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Response to Anonymous Referee #1 comments

The manuscript of Stavroulas et al., presents and analyzes the organic aerosol sources over Athens (Greece) using long term observations (1 year) and 2 intensive campaigns measurements. The source analysis is based on the Aerosol Chemical Speciation Monitor (ACSM). The finding are very important for the region of Athens but also crucial for the atmospheric science community as they found that during the winter a significant fraction of the secondary organic aerosol is clearly connected to the biomass burning organic aerosol. The paper is very well written and organized. I definetely recommend publishing of this paper, after some minor changes:

Response: *We thank the anonymous referee for the thoughtful review. We have further elaborated on these points in the revised manuscript.*

(1) The introduction contains information about Athens topography and biomass burning aerosol (BBOA). However, since in the paper are discussed additional sources found (e.g., LV-OOA, SV-OOA, HOA and COA) I suggest adding a paragraph giving some information about these sources and provide previous measurements for Athens. For example Kostenidou et al., 2015 have measured the OA sources for Athens suburban area during an intensive summer (2012) camping using HR-AMS data.

Response: *Indeed, the introduction focuses mostly on winter time conditions and mainly discusses the biomass burning related atmospheric chemistry and its effect on air quality. The introduction in the revised version of the manuscript now adopts a wider perspective and addresses the referee's comment.*

See rewritten section 1 (Introduction)

(2) Page 3, line 62: please add Florou et al. 2017 after Kalogridis et al. 2017 reference.

Response: *Reference added.*

(3) I suggest replacing the sentence: "Respective measurements using high resolution techniques are scarce and limited in time (Florou et al., 2017)" with: "Florou et al., 2017 have measured the chemical composition and the OA sources during a wintertime intensive campaign in the center of Athens using an HR-AMS an however their data are limited in time."

Response: *Amended.*

See P3, L78.

(4) Page 4, line 119: Please provide the RIENH4 and RIESO4 with the corresponding standard deviations.

Response: *Response factor and relative ionization efficiencies of* NH_4^+ *and* $SO_4^=$ *are now added to the revised supplementary material.*

See P5, L132.

(5) Page 6, line 162: the right parenthesis should not be in bold form.

Response: *Amended.*

(6) Page 9, line 261: please add domestic or residential before heating.

Response: *Amended.*

(7) Pages 12-14, lines 353-425 (warm period section): It would be interesting to compare the HOA, COA, SV-OOA and LV-OOA mass spectra of the warm period in terms of angle theta with the corresponding spectra of Kostenidou et al. (2015) that they found for a suburban area of Athens during summer.

Response: *A comparison with the summertime factors from Kostenidou et al. (2015) has now been added. Primary factors correlate well, namely HOA with* $R^2=0.92$ *for the 2016 dataset and* $R^2=0.94$ *for 2017, COA with* $R^2=0.75$ *for 2016 and* $R^2=0.77$ *for 2017. On the other hand, the semi-volatile component correlates moderately (*$R^2=0.50$ *and 0.56 for 2016 and 2017 respectively), mainly because of the least oxidized nature of this study's SV-OOA which is probably related with the fact that the Thissio station is urban (city-center) in contrast to the suburban Demokritos station where the measurements of Kostenidou et al. (2015) took place. Finally, the LV-OOA factor shows a slightly better correlation (*$R^2=0.61$ *and 0.59 for 2016 and 2017 respectively). The fact that the LV-OOA factor does not exhibit better correlation, is driven mostly by the elevated signal at m/z=18 (*H_2O^+*) attributed to this factor in this study, in contrast to its almost complete absence in the Kostenidou et al. (2015) spectra, performed with a High Resolution Time-of-Flight Aerosol Mass Spectrometer. If m/z=18 of this study is excluded from the correlation exercise the derived values for* R^2 *are of 0.85 and 0.84 for 2016 and 2017 respectively.*

See P16, L490-492, P17, L496-499.

(8) Pages 14-15 lines 426-459 (cold period section): It would be nice to also compare the BBOA, HOA, COA and LV-OOA mass spectra from the winter period with the BBOA, HOA, COA and

OOA mass spectra of Florou et al. 2017 that they measured during the winter at the same site. Florou at al. (2017) found two BBOA factors during the winter for a study in Patras (Greece); one of them (BBOA-II) was less oxygenated and its origin was not fully explained i.e., it could be due to the different types of fuel orcombustion or due to different degree of BBOA aging. What is the angle theta between the SV-OOA mass spectrum of this study (that is linked to aged BBOA) and the BBOA-II of Florou et al. (2017)?

Response: *A comparison of the mass spectra for HOA, COA, BBOA and LV-OOA to the ones obtained by Florou et al (2017) for Athens has been added to the revised version. Correlations are very good for all primary factors, e.g. HOA with* $R^2=0.92$*, COA with* $R^2=0.96$ *and BBOA with* $R^2=0.88$*. For the LV-OOA factor the same issue as when comparing with the summertime factors arises. When taking into account the m/z=18 fragment* R^2 *is 0.57 while when excluding it correlation is stronger with* $R^2=0.78$*. For the Patras site, as well, the correlation of the primary factors is very good (HOA:* $R^2=0.97$*, COA:* $R^2=0.93$ *and BBOA:* $R^2=0.89$*). LV-OOA correlates well when not taking into account the contribution of m/z=18 (*$R^2=0.88$*) while correlation less strong otherwise (*$R^2=0.68$*)*

See P20, L596-602 and L608-610.

(9) Page 17, line 496: there is a “t” alone in that sentence which it should be deleted.

Response: *Amended.*

(10) For the winter case you show in Table 2 that the BBOA mass fraction is around 8-10%. How about the absolute mass concentration? Did you see any correlations with temperature?

Response: *As seen from the factor's time-series, BBOA exhibits the highest concentrations during nighttime, when temperatures are lower and people resort to biomass burning for heating purposes. However, temperature alone cannot explain the high values of BBOA as high values have been also observed during smog periods (SP, Fourtziou et al., 2017), characterized by low wind speed, which does not allow dispersion of air masses.*

(11) I believe that a comparison with summer sulfate measurements from previous years should be made. It could be a paragraph before the conclusion part. How did the PM1 sulfate mass concentration and mass fraction change over the years? You could use the data of Kostenidou et al. (2015), for Athens during the summer and Bougiatioti et al., (2014) and Hildebrandt et al., (2010), which are for summer but for the Finokalia station (different location) given the fact that the sulfate concentration is similar in many locations above Greece during the summer (Tsiflikiotou, Master thesis). Using this trend, could you make any implications? For example how did the economical crisis in affect the air quality (less industry that produces SO2, which is converted to particulate sulfate)?

Response: *We would like to thank the reviewer for his/her suggestion., The studies of Bougiatioti et al. (2014), Kostenidou et al. (2015) and this study were performed well within the economic recession, while only the short-term study of Hildebrandt et al. (2010) was performed before. . Thus by comparing levels at different locations, different months and given the limited amount of data such comparison could be biased. There is, indeed, an apparent reduction in the mean annual submicron sulfate levels, when compared with previous filter-based studies conducted in the area during the previous decade (Theodosi et al., 2011; Pateraki et al., 2012). We will keep however his/her suggestion and we plan in the future to collect all available data set from Greece to examine the impact of economic recession on* SO_4 *levels.*

(12) Figure 5. Please improve the resolution of this figure. Top graph: The left y axis should say “mass concentration (g m-3)” once. The right y axis should also say “mass concentration (g m-3)” once and for each sub-axis just indicate the name of the species without g m-3. Bottom graphs: again “mass concentration (g m-3)” or “% mass concentration and for each sub-axis just indicate the mane of the species without g m-3 or Contrib.(%). Please take care the numbers on the y axis, some fall on other and it is difficult to be read. Avoid gaps.

Response: *Figure 5 has now been redrawn in order to make the diurnal variability of each factor clearer. The referee’s suggestions/comments have been taken into account.*

See P49 new graph.

(13) Figure 6. The same as for Figure 5.
Response: *Figure 6 has been redrawn in the same manner as Figure 5.*

See P51 new graph.

(14) Figure 8. You should consider using a lighter green for the LV-OOA in order to be more distinguishable from the SV-OOA. May be use another color for the map behind (light blue)?

Response: *Figure 8 has been redrawn in the revised manuscript, so the information depicted is more clear.*

Figure 8 has been moved to SI as new graph SF.21.

References

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

Response to Anonymous Referee #2 comments

This manuscript presents a long-term dataset of near real time chemical composition of submicron aerosols in Athens, Greece. It is completed by two intensive campaigns during winter time. Statistical analysis was performed in order to apportion the sources of organic matter. The subject of this paper is of interest and falls within the scope of ACP, although in its current form neither the methodology (PMF) nor the results bring strikingly new outputs in this region. I am still favorable to publication after major revisions.

Response: *We thank the anonymous referee for the review and have incorporated his/her suggestions and comments in the revised version of the manuscript.*

Major Comments

1) Overall, the result section is too descriptive. Describing the angles between profiles impinges upon the actual results. The authors should re-focus the discussions on how this study slots into previous knowledge in Greece (Athens and their cities, such as Patras) and, why not, in the Eastern Mediterranean.

Response: *We would like to thank the reviewer for this comment. Given the fact that matters of clarity and focus have been also pointed out by some of the other reviewers, the results section and especially §3.3, has now been revised in the new version of the manuscript. Similarity with literature spectra is now presented in a more systematic and clear way, while the discussion incorporates a more in depth analysis of the novel findings that complement the knowledge obtained regarding submicron aerosols and more specifically the organic fraction, for the region of the Eastern Mediterranean.*

See P15 new Section 3.3.

Moreover, strong assessments are made regarding SOA, simply from diurnal variations. The authors should either tone down these statements or add much more discussion and figures.

Response: *We do not feel that our assessment of the nature/origin of SOA is simply based on diurnal variability. SV-OOA which is believed to originate from the fast oxidation of primary combustion sources is correlated during winter-time both with external tracers such as* BC_{wb} *and fine-mode nss-*K^+*, as well as with mass spectra from oxidized biomass burning. Additionally, the contribution of m/z=60 and m/z=73, well known fragments of levoglucosan, is significant to this secondary factor. Additional information for* *compounds such as VOCs would be useful, but this is outside the purpose of this manuscript. Nevertheless, the fast oxidation of fresh biomass burning in plumes within just a few hours after emission has been documented in literature (Lathem et al., 2013; Cubison et al., 2011), supporting our present assessment. Furthermore, the LV-OOA spectrum exhibits a highly oxidized nature, correlating very well with literature spectra of OOA attributed to regional processes from earlier studies in the region (Bougiatioti et al., 2014). In any case, we have tried in the revised version to tone down the statements, where not fully supported by experimental results.*

See P15 new Section 3.3.

Then, organonitrates have been found to have significant contributions in Greece (Florou et al., 2017). Can the authors add some more knowledge about that? (especially regarding the role of primary combustion sources in their formation?)

Response: *We would like to thank the reviewer for pointing out the issue of organic nitrate contribution to nitrate measured by the ACSM, a matter of rising concern among the scientific community. For pure ammonium nitrate, Fry et al. (2009) report a* $NO^+:NO_2^+$ *ratio of 2.7, while Farmer et al. (2010) report 1.5. Older studies using AMS, report ratios ranging from 1.18 (Cottrell et al., 2008) to 2 or 3 (Alfarra et al, 2006), while more recently Kindler-Scharr et al. (2016) report values ranging from 2.04 to 3.45. Using data from the ammonium nitrate calibration of our instrument we calculate a* $NO^+:NO_2^+$ *ratio of 3.84, slightly higher than those presented in the literature. Given that the* $NO^+:NO_2^+$ *ratio highly depends on each instrument and it's tuning, and also due to the fact that the instrument's response - in terms of this ratio - when sampling specific organic nitrate standards was not explored during this study, some uncertainty is expected when calculating the fraction of nitrate signal attributed to organonitrates (*R_{ON}*). These uncertainties are expected to be even larger since the limited sensitivity of the instrument does not allow to distinguish the interference of the* CH_2O^+ *ion at m/z=30, thus potentially leading to an overestimation of the measured* $NO^+:NO_2^+$ *ratio.*
In our study, for the 2016-2017 period the $NO^+:NO_2^+$ *ratio ranged roughly from 3.20 (10th percentile) up to 9.83 (90th percentile), thus yielding several negative values for* R_{ON} *and a few values larger than 1, when calculated according to Farmer et al. (2009). Eventually the* R_{ON} *data acquired had to be treated so that negative values correspond to a fractional contribution of organonitrates to* NO_3 *signal of 0, meaning that we assume that those negative values correspond to pure ammonium nitrate particles. Furthermore, we assume that larger values of* $NO^+:NO_2^+$*responsible for elevated* R_{ON} *values are not due to other inorganic salts such as* $NaNO_3$ *and* $Ca(NO_3)_2$*. In the above context we find that during the cold season* R_{ON} *is pretty low with an average value of 0.19. Diurnal variability during the cold season shows minima during night time while a maximum is evident in the afternoon. The opposite trend is observed in the warm season were* R_{ON} *averages at 0.62, exhibiting maxima during night time. Given all the points presented above we believe that although organonitrates is a very important subject, we feel that first it is beyond the scope of this manuscript and second that the overall uncertainties of the ACSM do not allow an accurate and qualitative determination of their levels in the present work.*

2) The method used by the authors to select the appropriate solution is not clearly stated, although it was inspired by Crippa et al. (2014). From the first ACSM intercomparison, Frohlich et al. (2015) proposed a methodology of find optimal solution, and stated some recommendations. Why did the authors prefer Crippa et al.?

