{2.5}$ 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 μg m^{-3} for $PM_{2.5}$ in suburban Athens. The overall contribution of the factor to $PM_{2.5}$ mass would be then 28% (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 $PM_{2.5}$.

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, quantatively. 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. Fameli 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 PM_{10} 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 concentrations.
Overall, as stated in the manuscript, the night-time contributions of the vehicular source is 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 that is around 10%.
The mass fraction of sulphate in the source profile (0.07μg/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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