Response: *We agree with the anonymous referee that the presentation of the PMF strategy used, which is indeed the one proposed by Crippa et al. (2014), has to be described in a more clear and systematic way. In the original manuscript the results of each step of the process were not presented, in an effort to keep the manuscript short and easy to follow. Both those issues are addressed in the revised version. . The steps of the strategy are clearly presented and PMF solutions of a) the unconstrained runs, b) runs with a constrained HOA factor and c) runs with both HOA and BBOA factor constrained for the cold season dataset are now presented in the revised supplement.*

Regarding the methodology selected, we believe that Frohlich et al. (2015) performed such a detailed optimization of the alpha values used to constrain each factor, due to the scope of their work, which was specifically to explore the performance of the ME-2 method itself across different instruments, thus trying to assure a high level of compatibility amongst 15 different ACSM datasets. However, in order to fully address the reviewer's comment, the revised version of the manuscript and supplement now incorporates results from a sensitivity analysis performed on the alpha value approach.

See P9, Section 2.3.2.

3) The local vs regional vs advected features are not well characterized, and I would strongly recommend the authors to perform a wind analysis, especially for the "local" sources (eg traffic & biomass burning).

Response: *According to the reviewer's suggestion, wind effects have been examined in the revised manuscript, focusing on the sources of local character, namely traffic and biomass burning, as expressed by the HOA and BBOA time-series. The concentrations of these parameters, when regressed against wind speed, decline exponentially for winds exceeding 2 m sec^{-1}, indicating the locality of the respective sources (Fourtziou et al., 2017). The examination of bivariate wind direction and speed plots (Grivas et al., 2018) further corroborate that organic aerosols characterized as HOA and BBOA are mainly produced in the vicinity of the sampling location, rather than advected from the extended area of Athens. This information, is included in the revised manuscript, accompanied by relevant supplementary figures.*

See SI, SF.20, the wind analysis is provided.

Minor comments

P3 l78: the introduction mainly focuses on wintertime biomass burning, so why would you need long-term datasets?

Response: *The introduction has now been revised so as to be much more balanced and provide discussion also related to the warm periods of the year. Furthermore, the importance of long-term chemical composition datasets with high temporal resolution, in the urban setting, is highlighted.*

See rewritten section 1 (Introduction)

P4 l120: please indicate the calibration values

Response: *Calibration values have been added to the supplement.*

See P5, L132.

P4 l103: the ACSM does not measure "aerosol mass" but only the chemical composition; it is not equivalent to a TEOM-FDMS.

Response: *This phrasing has been corrected in the revised manuscript.*

See P11, L309-314.

P5 l123: it is not clear why a chemical-dependent CE has not been applied. Although it is discussed later on, it could be quickly stated here.

Response: *We would like to thank the reviewer for pointing this out. A chemical dependent CE according to Middlebrook et al., 2011, has been now applied on the dataset and will be incorporated in the revised version. Concentrations have been updated accordingly.*

See P5, L146.

P5 l125: did the authors use denuders ahead of the PILS in order to prevent nitric acid, sulfuric acid and ammonia to be respectively confused with particulate nitrate, sulfate and ammonium?

Response: *Two denuders are placed in front of the PILS inlet, which is now added as information in the revised version of the manuscript. Note also that PILS was operating in cation mode and mainly nss-K were used in this manuscript.*

See P5, L153.

P5: filter samplings are not presented.

Response: *Details on filter sampling and analysis has been added.*

See P6, L160-168.

P10 l292: See major comment. I don’t think that the only fact that nitrate has a morning peak similar to BC is enough to link it with morning traffic. More discussion would be needed.

Response: *We agree that a direct comparison between nitrate and BC is not enough to link with morning traffic. Nitrate is an oxidation product, probably what we see is the combined result of several factors like nighttime oxidation, pH, BL. and therefore we have decided to remove this sentence from the revised text.*

P11 l318-319: Datasets have been separated into cold and warm months prior to PMF. Why not seasonally? Not just cold and warm months influence the characteristics of secondary organic aerosols, it could also be related to air masses. So the approach chosen here is not well justified.

Response: *According to studies on the climatology of Southern Greece, the transient period (spring and fall seasons) in Athens doesn't exceed 60 days on average (Argyriou et al., 2004), covering mainly the months of April and October - which were excluded from the seasonal analysis. As a result, the vast majority of air pollution studies in the area have examined the seasonal variability on a cold-warm season basis (Grivas et al., 2008 and reference therein). This classification reflects the contrast between dry/sunny summer and humid/cloudy winter conditions which are typical in the Mediterranean climate setting. Moreover, this split is representative of the relative intensity of local sources and processes, since the cold period effectively includes the time-span when residential heating is active as a source. On the other hand, the warm period essentially coincides with the photochemical season, also being characterized by an absence of precipitation and therefore a larger impact from regional sources.*

See P8, L245-251.

P11 l329: why the HOA from Ng et al. has been used? Why not any other profiles, especially gotten from previous studies in Greece?

Response: *The HOA profile from Ng et al. (2011) is an average of profiles derived from different environments in Europe, Asia and North America, covering different seasons of the year and countries with different types of vehicular fleet. Consequently, we consider that the HOA factor of Ng et al. (2011) can be suitable as an anchor profile for constrained runs in the present study. The results obtained using this factor as an anchor are proven to be representative. Correlation with HOA factors from other studies in Greece is very good for all seasons. Correlation with the wintertime HOA obtained by Florou et al. (2017) at the same measuring site yields an* R^2*=0.92 while correlation of this study’s deconvolved factors for HOA during summertime of 2016 and 2017, with the HOA factor of Kostenidou et al. (2015) measured at a suburban site in Athens during the summer of 2012, was also excellent (*R^2*=0.92 and* R^2*=0.94 respectively). All of this information has now been added to the revised manuscript.*

See P8, L231-234.

P11 l333: Do the authors have any hint of how representative the BBOA of Ng et al. is in Greece?

Response: *We agree with the reviewer that the nature of the biomass burning fuel may vary considerably depending on the location. Especially in Athens, Fourtziou et al. (2017) have reported that a wide variety of hardwood and softwood types are commonly used for heating purposes. This is why an average BBOA spectrum has been selected, and a large alpha value imposed. The BBOA spectrum from Ng et al. (2011) exhibits very good correlation with BBOA factors identified in previous studies for two major Greek cities. Comparison with the Florou et al. (2017) BBOA factor for Athens yields an* R^2*=0.91 while comparison with the factor for Patras yields an* R^2*=0.90. BBOA from this study for the 2016-2017 winter, also correlates very well with* R^2*=0.94. Finally BBOA from Ng et al. (2011) correlates well with BBOA obtained at Finokalia, a regional background site (Bougiatioti et al., 2014) yielding* R^2*=0.78. The results obtained during this study justifies our decision, as the derived BBOA is in excellent correlation with the respective ones found in the literature. one obtained during wintertime by Florou et al. (2017) in Athens (*R^2*=0.89), and in Patras (*R^2*=0.89), even with the BBOA from Bologna during winter (*R^2*=0.85; Gilardoni et al., 2016).*

See P20, L607-610.

P12 l340-341: it could be appreciable if the authors provide a bit more details on the metrics used through the correlation of PMF timeseries with external tracers.

Response: *Even though it is stated at the supplementary material, we agree with the reviewer that this piece of information was obscured by the way the correlation tables were presented. This matter has been considered in the revised version of the supplement.*

See P9, L252-254.

P12 l351: a correlation coefficient of 0.86 corresponds to a r2 of 0.63, which is still a good statistical correlation. Ranges of r2 are by the way not consistent throughout the manuscript.

Response: *The inconsistency in terms of reported correlations was also pointed out by some of the other referees. In the revised text all correlations are given in terms of the square of the Pearson correlation coefficients (*R^2*).*

P13 l397 and p14l400, r2 of 0.32, 0.36 and 0.39 are considered as “moderate”, which should rather be a poor correlation. Later, p16 l477, a r2 of 0.53 is considered as “very well”. I strongly suggests the authors to use a consistent description of correlation coefficients.

Response: *Both of the abovementioned comments have been addressed in the revised manuscript. Characterization of the derived correlations is now uniform in the revised version. Correlations are presented in a more systematic way. Only one metric is used when investigating both affinity with other* *mass spectra and correlation with external time series. Quantitative criteria regarding the description of correlations are also set.*

P13 l388-390: See major comment. Linking SVOOA with primary sources only from mean diurnal variations is not convincing. Please add more discussion.

Response: *The phrasing of this sentence has been changed in the revised version of the manuscript, even though the assumption made, does not refer to the diurnal variability of the factor, but rather to its comparison with reference mass spectra obtained in other studies. In this context, it is now made clear, that since the warm season SV-OOA factor spectrum, obtained during this study, correlates better to factors related with the oxidation of biogenic VOCs together with SOA factors related to primary sources such as cooking and traffic an assumption linking the factor to primary sources can be made.*

See P17, L505-215 & P20, L611-618.

P14 l400: See major comment. Same comment, the statement "SVOOA may, to some extent, partially originate from a combustion source" seems random and hardly quantifiable.

Response: *We agree with the reviewer that the fact that SV-OOA may originate from a combustion source is not quantifiable, but, nevertheless, it must originate from the oxidation process of some kind of primary organic aerosol. Its good correlation with external spectra of aged combustion emissions (aged diesel exhaust, as well as aged BBOA), supports the validity of the statement.*

P14 l407: "HOA emissions are very low", compared to what?

Response: *This sentence should rather read "HOA concentrations are very low compared to the cold season" since HOA concentration during the warm months is on average more than five times lower than during the cold season. This information has been added to the revised manuscript.*

See P18, L549.

P14 l422: the authors would need to prove the link between SOA and regional biomass burning.

Response: *The link between SOA from the oxidation of primary biomass burning emissions is not new in the literature. It has been demonstrated that OOA of a mixed nature, but which is also made up of aged BBOA, has been observed in a regional background site in Spain, 100 km away from a wildfire (Minguillón et al. 2015) and also in a regional background site in Greece, affected by plumes from wildfires over even longer distances (Bougiatioti et al., 2014). With air masses during the warm period originating mostly from the north, northeastern sector, it is clear that part of the transported OOA is bound to include to some extent (nonetheless non-quantifiable) processed, regional biomass burning from the Balkans and the area of the Black Sea, where hotspots of fires are peaking during July-September (Sciare et al., 2008).*

See P19, L570-575.

P15 l444-448: how does BBOA compare with BBOA profiles from other studies in Greece? Or in other Mediterranean sites?

Response: *BBOA correlates very well with the spectra reported by Florou et al.,2017 both for the BBOA factor obtained at the same site (R^2=0.88) and BBOA in Patras (R^2=0.89). It also correlates well with the BBOA factor obtained at Finokalia (Bougiatioti et al., 2014) exhibiting an R^2 of 0.81 as well as with the BBOA obtained in Bologna by Gilardoni et al., 2016 with an R^2 of 0.85.*

See P20, L607-609.

P16 l477-479: HOA correlates moderately with CO, BC and NO. So is HOA representative of traffic?

Response: *HOA is representative for fossil fuel combustion processes, and it may originate from both traffic and domestic heating oil emissions. Performing a linear regression exercise for the cold period data set, excluding values obtained during night-time (19:00 – 05:00) the HOA factor exhibits stronger correlation with tracers that are related to traffic emissions, than when using the entire dataset. Indicatively, during the day-time period including the traffic rush hour peak, HOA correlates well with BC_{ff} (R^2=0.71).*

See P23, L699-700.

Technical corrections and suggestions
P1 l22: replace “fine” by “submicron”
Response: *Amended.*
P1 l24: rephrase to “with concentrations during wintertime sporadically reaching up to 200 µg/m3”. Please also indicate the time resolution for this (daily/hourly concentrations?)
Response: *Amended.* P1, L25.
P2 l50: replace “namely” by “such as”
Response: *Amended.*
P4 l92: “105 m above sea level”
Response: *Amended.* P4, L109.
P4 l105-109: these information are redundant and/or well known. It could be removed.

Response: *This information has been now removed.*

P6 l165-172: I don’t think a thorough description of PMF and ME-2 is necessary here. Please shorten or remove this section.
Response: *Amended* P8, L215.

P8 l237: rephrase to “The other striking feature is that”

Response: *Amended.*

P8 l241: rephrase to “average 8 of such”

Response: *Amended.*

P8 l242: please add “to our knowledge”

Response: *Amended.* P12, L348.

P8 l243: rephrase to “highlight the strong impact”

Response: *Amended.*

P10 l286: rephrase to “to the regional character”

Response: *Amended.*

P11 l231: one could cite here Canonaco et al.(2015): Canonaco, F., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: Seasonal differences in oxygenated organic aerosol composition: implications for emissions sources and factor analysis, Atmos. Chem. Phys., 15, 6993-7002, https://doi.org/10.5194/acp-15-6993- 2015, 2015. -

Response: *The proposed references are now added in the revised text.* P8, L226.

P12 l343-350: I think this has already been presented elsewhere, so I don’t think it is necessary here.

Response: *Given the fact that a new approach in describing correlations, has been adopted for the revised manuscript, omitting the use of the theta angle, this description has now been removed.*

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Response to Anonymous Referee #3 comments

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

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

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

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

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

Major comments

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

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

See rewritten section 1 (Introduction)

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

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

See P8, L215

3. Page 11, line 323; unconstrained runs, the results from unconstrained runs need to be presented in supplement. It is very difficult for the reader to trust the results (especially BBOA and COA

factors) if unconstrained results are not shown. The technical guidelines for constraining are given in Crippa et al. (2014) and the results for each step needs should be presented.

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

See P8, L224-234.

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

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

See P9, L252-254.

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

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

See P6, L183-185.

Minor comments

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

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

See P2, L33.

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

Response: *The term non-refractory part is now omitted.* See P4, L124.

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

Response: *The instrument's serial number has been removed from the revised manuscript* See P4, L119.

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

Response: *Amended* See P4, L119.

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

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

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

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

See P5, L132.

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

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

See P5, L146.

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

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

See P11, L308-313.

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

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

See P6, L180.

15. Page 5, line 144; remove "Necessary"
Response: *Amended.* See P6, L183.

16. Page 5, line 145; remove "historic"
Response: *Amended.* See P5, L184.

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

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

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

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

See P6, L160-168.

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

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

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

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

See P12, L350-353.

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

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

See P12, L367-369.

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

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

See P13, L381-385.

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

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

See P17, L505-514.

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

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

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

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

See P17, L511-513.

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

Response: *A correlation coefficient for the comparison with the mass spectra obtained by Sage et al. (2008) has been added to the revised version of the manuscript.*

A concrete number for the diesel vehicles in Athens is not available. According to local authorities, the number of new diesel passenger vehicles sold in Greece since the lift of the long-standing ban in the two major cities exceeds 300,000. The larger part of these vehicles are expected to circulate in the area of Athens.

See P17, L514-515.

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

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

See P18, L532.

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

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

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

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

See P18, L551-553.

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

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

See P19, L557-562.

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

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

See P6, L157-159.

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

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

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

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

See P22, L652-654.

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

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

See P22, L663-665.

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

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

See P23, L677-681.

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

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

See P23, L685-688.

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

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

See P23, L700-704.

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

Response: *Organics and BC are indeed mostly from heating. If the increase would mostly be due to the boundary layer, similar concentrations would also be seen during the warm season, as well, as the boundary layer height is not that different between warm and cold season (Alexiou et al., 2018). The significant enhancement of winter-time fine PM levels due to heating emissions has been well-documented for Athens, even prior to the advent of the economic recession (Chaloulakou et al., 2005).*
On the other hand, nitrate is not directly emitted, but the higher concentrations are due to the combined effect of temperature and reduced acidity to the partitioning in the aerosol phase, as it has already been mentioned. These are further clarified in the revised text.

See P24, L728-735.

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

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

See P25, L755.

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

43. Figure 4; in upper figure you use “organic aerosol” but in lower figure “Organics”. Please be consistent with the names.
Response: *Amended.* See P46-47.

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

Response: *The selected pairs in Figure 6 have been rearranged in order to be in accordance with those presented in figure 5.* See P51.

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

Response: *Amended.* See P53.

Technical comments:

46. Page 6, line 163; time series

Response: *Amended.*

Rerefences

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Atmos. Chem. Phys. Discuss.,
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Response to Anonymous Referee #4 comments

The manuscript presents a one-year dataset (2016/2017) of near real time chemical composition of submicron aerosol particles measured in Athens and its subsequent PMF analysis. This dataset is complemented by 2 intensive campaigns carried out in winter (2013/2014 and 2015/2016). While these data are of prime interest, the manuscript is very descriptive and do not bring significant new results for the scientific community. However, I support the publication of this manuscript after major modifications.

Response: *We would like to thank the anonymous referee for the review and have incorporated the suggested comments in the revised version of the manuscript.*

1/ The PMF analysis and the constraints applied are somewhat confusing and the methodology should be described more clearly and in a more systematical way. A lot of different alpha values are selected (arbitrarily?) for the different factors. For a given source profile authors choose different alpha values for the different dataset. This must be explained and justified. Did the authors studied the influence of the alpha values on the sources contributions in a more systematic way? An alpha value of 0.1 is, from my point of view, too low for COA. Same for HOA, an alpha value of 0.05 is, in a first approach, too low considering the variability of the vehicular fleet (diesel/gasoline share, ...).

Response: *Since this has been pointed out in other reviewer reports, the revised manuscript attempts a clearer approach in presenting those results, reporting all the steps of the strategy and the evaluation of the results in a systematic way. A sensitivity analysis of the alpha values used is also presented.*
Affinity of the resulting factors with deconvolved factors from the literature as well as correlation of the respective time series with external tracers is the criterion of selection for the preferable PMF solution. In this manner different alpha values for the split dataset concerning the same factor shouldn't be unreasonable. Specifically, the two HOA factors obtained for the warm months of 2016 and 2017 with different a-values (0.05 and 0.1 respectively) show excellent correlation (R^2=0.99).
On the other hand, an alpha value of 0.1 for COA has been reported earlier (Cannonaco et al., 2015). Actually Crippa et al. (2014) suggest that a lower alpha value (e.g. 0.05) should be used to constrain the COA factor. Furthermore, an alpha value in the range of 0.05 to 0.1 for HOA is suggested in the same study, and has been used in several different studies implementing the a-value approach (Frolich et al., 2015; Bressi et al., 2016).

See P7, Section 2.3.1.

2/ Authors should convince the reader of the validity of the COA factor extracted from their analysis. The COA factor extracted here from the PMF analysis represents a contribution as high as BBOA in winter. It seems well correlated with the BBOA factor and other combustion markers (nssK+ for instance) and do not exhibit the classical midday hump. As the COA MS profile contains a slight contribution of m/z 60, I suspect a mix of both COA and BBOA factor.

Response: *It is evident, in the revised version of the supplementary material, where results from unconstrained PMF runs as well as runs only constraining an HOA factor have been added, that a factor resembling cooking-like organic aerosols, arises in both the warm and cold periods. When replicating the methodology of Mohr et al. (2012) thus calculating* $f_{55,OOAsub}$ *and* $f_{57,OOAsub}$ *and plotting them against each other, it can be observed that points lying closer to the steeper slope – obtained by fitting a line through zero and* $f_{55,OOAsub}$ *vs* $f_{57,OOAsub}$ *of deconvolved COA spectra from the literature – correspond to measurements during the afternoon (~16:00) coinciding with this hump observed in the mean diurnal variation, and to night time measurements coinciding with the maximum observed in the diurnal variability of the factor (Figure below).*

Lunch hours in Greece are known to be stretched towards late afternoon (15:00 – 17:00 LT). This fact has alson been demonstrated by Florou et al. (2017), where the COA factor obtained for the same site was found to be dominated by the evening peak exhibiting slightly elevated concentrations around 15:00. Note also that the same diurnal variability and contribution of the cooking to the total mass, was reported by Florou et al., 2017 for the same site in Athens, and especially during night also in Patras, another Greek city indicating that our findings have not a local character but probably represnts all major Greek cities.

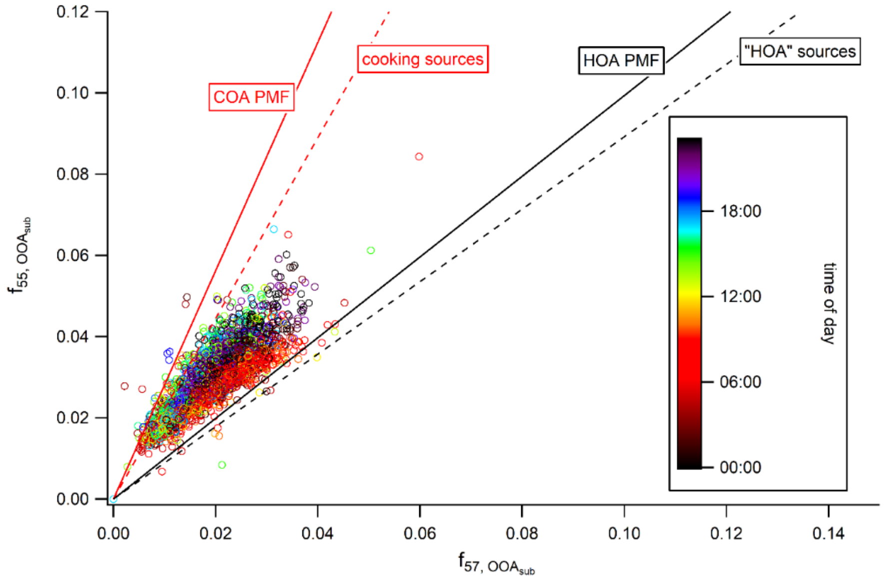

Figure 1. $f_{55,\ OOAsub}$ *plotted against* $f_{57,\ OOAsub}$*. Data points are colored according to time of day. Lines correspond to linear fit results conducted using COA and HOA results both from PMF and laboratory standards studies (Mohr et al., 2012).*

See P10, L279-282.

Also, the reference mass spectra chosen to constrain COA has been obtained in Paris. In Paris, the main site was located in the local Chinatown and was surrounded by well-known fast food brands. One could assume that the cooking emissions in Athens are slightly different than those of Paris for this specific study.

Response: *We agree with the reviewer concerning the reference mass spectra chosen to constrain COA. The same concern was also raised by some of the other reviewers. Nevertheless, when comparing our resulting COA with the respective ones from Florou et al. (2017) (Athens, same site) and Patras (3rd largest city in Greece), the squared Pearson correlation coefficients are 0.96 and 0.93, respectively.*

See P16, L488-491.

3/ The split of the data series between warm and cold period sounds quite arbitrary. Does it actually rely on temperature? If yes, this should be explicitly discussed in the text. While necessary for such long data series, splitting the dataset can induce a discontinuity of the sources contributions. Are such discontinuities observed here?

Response: *The warm period is characterized by absence of precipitation and increased photochemistry which allow especially the influence from regional sources. Splitting of the data series is actually necessary when dealing with long term datasets that incorporate different sources of OA for different times of the year and splitting approaches have been utilized in numerous studies that deal with long term datasets around the world (Bressi et al., 2016; Minguillon et al., 2015; Budisulistiorini et al., 2016). Given the fact that the mass spectra of the factors, present during the warm period, namely HOA, COA, SV-OOA and LV-OOA are very similar for the two parts of the warm season, e.g. July – September 2016 and May – July 2017, we can be confident that no discontinuities are present in our analysis.*

See P8, L244-251.

4/ If the data are available, I strongly suggest that the authors carry out a local winds analysis. From my experience such high nocturnal peaks are often mostly associated to local wind changes and in this case the occurrence of nocturnal breezes. In such cases (heavily polluted urban area), a local wind analysis is, from my point of view, much more relevant than a long-range transport analysis. Also, the influence of local wind patterns can induce strong correlation within the dataset which cannot be related to sources intensities or atmospheric transformation processes.

Response: *According to the suggestion of the reviewer, as well as to that of reviewer #2, a wind analysis has been performed. Although it has been verified that HOA and BBOA are related with local emissions and record high concentrations during calm and low-wind conditions, increased levels of other components, such as LV-OOA, summer-time SV-OOA and sulfate are observed during stronger winds which are linked to regional advections and long range transport. This difference, indicates that common diurnal patterns shouldn't be attributed solely to meteorological conditions. Although the reviewer is correct to indicate the importance of mesoscale circulation for receptor sites, in our case the site is located in an urban area and is additionally affected by local primary sources. Moreover, for the inner Athens basin, nocturnal land-breezes are known to be very week (Kassomenos et al., 1998) to completely determine correlation patterns due to intra-urban transport. These are now discussed in the revised version of the manuscript.*

See P21, L640-647 & P22, L672-676.

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Response to Anonymous Referee #5 comments

This paper aims to identify sources of submicron organic aerosols in Athens with a major interest on quantifying the contribution of biomass burning. Results are based on high temporal resolution chemical measurements performed by an ACSM. As stated by authors, this is the first study on submicron aerosol by using high temporal measurements during a relatively long period (1 yr plus 2 winter periods). However, it is a very descriptive work that does not provide new knowledge on atmospheric processes and sources in the eastern Mediterranean. The study is focused on the organics and mainly in the contribution of wood burning, as stated in the introduction section and as deduced from the extension of measurements during the two winter periods. Impact of wood burning in air quality is a growing concern in Athens in the last years.

Response: *We would like to thank the anonymous referee for taking the time to review our manuscript. Nevertheless, we don't agree that this work does not provide new knowledge on atmospheric processes and sources in the area. For the first time such a long (20 months) high-resolution time series is presented in the literature for Athens one of the biggest cities in the eastern Mediterranean. As the reviewer claimed* “Impact of wood burning in air quality is a growing concern in Athens in the last years” *and indeed this was one of our aims. The final aim was to understand the sources of submicron organic aerosol in an urban location on an annual basis and not “to provide new knowledge on atmospheric processes and sources in the eastern Mediterranean”. This issue which is very important necessitates measurements at multiple background sites and it was out of our scope. Note however that the Introduction was re-written to clearly address all these issues mentioned above and better highlight the importance of our work for southern European urban environments.*

Thus, the authors (5 of 7) co-authored a paper currently on ACPD (https://doi.org/10.5194/acp-2018-163) focused on the impact of residential heating on fine particulate matter by applying PMF to the chemical characterization of filters (24 and 12h resolution). This study was performed in the same place and during part of the period covered by the present study.

Response: *In contrast with the study of Theodosi et al. (2018) which reports filter-based analytical data, our manuscript presents 30-min resolution on-line measurements showing in detail the diurnal variability of components, and specifically focusing on the different fractions of the organic aerosol and addresses among others the diurnal profiles of the organic fractions. Note that in the revised version of Theodosi et al., authors clearly differentiate between these two studies. Finally, less important but worth mentioning is* *that the two first authors are not the same in these two studies and in addition not participating in both works.*

I have read the comments by the other reviewers and I strongly agree with the remarks form RC2, and also 3 and 4. I would like to add some minor comments and insist on some of the comments already mentioned by the other referees. My major concern is the use of constrains based on measurements performed in very different areas (HOA, COA and BBOA form north Europe) for the PMF of organics. Are these profiles usable in the study area? The profiles used should be more similar to the profile emissions in the area. Do the authors have some information about COA and BBOA profiles from the eastern Mediterranean area? Most statements about the origin of the SVOOA and SOA are hard to demonstrate based only in the interpretation of the diurnal variation.

Response: *As also stated by the anonymous referee himself/herself most of the issues raised are common with the ones of Referees #2, #3 and #4. The revised version of the manuscript describes in detail the unconstrained and constrained runs, as well as correlations of the derived spectra of the factors with the respective ones from Greece and neighboring areas (e.g. Bologna, Italy). Furthermore, the origin of SV-OOA is clearly demonstrated for the winter period as mainly being derived from the fast oxidation of primary combustion sources, while during summer our suggestions are backed up by correlations with SOA from the oxidation of biogenic components and, to some point, regional biomass burning aerosol.*

See P8, L224-243.

Minor comments

Experimental methods; Page 5. Was the ACSM calibrated on field?

Response: *The IE for NO3 and RIEs for NH4 and SO4 are now reported in the revised Supplementary material. The ACSM was calibrated just before its deployment to the site and successfully participated in the ACSM intercomparison exercise.*

See P5, L130-136.

No information about filters sampling and analysis is provided. Please, indicate sampling period and frequency and the methods of filters treatment and analysis.

Response: *All the relevant information, sampling period, frequency and filters treatment, related to filter sampling has now been added to the revised version of the manuscript.*

See P6, L160-168.

Please, indicate the size range of SMPS TSI3034.

Response: *This piece of information was reported in section 3.1, P7, L211 of the manuscript and has been moved to Section 2.2 "Instruments and methods" of the revised version. We would like to thank the reviewer for pointing this out.*

Results and discussion

In the supplementary, authors show the correlations between filters and ACSM for the whole period (SL1.1) and for the winter periods (SL1.2). Is there any reason for the different slopes determined for each period? Do you expect the presence of coarse nitrate in the 1-2.5 µm fraction?

Response: *We believe that the slopes for NO_3^-, which are 0.99 for 2016 – 2017 versus 1.02 for the winter of 2015 – 2016, the slopes for regression of NH_4^+ from the ACSM versus the PILS, which are 0.98 for 2016 – 2017 and 0.97 for 2013 – 2014 are not significantly different. For sulfate the small difference (0.87 for 2016 – 2017 versus 0.93 for 2015 – 2016) could be because of the different way used to calculate RIE $SO_4^=$. For the 2016 – 2017 this value is derived by calibrating the instrument with ammonium sulfate, while for 2015 – 2016 RIE was derived using the approach of Budisulistiorini et al. (2014).*

Did the OA/OC ratio keep constant along the sampling period?

Response: *Unfortunately, no $PM_{2.5}$ filter sampling data are available for the months prior to November 2016. Furthermore, IC analysis on filters obtained through the warm period of 2017 is not yet available. In this context, even though the OM to OC ratio varies during the cold season of 2016-17, not enough information is available in order to be able to formulate an in-depth analysis of the issue.*

Did you compare EC vs BC? Is this ratio constant along the study period? Is any difference in winter with respect summer?

Response: *A comparison between EC and BC hasn't been performed in the context of this study. We feel that a detailed description of the absorbing particles' behavior, falls outside the scope of this manuscript. We have to note here, that BC concentrations were used as reported by the aethalometer AE-33 deployed at the Thissio station, thus using default MAC values.*

Line 256. Contribution of nitrate in summer?

Response: *The contribution of nitrate during summer has been added.*

See P12, L363.

Line 260. There is a BC peak in June not related to any other compound (figure 3). What is the cause of this maximum? Any information from the measurements by means of Aethalometer?

Response: *When moving from May to June, an increase is also observed in organics, sulfate, and ammonium. The increase is most likely due to the relatively stagnant conditions that prevailed during June 2017 in the area (mean monthly wind speed 27% lower than the study average).*

Line 265 semi-volatile inorganics; and organics?

Response: *Organics have now been added to the sentence.* See P13, L374.

Lines 290 293: Is nitrate primary emitted? Do you mean that nitrate is quickly formed from primary NOx? Can be the relatively high levels of nitrate be related to the low stability of nitrate with temperature? It is risky to assign a source origin to nitrate only form the diurnal variation.

Response: *This issue was also raised by referee #3. As nitrate follows the same trend with organics and BC, it is clear that the chemical composition during nighttime is very different than the one during day. High levels during night time is certainly related to the semi volatile nature of nitrate and its partitioning between the particle and gas phase, rather than its primary emissions. The low temperatures combined with reduced aerosol acidity, favors the partitioning of nitrate in the aerosol phase.*

See P13, L381-385.

Line 296: What do you mean with “normalizing the diurnals?

Response: *The same approach is used as the one described in Lines 286 – 288. Each hourly value has been divided by the respective species mean concentration.*

See P13, L398-399.

Line 363: Please, replace “2016 and 17” by “2016 and 2017”

Response: *Amended.*

Line 477. Did you check the correlation with the BC factions? Does the HOA factor correlated better with BCff than with BCwb?

Response: *Yes, as can be seen in the supplementary material tables, summarizing the correlations of each selected solution with external time series, the identified HOA factors are consistently better correlated with* BC_{ff} *than with* BC_{wb}*.*

See P22, L649-651.

Figure 8. Why COA factor increased with wind form the eastern sector?

Response: *The COA fraction for the Eastern sector in the cold period appears slightly increased (4.7% compared to the mean), due to largely decreased fractions of BBOA and SV-OOA, as compared to the Northern sectors. In fact, the mean COA concentration in the cluster, is within 0.1 μg m-3 of the mean COA concentration, a difference not statistically significant (p>0.05).*

Line 480-483. During the cold period nitrate correlates with LV-OOA while in summer it correlated with SV-OOA. Could you explain the reasons of it?

Response: *During the warm period nitrate correlates with SV-OOA because of the semi-volatile nature of the precursors of SV-OOA. On the other hand, during the cold period when temperatures are lower, and because of the different chemical composition aerosol is less acidic, the low temperature and higher pH "stabilizes" more the partitioning of nitrate in the aerosol phase (Guo et al., 2017; Nah et al., 2018), therefore nitrate could correlate more with the less volatile component, which is LV-OOA.*

Summary and conclusions

Line 535. Sulfate and ammonium concentrations are not lower in summer

Response: *This fact has now been clarified.* See P24, L728-732.

Line 571. What do you mean with "central heating"? Fuel-oil heating?

Response: *Indeed, the fuel used in most buildings central heating installations is diesel oil. This clarification has been added in the text.*

See P25, L755.

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Sources and processes that control the submicron organic aerosol in an urban Mediterranean environment (Athens) using high temporal resolution chemical composition measurements.

Iasonas Stavroulas[1,2,3], Aikaterini Bougiatioti[1,3], Georgios Grivas[3], Despina Paraskevopoulou[3], Maria Tsagkaraki[1], Pavlos Zarmpas[1], Eleni Liakakou[3], Evangelos Gerasopoulos[3] and Nikolaos Mihalopoulos[1,3]

[1]Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, 71003 Crete, Greece
[2]Energy Environment and Water Research Center, The Cyprus Institute, Nicosia 2121, Cyprus
[3]Institute for Environmental Research and Sustainable Development, National Observatory of Athens, Lofos Koufou, P. Penteli, 15236, Athens, Greece

Correspondence to: A. Bougiatioti (kbougiatioti@gmail.com) and N. Mihalopoulos (nmihalo@noa.gr)

Abstract. Submicron aerosol chemical composition has been studied during a year-long period (26/07/2016-31/07/2017) and two winter-time intensive campaigns (18/12/2013 – 21/02/2014 and 23/12/2015 – 17/02/2016), at a central site in Athens, Greece, using an Aerosol Chemical Speciation Monitor (ACSM). Concurrent measurements include a Particle-Into-Liquid Sampler (PILS-IC), a Scanning Mobility Particle Sizer (SMPS), an AE-33 Aethalometer and Ion Chromatography analysis on 24 or 12 hour filter samples. ~~Quality of the ACSM data was assured by comparison versus the above mentioned measurements.~~ The aim of the study was to characterize the seasonal variability of the main ~~fine~~ submicron aerosol constituents and decipher the sources of organic aerosol (OA). Organics were found to contribute almost half of the submicron mass, with 30-min resolution concentrations during wintertime ~~sporadically~~ reaching up to 200 μg m^{-3}~~, on occasions~~. During ~~this season~~winter (all three campaigns combined), the primary sources contribute about 33% of the organic fraction, comprising of biomass burning (10%), fossil fuel combustion (~~16~~13%) and cooking (~~8~~10%), while the remaining ~~66~~67% is attributed to secondary aerosol. The semi-volatile component of the oxidized organic aerosol (SV-OOA; ~~31~~21.8%) was found to be clearly linked to combustion sources and in particular biomass

burning, and even a part of the very oxidized, low-volatility component (LV-OOA; ~~35~~44%) could also be attributed to the oxidation of emissions from these primary combustion sources. These results, based on the combined contribution of BBOA and SV-OOA, highlight the rising importance of biomass burning in urban environments during wintertime, as revealed through this characteristic example of Athens, Greece, where the economic recessions led to an abrupt shift to biomass burning for heating purposes in winter. During summer, when concentrations of fine aerosols are considerably lower, more than 80% of the organic fraction is attributed to secondary aerosol (SV-OOA ~~30~~31% and LV-OOA 53%). In contrast to winter, SV-OOA appears to result from a well-mixed type of aerosol, linked to fast photochemical processes and the oxidation of primary traffic and biogenic emissions. Finally, LV-OOA presents a more regional character in summer, owing to the oxidation, within a few days, of organic aerosol.

1. Introduction (This sections has been rewritten)

Exposure to fine particulate matter is recognized as a leading cause of premature mortality in Europe. Even if the annual limit value is not exceeded at the majority of regulatory monitoring stations in European countries, health effects are expected to appear at lower levels as well, even below the WHO guideline values (EEA, 2017).

Organic carbon (OC) is among the key PM components which record the strongest associations with short-term mortality (Ito et al., 2011; Klemm et al., 2011). Moreover, short-term exposure to OC has also been linked to respiratory and cardiovascular hospital admissions (Levy et al., 2012; Zanobetti et al., 2009) and pediatric asthma ED visits (Strickland et al., 2010).

It appears that the characterization of fine aerosol chemical properties and their short term variability is critical, especially at the urban background level which is more relevant for the average population exposure. While the majority of transformations related to particle sulfate and nitrate have been well described, there is much progress to be made regarding the mechanisms and characteristics of secondary organic products.

The development of the Aerosol Mass Spectrometer (AMS) technology has been an important breakthrough in the study of aerosol chemical composition, in high temporal resolution. The ability to further differentiate between primary and secondary components, based on specific markers, introduces an important advancement to organic aerosol (OA) source apportionment (Jimenez et al., 2009), which otherwise mainly relied on a statistical approach using elemental and organic carbon thermal-optical data (EC tracer method and variants; Turpin and Huntzicker, 1995). Capitalizing on abundant spectroscopic data, PMF (Positive Matrix Factorization) source apportionment (SA) is used to discern between various primary sources like traffic and biomass burning, and to categorize secondary aerosols depending on their degree of oxidation.

The ACSM (Aerosol Chemical Speciation Monitor) is an instrument relying on AMS technology and is specifically designed for long-term routine monitoring (Ng et al., 2011). While many studies have focused at regional and rural background areas, ACSM results from large European urban centers are relatively scarce. Canonaco et al. (2013) have performed one year of measurements at an urban background site in the center of Zurich. Aurela et al. (2015) have deployed an ACSM at residential, traffic and highway sites within the Metropolitan Area of Helsinki, for a total of five months. Findings from 10 months of measurements at the North Kensington urban background site in London are reported by Reyes-Villegas et al. (2016).

Regarding Southern European cities, results have been presented from the intensive ~~one-month~~ ACSM campaign of Minguillon et al. (2016), at an urban background site in Barcelona. Short-term – up to one month - studies in Southern Europe using the AMS have also been conducted in Barcelona (Mohr et al., 2012), Bologna (Gilardoni et al., 2016) and Marseille (El Haddad et al., 2013). In urban Athens, a~~n intensive~~ ~~one~~ one-month ~~-~~AMS campaign during winter 2013 has been carried out for chemical composition and OA sources (Florou et al., 2017).

The Greater Athens Area (GAA) appears as a challenging urban milieu for the study of aerosol dynamics, as it combines a large population (about 4 million) and intense primary emissions, with complex topography and meteorology, that lead to high levels of atmospheric pollutants and significantly deteriorate air quality (Kanakidou et al., 2011; Pateraki et al., 2014). The characteristics and related processes of secondary organic aerosols, in the long-term, have received up to this point limited attention (Grivas et al., 2012; Paraskevopoulou et al., 2014).

Moreover, since 2013, due to the economic recession in Greece, primary and secondary precursor emissions emerge altered and intensified, as the residents have switched from fossil fuel combustion to uncontrolled burning of wood and biomass for space heating (Saffari et al., 2013, Fourtziou et al., 2017, Gratsea et al., 2017). Existing measurements of aerosol chemical composition in Athens have mainly been performed using filter sampling (Theodosi et al., 2011, 2018; Paraskevopoulou et al., 2014) and have indicated the dominant role of organic aerosols in the fine particle fraction.

In this study we present, for the first time, long-term results on the sources of submicron organic aerosols in Athens from high temporal resolution measurements during a year-long period, complemented by two intensive winter campaigns. For the collection of data, we deployed an Aerosol Chemical Speciation Monitor (ACSM) and in addition a Particle Into Liquid Sampler (PILS) coupled with ion chromatography, an AE-33 Aethalometer, while also conducting auxiliary aerosol (filter-based) and gas phase measurements.

The main objectives of this are (i) to characterize the submicron aerosol and its variability using high temporal resolution, (ii) to quantify the sources of the organic aerosol and their seasonal variability (via PMF analysis) and (iii) to study the year-to-year changes of aerosol sources during winter time, with special emphasis on wood burning.

2. Experimental Methods

2.1 Sampling site and period

The measurements exploited in this study were conducted, at the urban background site of the National Observatory of Athens at Thissio (37.97N, 23.72E), as representative of the mean population exposure over Athens metropolitan area (Fourtziou et al., 2017). The site stands at an elevation of 105 m above sea level, in a moderately populated area, where the influence of direct local emissions is limited.

The measurement period lasted for an entire year, from July 2016 to July 2017. Additionally, two intensive winter campaigns took place at the same site, the first from mid-December 2013 to mid-February 2014 and the second from 23 December 2015 to 17 February 2016. These intensive campaigns aimed at studying the year-to-year variability and impact of biomass burning on the air quality of the city of Athens during wintertime.

2.2 Instruments and Methods

Measurements were performed with an Aerosol Chemical Speciation Monitor (ACSM~~, s/n 140 139~~) by Aerodyne Research Inc. (Ng et al. 2011a), measuring the non-refractory PM_1 ($NR-PM_1$) ~~aerosol mass and~~ chemical composition in near real-time (30-minute temporal resolution). The instrument was sampling through a BGI Inc. SCC 1.197 Sharp Cut Cyclone operated at 3 L min^{-1}, yielding a cut off diameter of approximately 2 μm. ~~The ACSM measures mass and provides real time chemical composition (organics, sulfate, nitrate, ammonium and chloride) for non-~~

~~refractory aerosol particles. The design of the instrument limits these measurements in the submicron range; more specifically the particles that reach the final stage of the instrument lie in the size range from 40 to 700 nm.~~ Practically the ACSM operates following a similar principle as the Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000) where ambient air is drawn through a critical orifice to a particle focusing aerodynamic lens; the resulting particle beam is flash-vaporized at 600ºC, ionized via electron impact ionization and guided through a quadrupole mass spectrometer. Ammonium nitrate and ammonium sulfate calibrations were performed prior to the ACSM's deployment on the site for the period of 2016 – 2017 and the response factor (RF) for nitrate along to the Relative Ionization Efficiencies (RIEs) for ammonium and sulfate were determined. For the 2013 – 2014 and 2015 – 2016 intensive winter campaigns ammonium nitrate calibration were performed and the RIE for sulfate was determined according to the fitting approach proposed by Budisulistiorini et al. (2014). Values are presented in Table ST1 of the supplementary material. ~~The instrument has participated in an intercomparison study of 15 Q-ACSM instruments organized by the European Center for Aerosol Calibration (ECAC) at the Aerosol Chemical Monitor Calibration Center (ACMCC) at Site Instrumental de Recherche par Télédétection Atmosphérique (SIRTA, Paris) during March 2016 (). It showed excellent agreement (well below ±20%) with the ACMCC's reference instrument, in both pre- and post-calibration periods of the intercomparison study, while the relative ionization efficiencies (RIE) for ammonium and sulfate, obtained by the on-site calibration, were very close to the ones previously used, indicating a stable performance of the instrument.~~ The detection limits for the ACSM provided by Ng et al. (2011a) are: 0.284 μg m^{-3} for ammonium, 0.148 μg m^{-3} for organics, 0.024 μg m^{-3} for sulfate, 0.012 μg m^{-3} for nitrate, and 0.011 μg m^{-3} for chloride. Mass concentrations are calculated ~~with the recommended~~ using a chemical composition dependent collection efficiency (Middlebrook et al., 2012) (Fig. SF.1)~~of 0.5 for all constituents~~.

Parallel measurements were performed for biomass burning identification, but also for quality control purposes. In this context, a Metrohm ADI 2081 Particle Into Liquid Sampler (Orsini et al., 2003) coupled with Ion Chromatography (Dionex ICS-1500) was used, which was sampling ambient air from a different, but adjacent to the ACSM's, PM_1 inlet. Two denuders were placed inline, upstream of the instrument in order to remove gas phase species (e.g. NH_3, HNO_3, SO_2) The ion Chromatograph was set to measure cations such as ammonium and potassium at a time resolution of 15 minutes. The resulting concentrations from the ACSM were tested against filter measurements and the concentrations provided by the PILS. For the PILS, the detection limit was calculated at 1 ppb for Na^+, NH_4^+~~, Mg^{+2} and Ca^{+2}~~ and 2 ppb for K^+. nss-K^+ concentrations ~~could be~~ were calculated using the Na^+ concentrations and the Na^+/K^+ ratio in seawater as a reference (Sciare et al., 2005). Reported concentrations were blank corrected.

Furthermore, filter sampling was also conducted in parallel at the Thissio station. $PM_{2.5}$ aerosol samples on Quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47mm, PALL) were collected on a daily basis while during the winter periods the sampling frequency was set to 12h. A Dichotomous Partisol Sampler 2025 (Ruprecht & Patashnick) was used at a flow rate of 16.7 L min^{-1}. The samples were analyzed for organic and elemental carbon (OC, EC) with the Thermal-Optical Transmission technique, using a Sunset Laboratories OC/EC Analyzer and applying the EUSAAR-2 protocol (Cavalli et al., 2010). Filters where also analyzed for determination of the main ionic species~~SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}~~ using ion chromatography as described in Paraskevopoulou et al. (2014).

Two different absorption photometers were monitoring Black Carbon (BC) concentrations. A 7-wavelength Magee Scientific AE-42 portable aethalometer was used for the 2013-14 and 2015-16 winter campaigns, providing 5-min resolution measurements. For the year-long period a dual spot, 7-wavelength Magee Scientific AE-33 aethalometer (Drinovec et al., 2015) was used, operating at 1-min resolution. Standard gas analyzers ~~monitoring, like~~for O_3 (Thermo Electron Co., model: 49i), CO, SO_2 and NO_x ~~concentrations~~ (HORIBA, 360 series)~~, a PM_{10} beta-attenuation monitor for aerosol mass concentration (Eberline, FH 62 I-R)~~ and a Scanning Mobility Particle Sizer for PM_1 size distributions (SMPS 3034, TSI Inc.) measuring in the range of 10.4 – 469.8 nm, were also operating at the sampling site~~, as part of its routine measurements~~. Wavelength dependent source apportionment of the BC load was performed by the AE-33 Aethalometer, based on the approach of Sandradewi et al. (2008) providing a fossil fuel (BC_{ff}) and a wood combustion (BC_{wb}) ~~generated factor~~component. ~~An~~ The default absorption exponents of 1 for fossil fuel combustion and ~~1.9~~2 for pure wood burning, as incorporated in the AE-33 software, ~~based on the approach of Sandradewi et al. (2008)~~ was used, very close to the respective values of 0.9 and 2, used in a suburban site in Athens (Kalogridis et al., 2017). ~~Necessary m~~Meteorological parameters for the study were taken from the ~~historic~~ actinometric meteorological station of NOA, at Thissio (Kazadzis et al., 2018) (Fig. SF.2). All measurements were averaged to 1-hour intervals in order to synchronize the different data sets.

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The bivariate wind speed-direction plotting methodology developed by Carslaw and Ropkins (2012) in the Openair R-package, was used for the identification of source areas, as incorporated in the Zefir Igor Pro-based tool (Petit et al., 2017). Four-day back trajectories were calculated using the HYbrid Single-Particle Langrangian Integrated Trajectory (HYSPLIT_4) model (Draxler and Hess, 1998) developed by the ARL/NOAA, and 1-degree GDAS (NCEP) meteorological data. Trajectories were computed every 3-h, for air masses arriving at Athens at a height of 1000 m. The selected height is considered suitable to capture transport at a representative upper limit of the boundary layer in Athens (Markou and Kassomenos, 2010). Trajectory clustering was performed using the TrajStat plugin (Sirois and Bottenheim, 1995; Wang et al., 2009) of the MeteoInfo GIS software~~ (http://www.meteothinker.com/products/meteoinfo.html)~~. The change of the total space variance for decreasing number of clusters was examined as a criterion for cluster number selection. The analysis was performed separately for summer and winter, resulting in 5 clusters for each period.

2.3 Source apportionment of the submicron organic fraction using ~~Positive Matrix Factorization~~PMF analysis.

2.3.1 PMF strategy.

Positive Matrix Factorization (Paatero and Tapper, 1994) was performed on the organic mass spectra obtained by the ACSM. The graphic interface SoFi (Source Finder) version 6.1, developed at PSI, Zurich (Canonaco et al., 2013) was used. SoFi implements the multilinear engine algorithm ME-2 (Paatero and Hopke, 2003), analyzing the acquired mass spectral timeseries matrix into a linear combination of ~~source~~ factor profile (FP) and time series sub-matrices. Detailed description of the method can be found in the above referenced studies.

For our datasets ~~O~~only m/z ≤ 125~~0~~ were used in order to avoid interferences from the naphthalene signal (m/z 127, 128 and 129). Weak signals, with signal-to-noise ratio (S/N) below 0.2 were downweighted by a factor of 10, and those with S/N between 0.2 and 1 were downweighted by a factor of 2 (Ulbrich et al., 2009), using ~~the aforementioned customized software~~built in utilities of the SoFi toolkit.

~~Briefly, the organic mass spectra measured by the ACSM are represented as a matrix X, with columns representing the different m/z's and rows the time series of the mass spectrum. Then the measured matrix X is approximated by the product of F and G, added to E (X=GF+E) where each~~

~~column of matrix G represents the time series of a factor and each row of F represents the profile (mass spectrum) of this factor and E is the model residual. The entries in F and G are then fitted using a least squares algorithm that iteratively minimizes the quantity Q^m, which is the sum of the squared residuals weighted by their uncertainties. Finally, at each step of the solution process, outliers are defined based on the ratio of residuals to uncertainties (Canonaco et al., 2013).~~

The input organics and organics' error matrices are derived automatically from the ACSM data analysis software~~, using a simple automated procedure~~. Several ~~PMF~~ model runs were ~~realized~~performed, with and without applying constrains to the derived FPs, using the *α* value approach (Canonaco et al., 2013; 2015) and following the methodology proposed by Crippa et al. (2014). ~~In brief, i~~Initially unconstrained PMF runs provided insight on the potential number and type of factors. For the following steps, reference factor profiles (RFPs) were introduced in order to constrain primary OA factors, (i) first for the Hydrocarbon – like organic aerosol (HOA), (ii) then for both HOA and BBOA and (iii) finally for HOA, BBOA plus cooking – like organic aerosol (COA). Potential FPs for secondary organic aerosols were left unconstrained. A thorough discussion on the choice and representativeness of the RFPs used can be found in section SI.4.1 of the supplementary material.~~-~~ Each factor was constrained using different *α* values within the limits suggested by Crippa et al. (2014). ~~were deconvolved by introducing constrains to known factor profiles, implementing the *α* value approach, while potential secondary oxygenated components were left unconstrained. The *α* value ranges between 0 and 1 and is a measure of how much the resolved factors are allowed to vary from the input ones.~~ Next, the model's residuals, for each different model setup, were analyzed in search of structures that could indicate underestimation or overestimation of the number of separated factors. Stability of factors for different model seeds and correlations of the obtained FP spectra with FPs reported in similar environments and conditions were examined (Section SI.4.8). Finally, correlations of the time series of the selected optimal solutions to both gas phase and particulate independent measurements such as BC, BC_{ff}, BC_{wb}, CO, nss-K^+, NO_3^-, $SO_4^{=2=}$ and NH_4^+ was examined to solidify the selection (Section SI.4.9).

The year-long data series was divided into a cold period, from ~~(~~November 2016 to March 2017~~)~~ and warm period consisting of two sub-periods from ~~(~~August to September 2016 and from May to July 2017 which were treated separately.~~) period as sources of organics and thus mass spectra and intensities are expected to differ considerably.~~ According to studies on the climatology of Southern Greece, the transient period (spring and fall seasons) in Athens doesn't exceed 60 days on average

(Argyriou et al., 2004), covering mainly the months of April and October - which were excluded from the seasonal analysis (Figure SF.1). The two wintertime campaigns of 2013-2014 and 2015-2016 were also treated separately.

The coefficient of determination r^2 for simple linear regression is used as a metric for all comparisons, e.g. both affinity of obtained FPs with literature spectra and correlation of the respective time series with independent measurements.

~~A detailed description on the source apportionment method applied can be found in the following section.~~

2.3.2 Choosing the optimal configuration

Presentation of, and discussion on the optimal configuration chosen for the ME-2 model, as well as results from each step of the implemented strategy described above, followed by a sensitivity analysis on the α value influence on the obtained factors, can be found in section SI.4. In brief, for the cold period and the two winter – time intensive campaigns, constraining three factors, namely HOA, BBOA and COA, and leaving two unconstrained SOA factors, produces a solution that is characterized by minimal seed variability and model residual structures, while FPs, time-series, relative contribution and diurnal variability of the factors appear to be environmentally relevant, resembling solutions proposed earlier for the region (Kostenidou et al., 2015; Florou et al., 2017). Leaving factors unconstrained leads to an unstable model behavior such as diurnal residual structures for key variables (e.g. alkyl fragments like m/z=55 or 57) and large FP variability for different model seed runs. Furthermore, deconvolved spectra were missing expected variable contributions in profiles such as BBOA (very low m/z=41 and 43 relative contributions), while the COA – like factor was dominated by the CO_2^+ fragment at m/z=44. Configuring less or more than five factor solutions, resulted either in an even more pronounced residual diurnal cycle, pointing to poor factor separation or in splitting behavior and resulting factors which were environmentally irrelevant.

On the other hand, for the warm period constraining two factors, namely HOA and COA, and leaving two unconstrained SOA factors was found to be the solution exhibiting higher relevance while being robust and close to previou-s knowledge related to OA in the Greater Athens Area. A BBOA factor could not be identified for the warm periods, since contribution of the marker fragments for biomass burning m/z=60 and m/z=73 are almost absent in these periods dataset. The

COA factor is present in all the studied periods, validated following the approach of Mohr et al. (2012) (Fig. SF.9), and emerged in all the steps (unconstrained and constrained runs) of the implemented strategy (Figures SI.4 through SI.7 and related discussion in section SI.4).

3. Results and Discussion

3.1 Comparison of ACSM data with ancillary measurements

As a first quality control/quality assurance of the ACSM data, the ammonium concentrations are compared to the respective ones derived from the PILS, on an hourly basis for winter 2016-17. A good agreement is found (r^2=0.~~83~~80, slope of 0.~~98~~82). The sulfate and nitrate concentrations for the winter 2016-2017 period are compared to the respective ones from the ion chromatography analysis (PM$_{2.5}$ filters), on a daily basis (r^2=0.75, slope of 0.81 and r^2=0.78, slope of 0.95, respectively). The organics concentrations are compared to the organic carbon concentrations of the PM$_{2.5}$ filters~~ determined by the thermal-optical method (SUNSET Laboratory Inc.) using the EUSAAR-2 protocol (Cavalli et al., 2010)~~. An ~~very good~~excellent agreement is found (r^2=0.93, slope of 1.59) with the slope being close to values reported for urban areas (Petit et al., 2015) and OM:OC calculations from AMS measurements in polluted environments (Saarikoski et al., 2012). The results from the aforementioned comparisons are provided in the Supplementary material (SF.3).

During the intensive winter 2015-2016 campaign, the concentrations of the ACSM components are compared to those determined from the ion chromatography, based on concurrent filter samples collected at the same site, twice per day, (06:00 - 18:00 pm and t 18:00 - 06:00 local time). Results indicate an excellent agreement for sulfate (r^2=0.88, slope of ~~0.92~~1.0), ammonium (r^2=0.~~81~~82, slope of 1.~~04~~06), and nitrate (r^2=0.~~87~~88, slope of 1.~~08~~12) (Figure SF.4). During the intensive winter 2013-2014 campaign, the ammonium concentrations from the ACSM showed significant correlation with the respective ones from the PILS (r^2=0.~~81~~80, slope of ~~0.97~~0.81).

Finally, the sum of the ACSM component concentrations plus BC, measured with the 7-wavelength aethalometer was compared with the mass concentrations determined by ~~a~~ the ~~Scanning Mobility Particle Sizer (SMPS; TSI 3034)~~SMPS ~~measuring particle number concentrations in the range of 10.4-469.8 nm (~~since February 2017 at Thissio~~)~~. The density used to convert volume distributions and consequently volume concentrations of spherical particles to mass concentrations, was obtained by applying the methodology of Bougiatioti et al. (2014)

assuming that the aerosol PM$_1$ population was dominated by ammonium sulfate and organics and calculating the respective mass fractions time series based on the ACSM measurements. A density of 1.77 g cm^{-3} was used for ammonium sulfate and 1.3 g cm^{-3} for organics (Florou et al., 2017). The results obtained using a ~~constant collection efficiency of 0.5~~chemical dependent collection efficiency to determine the ACSM derived mass concentrations, are portrayed in Figure 1 and indicate ~~strong~~ excellent correlation (~~squared Pearson correlation coefficient~~ r^2=0.89~~8~~) a slope of 0.96 and an ~~insignificant~~ intercept of 0.60~~01~~. ~~The slight underestimation of the SMPS-derived submicron mass can be attributed to the instrument's upper limit diameter (469.8 nm versus 700 nm for the ACSM). It should also be noted that this discrepancy could be attributed to the uncertainty in the estimation of aerosol density used for the conversion of volume to mass concentration of the SMPS (Bougiatioti et al., 2014).~~

3.2 PM$_1$ average chemical composition and ~~seasonality~~temporal variability

3.2.1 Chemical composition and characteristics

The time series of the main submicron aerosol components measured by the ACSM and the black carbon concentrations are presented in the upper panel of Figure 2 (one complete year period). The periods average cumulative concentration of the ACSM components and BC was ~~15.1~~12.4±~~16.7~~12.5 μg m^{-3}. The highest concentrations were measured during winter (average ~~20.9~~16.1±~~26.4~~19.5 μg m^{-3}) and the lowest during summer (average ~~9.1~~10.3~~.~~±~~6.2~~5.6 μg m^{-3}). On an annual basis, the most abundant component was organic aerosol, followed by sulfate, contributing ~~46.1~~44.5 and ~~29.1~~27.8% to the total submicron mass, respectively, while BC contribution was calculated at ~~12~~15.1%, ammonium ~~8.5~~7.9% and nitrate 4.3%. In the middle and bottom panels of Figure 2 the respective time series of the main submicron aerosol components during the two intensive 2-month winter campaigns are presented. During winter 2013-14 the average mass concentration of the ACSM components (plus BC concentrations) was ~~25.1~~24.5±~~29.9~~24.7 μg m^{-3}, with organics and ~~sulfate~~ BC contributing ~~53.5~~55.6 and ~~15.9~~14.6% to the total submicron mass, respectively, followed by ~~BC~~ sulfate (~~12.9~~13.6%). During winter 2015-16 the average concentration was ~~19.5~~21.2±~~25.3~~27.4 μg m^{-3}, with organics and BC contributing 51.~~2~~ 6 and ~~17.9~~15.2% to the total submicron mass, respectively, followed by sulfate (~~17.6~~14.8%), nitrate (6.~~7~~5%) and ammonium (6.~~6~~7%). It is clearly deduced that during the last winters, organics constitute half or even more of the total PM$_1$ mass, sulfate around 20% and BC around 14%.

~~What is also striking is~~is tThe other striking feature is that ~~the fact that~~ during wintertime, PM_1 concentration spikes can reach up to 22~~4~~0 μg m^{-3} hourly values, with organics taking up most of the mass. Maxima are recorded during night-time and mostly during meteorological conditions favoring pollutants emission and accumulation, such as low wind speed and low temperature (Fourtziou et al., 2017). There are on average 8 such incidents occurring during each winter (10 in 2013-14, 7 in 2015-16 and 7~~8~~ in 2016-17), with organic levels being higher than 100 μg m^{-3}. To our knowledge, ~~Such~~ such levels are the highest reported for Europe during wintertime and highlight the strong impact of local emissions and especially those related to heating/wood burning (see below), ~~to~~ on the levels of organics and consequently PM_1. ~~These~~Similar maxima ~~observations~~ to the ones observed in this study are ~~in accordance with~~ also reported by Florou et al. (2017, same site from 10 January until 9 February 2013), where~~as~~ organics concentration alone reached up to 125 μg m^{-3} and maxima of 8 μg m^{-3} for BC and up to 5 μg m^{-3} for nitrate, were recorded. Similarly, wintertime pollution events with increased local character and elevated organics concentrations (around 100 μg m^{-3}, average of 22.6 μg m^{-3}) have been reported at a regional background site, just outside of Paris, during February 2012 (Petit et al., 2015).

3.2.2 Seasonal variability

The seasonal variability of the main measured species, along with the average PM_1 concentration (μg m^{-3}), as calculated from the ACSM+BC measurements is shown in Figure 3 and the basic statistics are included in Table 1. Organics contribute ~~43.9~~46% to the total submicron aerosol mass in summer, followed by sulfate (~~33.1~~30.5%), BC (12.6%), ammonium (~~12.5~~8.3%) and nitrate (2.6%) ~~and BC (7.6%)~~, while in winter, organics and sulfate contribute ~~49~~48.1 and 2~~4.1~~3.2%, respectively, followed by BC (1~~2.1~~4.7%), ammonium (6.9%) and nitrate (6.~~7~~3%).

The mass concentrations of organics, nitrate, chloride and BC exhibit a clear annual cycle, with minimum during summer and maximum in winter. This pattern seems to be due to a combination of three simultaneous processes. At first, the additional primary emissions from domestic heating play an important role, as is evident by the largely elevated concentration levels of organics and BC, which during winter are also emitted by central heating systems and fireplaces. A second reason could be the decreased boundary layer depth during winter. According to Kassomenos et al., 1995 and Alexiou et al., 2018, daytime PBL depth shows a clear annual cycle, with maxima during the warm months (June to September) and exhibiting a two-fold decrease during wintertime. Finally, the effect of temperature to the partitioning of the semi-volatile inorganics and organics can also contribute to the processes leading to the observed pattern. In support of the above, larger standard deviation is found in winter, demonstrating the frequency and magnitude of the observed pollution events due to the increased need for heating purposes (Fourtziou et al., 2017). Independently of the year, it can be seen that winter concentrations of organics, nitrate, chloride and BC are very similar and more than twice the respective ones during the rest of the seasons (Table 1).

Organics concentration are consistently high during all studied winters (from December to February), while the higher nitrate values, exhibiting similar trend with organics and BC can be ~~also attributed to the increased local sources combined with the overall lower temperatures, which favor the stability of ammonium nitrate~~attributed to the combination of lower temperatures during night-time along with the increased combustion sources which lead to reduced acidity, resulting at the favorable partitioning of nitrate in the aerosol phase. (Park et al., 2005; Mariani and de Mello, 2007; Guo et al., 2016). Ammonium and sulfate exhibit the opposite seasonal cycle, with maximum values in summer and minimum during winter and spring. The higher summer sulfate levels are the result of enhanced photochemistry associated with more intense insolation, combined with less precipitation, favoring the regional transport of polluted air masses (Cusack et al., 2012). The seasonal variation of concentrations is in agreement with that observed in Athens, during prior long-term measurement campaigns based on analysis of daily filter samples (Theodosi et al. 2011, Paraskevopoulou et al., 2014; 2015).

3.2.3 Diurnal variability

When investigating the diurnal patterns of the measured species (Figure 4), it is observed that during wintertime, ammonium and sulfate do not exhibit any significant variability, which is due to the ~~more~~ regional character of ammonium sulfate~~ (Seinfeld and Pandis, 2016)~~. In order to quantify the extent of this variability we calculated the normalized diurnal pattern by dividing each hourly value with the respective mean concentration. More specifically, sulfate varies by ~~12.5~~13% around the mean value while ammonium varies by ~~33~~40%. On the other hand, organics, BC and nitrate vary significantly during the day (~~83.4~~183%, 79.8% and ~~74.3~~110% respectively). These species clearly double their concentrations during night-time, caused by the additional primary emissions. Furthermore, BC ~~and nitrate~~ also exhibits a second maximum during early morning hours, which should be attributed to the primary emissions during the morning traffic rush–hour.

During summer, all concentrations are significantly lower, especially organics (note scale change) which exhibit a 5-fold decrease of their mean maximum concentration during night-time. Normalizing the diurnal~~s~~ cycles, as mentioned above, reveals a much less pronounced variability for organics (~~46.9~~65%), implying a more regional character, while BC and nitrate exhibit the highest variability (67.7% and ~~57.6~~77% respectively) in accordance to their local nature. The night-time maxima of BC vanishes, while nitrate shows much lower concentrations, due to nitrate partitioning between gas and aerosol phase, favoring the vaporization of ammonium nitrate. BC still exhibits only one maximum during early morning hours owing to traffic emissions. Ammonium and sulfate diurnal profile follows expected photochemistry patterns, with peaking concentrations around 14:00 LT (UTC+2), consistent with secondary aerosol formation and increased vertical mixing with regional aerosol from aloft due to the evolution of the convective boundary layer which exhibits a bell shaped diurnal structure ranging from a few hundred meters to above one kilometer, with maximum heights during early afternoon (Asimakopoulos et al., 2004; Tombrou et al., 2007). ~~Sulfate concentrations exhibit lower night-time background, a concurrent (to winter) primary maximum (8:00-10:00 LT), and a secondary significant increase later in the afternoon (twice the night-time background).~~ Finally, organics concentrations are somewhat higher during early night which could possibly be associated with biogenic/vegetation sources either local or regional that produce volatile compounds and condense on the particulate phase during night when temperatures are lower, as is further elaborated during the source apportionment results discussion in section 3.3. Furthermore, organic variation also follows ~~the morning peak related to traffic and~~ the late afternoon peak also observed for ammonium and sulfate. Condensation of the particulate phase could ~~also~~ apply for nitrate as well, which also exhibits higher concentrations during night-time (almost double).

3.3 Source apportionment of organic aerosol

~~A source apportionment analysis of the organic aerosol data was carried out, separately for the cold (1 November to 31 March) and the warm period (July-August-September 2016 and May-July 2017). The separation served to better characterize the different profiles of the sources, as it is~~

~~expected that the different m/z intensities vary throughout the year. Several runs were performed, following the technical guidelines and methodology proposed by Crippa et al. (2014). Initially, an unconstrained run with the number of factors ranging from 2 to 8 was performed, allowing for a first estimate of the number of potential deconvolved primary and secondary OA spectra. After identifying the presence of primary OA, namely hydrocarbon-like organic aerosol (HOA), cooking organic aerosol (COA) for both periods and BBOA for the winter period, several constrained runs were performed using the~~ ~~*α* value approach.~~

~~In this context, the HOA mass spectrum was first constrained with a low~~ ~~*α* value, ranging from 0.05 to 0.1, using as reference the average HOA mass spectrum from Ng et al. (2011b). COA was also constrained with an~~ ~~*α* value ranging from 0.1 to 0.2, using as reference the mass spectrum from Crippa et al. (2013) reported for Paris. Finally, for the three wintertime periods, BBOA was also constrained with higher~~ ~~*α* values, (between 0.3 and 0.5) using as reference the average BBOA mass spectrum from Ng et al. (2011b). Only m/z ≤ 120 were used in order to avoid interferences from the naphthalene signal (m/z 127, 128 and 129). Weak signals, with signal-to-noise ratio (S/N) below 0.2 were downweighted by a factor of 10, and those with S/N between 0.2 and 1 were downweighted by a factor of 2 (Ulbrich et al., 2009), using the aforementioned customized software~~. ~~Solutions were chosen based on specific indicators, such as the Q/Q~~$_{exp}$ ~~ratio, residual analysis, reproducibility of factors for different model seeds, the affinity of the deconvolved spectra with spectra found in the AMS mass spectral database (http://cires.colorado.edu/jimenez-group/AMSsd/) and also the correlation of the time series with external time series (such as BC, NO, CO and nss~~ K^+~~). The profiles of all solutions were inter-compared as means for sensitivity analysis and the results are provided in the Supplementary material (SI.2). The affinity between spectra is expressed using the~~ ~~*θ* angle approach (Kostenidou et al., 2009). In this context each deconvolved mass spectrum represents a vector. The cosine of the~~ ~~*θ* angle between two such vectors (e.g.~~ MS_a ~~and~~ MS_b~~) is equal to the correlation coefficient~~ ~~*R* between them. The~~ ~~*θ* angle is calculated using the dot product formula:~~

Field Code Changed

$$\theta = cos^{-1}\left(\frac{MS_a MS_b}{|MS_a||MS_b|}\right)$$

~~Calculated angles less than 15° correspond to~~ ~~*R > 0.96* thus indicate spectra which are similar to each other, angles between 15° and 30° correspond to~~ ~~*0.96 > R > 0.86* and indicate some similarity but also some important differences between the compared spectra, while angles larger~~

~~than 30° correspond to correlation coefficient $R < 0.86$ and thus are considered to indicate spectra that do not compare well.~~

Warm period: In this period, the selected solution is a two factor constrained run (HOA using α =0.05 and COA using α =0.1) and consists of four factors: HOA~~ (hydrocarbon-like OA)~~, COA-like~~ (cooking-like OA,)~~, SV-OOA (semi-volatile oxygenated OA) and LV-OOA (low-volatility oxygenated OA). As already mentioned, ~~The ~~the two summer periods have ~~also ~~been treated separately, but the derived spectra were almost identical (~~θ angles between 1.6 and 11.9 for all derived factors, see Si~~r^2 ranging from 0.98-0.99). The time series of the four identified sources during summer 2017 is shown in Figure 5 along with their diurnal variability and the respective average daily contribution. The mass spectra of the selected solution are also provided in the supplementary material (Fig SF.12). No primary biomass burning aerosol could be identified, which is justified by the absence of fresh emissions over the city center during the warm period. In the summer periods HOA makes up ~~5.5~~4.3% of the total organic fraction, COA around ~~12~~10% on average (~~10.9~~7.3 and ~~13~~11.3% for 2016 and 2017, respectively). In summer 2016 SV-OOA made up ~~30.5~~32% and the rest ~~53~~56% is LV-OOA. In summer 2017, SV-OOA contributes ~~46~~34.6% to the total organic fraction while LV-OOA ~~35~~49.7%. The dominance of secondary influence (SV-OOA & LV-OOA) is apparent, and accounts for the majority of the organic aerosol. This finding is in accordance with Kostenidou et al. (2015), who reported that 65% of the sampled aerosol during summer can attributed to SOA (SV-OOA & LV-OOA), at a suburban site in Athens.

~~Since a strong constraint was used for COA (α =0.1), the derived COA mass spectrum is almost identical to the mass spectrum of wintertime COA in Paris (Crippa et al., 2013) with which the constraint was made, having a θ angle of 7°. COA also shares many similarities with the mass spectrum of fresh organic aerosol emissions from meat charbroiling (Kaltsonoudis et al., 2017) (θ=14.5°). ~~A comparison of the derived FPs with mass spectra in literature is shown in Fig SF.15-19 in the supplement. COA FP exhibits excellent correlation with spectra obtained in previous studies in the city (Florou et al., 2017; Kostenidou et al., 2015) as well as with spectra obtained in laboratory experiments investigating fresh OA emissions from meat charbroiling (Kaltsonoudis et al., 2017). When calculating the O:C ratio in COA following the study of Canagaratna et al. (2015) we find a ratio of 0.19, which is comparable to the value of 0.24 obtained for COA during summer at a suburban site in Athens (Kostenidou et al., 2015).

The HOA FP exhibits excellent correlation with literature spectra measured in cities located in the ~~Mediteranneean~~Mediterranean environment ~~setting~~ (Florou et al., 2017; Kostenidou et al., 2015; Gilardoni et al., 2016) as well as in other environmental and socioeconomical settings ~~ää~~(Crippa et al., 2013; Lanz et al., 2009). ~~Similarly, due to the constraint (α =0.05) HOA is identical (θ=2.5°) with the average HOA spectrum (Ng. et al., 2011b), obtained by averaging together different HOA mass spectra, but is also very similar to HOA reported by Crippa et al. (2014) (θ=4.5°) and HOA from Paris (θ=6.5°) (Crippa et al., 2013). SV-OOA is similar to the SV-OOA reported by Crippa et al. (2014) (θ=14°), and also has many similarities with the average SV-OOA (θ=16.5°) (Ng et al., 2011b) as well as with the laboratory-generated SOA from isoprene via the reactive uptake of epoxydiols (IEPOX) (θ=16.2°) (Budisulistiorini et al., 2013). This type of aerosol~~ According to Figure SF.18, where the affinity of SV-OOA with literature spectra is assessed, some assumptions could be made regarding the origin of the factor in this study. Similarity with IEPOX – OA, which is the oxidation product of isoprene, ~~denoting~~ could denote a possible link of SV-OOA with biogenic aerosol. This association is further strengthened by considering ~~its similarities~~the excellent correlation with SOA from biogenic precursors, such as a- and b-pinene ~~(θ=20° and 18°, respectively)~~ reported by ~~(~~Bahreini et al., (2005) (*r^2 of* 0.86 and 0.89, respectively). These precursors are found to exhibit maxima during ~~which are maximum during~~ night-time (Harrison et al., 2001~~;~~; Li et al., 2018; Hatch et al., 2011) ~~similarly~~ coinciding with the diurnal behavior of ~~to~~ SV-OOA in this study. On the other hand, comparison of the derived SV-OOA ~~shares some similarities~~ with SOA from diesel exhaust after 4 h of photochemical ageing (Sage et al. 2008) yields an *r^2 of* 0.89. Finally, SV-OOA ~~does not compare well~~exhibits the lowest correlations with the mass spectrum from aged organic aerosol emissions from meat charbroiling (Kaltsonoudis et al., 2017) ~~(32°<θ<37°)~~. The above mentioned comparisons with literature FPs~~This~~ provides some ~~indicates~~ indication that during summer, SV-OOA could be ~~it is not~~ linked to SOA formation from the oxidation of VOCs from both biogenic and traffic sources and is not linked to the oxidation of primary COA.~~, but rather to SOA formation from the oxidation of VOCs from both biogenic and traffic sources. Finally, LV-OOA is identical (θ=3.6°) with the very oxidized regional OOA found in the area (Finokalia, Crete) (Bougiatioti et al., 2014) and has many similarities with the LV-OOA reported by Crippa et al. (2014) (θ=11.7°) and with the average LV-OOA (θ=18.2°) (Ng et al., 2011b).~~ The low volatility component derived, exhibits excellent correlation to the very oxidized regional OOA found in the area (Bougiatioti et al., 2014) and good

Commented [IS3]: Ref #2, P13 l388-390 correlation with deconvolved OOA factors from previous studies in Athens (Florou et al., 2017; Kostenidou et al., 2015). When calculating the elemental ratios based on the study of Canagaratna et al. (2015), the O:C ratio for LV-OOA is 1.2, which is identical to the value of OOA obtained at Finokalia (Bougiatioti et al. 2014).

In terms of comparison with independent measurements, HOA ~~correlates significantly~~exhibits good correlation with nitrate (r^2=0.62) as well as with BC$_{ff}$ (r^2=0.63) while COA, as expected, shows ~~moderate~~ poor correlation with CO (r^2=0.33) and nitrate (r^2=0.36). SV-OOA is highly correlated with nitrate (r^2=0.86), implying common mechanisms in their variability, possibly linked with the partitioning between the gas and particulate phases. The ~~moderate~~ poor correlation with CO (r^2=0.4) and BC (r^2=0.35) implies that SV-OOA may, to some extent, partially originate from a combustion source. LV-OOA shows ~~moderate~~ good correlation with sulfate (r^2=0.62) and ammonium (r^2=0.63), consistent with the regional character of this factor. Results from the trajectory cluster analysis (Figure 8) show that enhanced LV-OOA levels are related to air masses originating from Eastern Europe and the Black Sea region, which have both been identified as the main areas of influence for secondary aerosols that are regionally processed and transported to Athens (Gerasopoulos et al., 2011; Grivas et al., 2018). The regional character of LV-OOA is confirmed by high concentrations associated with increased wind speeds (Figure SF.20), especially those that originate from the Northern sector. These results (presented in the Figure for the full dataset) are contrasted with HOA which displays a much less diffuse spread, due to the intensity of local emissions (mainly traffic in the center of Athens). The distant signal for LV-OOA to the SE direction could possibly be associated to processed aerosol deriving from shipping activity (Petit et al., 2014) in the Aegean Sea.

Primary fossil fuel emissions (HOA) are very low during summer exhibiting a fivefold decrease compared to the cold season, as in July and August most of the Athenians leave for their summer vacations, thus reducing local traffic. Concentrations peak around 7:00 and after 19:00 LT that corresponds to the early morning and evening rush hours in downtown Athens. COA exhibits a slight hump during lunch hours (13:00~~2~~-15:00 LT) where concentrations rise to 65% of the daily COA average after the morning minimum of around 50%, also seen in the relative contribution of the factor, while a large night-time peak is present at around 22:00 LT. This late peak, three times higher than the daily average value, is consistent with the late dinner hours and operation of ~~tavernas (typical~~grill houses and restaurants~~)~~ in central Athens ~~during the touristic~~

~~season~~. SV-OOA exhibits ~~two fold~~40% higher concentrations during night-time compared to the SV-OOA daily average, which apart from boundary layer dynamics may also be attributed to the condensation of semi-volatile compounds, as also implied by the excellent correlation of ~~SV-OOA~~the factor with nitrate~~s~~. During daytime, following the sharp decrease from the night time maxima, concentrations remain for some hours (10:00 to 14:00) close to 80% of the daily average before declining further in the afternoon. Finally, LV-OOA exhibits a peak during mid-day, consistent with increased photochemical processes during the peak of solar radiation intensity (Figure SF.1) that lead to further organic aerosol oxidation. ~~In coincidence to that a moderate hump is also observed for SV-OOA.~~

In summary, during the warm period, the vast majority (more than 80%) of organic aerosol in the area is linked to secondary organic aerosol formation. The semi-volatile product is of mixed origin, linked to quick atmospheric processes, within a few hours, such as photochemistry of primary sources, like biogenic emissions from vegetation, traffic emissions, or probably to a lesser extent regional biomass burning. This last assumption could be ~~backed by~~supported by the fact that OOA linked to aged BBOA has been reported in regional background sites in Greece (Bougiatioti et al., 2014) and elsewhere (Minguillon et al., 2015), as well as by the fact that during the warm season, air masses which mostly originate from the north, northeastern sector, carry pollutants from the Balkans and around the Black Sea, areas heavily impacted by wildfires from July to September (Sciare et al., 2008) (Fig. SF.21). On the contrary, the low-volatility product is the result of more extensive oxidation of organic aerosol in the area, within a few days, and has, thus, exhibits a more regional character.

Cold period: In this period, the selected solution is a three factor constrained run (HOA using α =0.1, COA using α =0.2, BBOA using α =0.4) and consists of five factors: BBOA (biomass burning OA), HOA, COA, SV-OOA and LV-OOA.~~ The HOA spectra are identical for all studied winter periods (1.2º<θ<5.2º) and so are the COA (3.3º<θ<3.9º) and LV-OOA spectra (3.2º<θ<3.6º). BBOA spectra still have many similarities between them (9.7º<θ<13.3º) while SV-OOA also exhibit similarities (12.9º<θ<17.1º). Indicatively, t~~The solution for winter 2016-17 is presented (Fig. 6), while the respective solutions for winter 2013-14 and 2015-16 are provided in the supplementary material (Fig. SF.13). The time series of the five PMF factors for winter 2016-

17 are shown in Figure 6 along with their diurnal variability and the hourly contribution of each factor.

~~HOA during wintertime 2016-17, is almost identical to the average HOA spectrum (Ng. et al., 2011b), as expected due to the constraint, having a θ angle of 5.1º, HOA from Crippa et al. 2014 (θ=5º) and HOA from Paris during winter (Crippa et al., 2013) (θ=5.8º) and from Hyytiälä (Äijälä et al., 2017) (θ=9.6º). COA is also almost identical to COA from Paris during winter (Crippa et al., 2013) having a θ angle of 6.2º. It is also very similar to fresh organic aerosol emissions from meat charbroiling (Kaltsonoudis et al., 2017) (θ=13.2º) and it shares similarities with COA from Hyytiälä (Äijälä et al., 2017) (θ=16.9º).~~ In terms of affinity with RFPs found in the literature, HOA for the cold season in this study is found to exhibit excellent correlations with spectra obtained during the same season in earlier studies in Athens as well as other Greek cities (e.g. Patras) (Florou et al., 2017) and also with HOA factors obtained in different environments, a fact also observed for the warm season obtained spectrum (Fig. SF.15). COA is excellently correlated with COA from Florou et al. (2017) in both Athens and Patras as well as with COA measured by Kaltsonoudis et al. (2017) (Fig. SF.16). When calculating the elemental ratios based on the study of Canagaratna et al. (2015) the O:C ratio for COA is 0.18, which is in accordance with the value of 0.11 derived for COA at the same site by Florou et al. (2017). ~~BBOA is very similar to the average BBOA spectrum (Ng. et al., 2011b) having a θ angle of 11.5º, sharing similarities with biomass burning aerosol from oak (θ=15.7º), spruce (θ=19.8º) (Schneider et al. 2006), BBOA from Crippa et al. (2014) (θ=20º) and with BBOA during wintertime in Zurich (Lanz et al., 2008) (θ=23.4º).~~ BBOA exhibits high correlation with factors form Zurich, Paris and Finokalia as summarized in Figure SF.17, while excellent correlation is found when compared to BBOA found in Bologna, earlier studies in Athens and in Patras. Once more, the calculated O:C ratio for BBOA is 0.25, which is in accordance with the value of 0.27 derived for BBOA at the same site by Florou et al. (2017). The SV-OOA spectrum ~~shares similarities~~exhibits high correlation with the average SV-OOA from Ng et al. (2011b) ~~(θ=21.3º)~~, as well as with the IEPOX-OA from Budisulistiorini et al. (2013) ~~(θ=22.8º)~~ (r^2=0.80 in both cases), as isoprene main oxidation products such as methyl vinyl ketone and methacrolein are often used as biomass burning tracers (Santos et al., 2017). Similar correlation is also found with IEPOX-OA and SV-OOA during the winter 2015-16 campaign ~~(Supplementary material, SI.2)~~. The factor ~~It shares some similarities~~exhibits high correlation with SV-OOA from wintertime in Paris (Crippa et al., 2013) ~~(θ=25.2º)~~ and SV-OOA from Hyytiälä (Äijälä et al., 2017) (Fig. SF.18)~~(θ=26.2°)~~. Finally, LV-OOA ~~is almost~~records an excellent correlation ~~identical (θ=8.3°)~~ with the LV-OOA from Crippa et al. (2014), the average LV-OOA from Ng et al. (2011b)~~ (θ=8.4°)~~, LV-OOA from Zurich during winter (Lanz et al., 2008~~; θ=9.3°~~) ~~while it also shares many similarities (θ=15.1°)~~as well as with the oxidized OOA found in the extended area (Finokalia~~-Crete~~) (Bougiatioti et al., 2014) (Fig. SF.19).

Since the identification of BBOA is mainly based on the two fragments of m/z 60 and 73, considered as the "fingerprint" fragments of levoglucosan and biomass burning tracers, BBOA exhibits indeed excellent correlation with these two fragments (r^2=0.94 and 0.9, respectively). Nss-K^+ is also proposed as a very good tracer for biomass burning and as is reported by Fourtziou et al. (2017), it shows a significant correlation with BC coming from wood burning (BC_{wb}), during wintertime in Athens. Consequently, the time series of nss-K^+ provided by PILS-IC and m/z 60 are studied together. It appears that during both winters (2013-14 and 2016-17) for which nss-K^+ data is available, m/z 60 is in very good agreement with nss-K^+ (r^2=0.85) (Figure 7a). Furthermore, BBOA ~~correlates well~~is highly correlated with BC_{wb} (r^2=0.~~78~~77), exhibits good correlation with nss-K^+ (r^2=0.~~62~~55) and with CO (r^2=0.51~~2~~). SV-OOA correlates ~~significantly~~ excellently with both wood burning "fingerprint" fragments of m/z 60 and 73 (r^2=0.99 for both), highly with BC_{wb} (r^2=0.~~82~~90~~),~~) and CO (r^2=0.~~6~~73~~1~~) (Figure 7b) ~~and~~ while exhibiting good correlation with nss-K^+ (r^2=0.~~61~~55), demonstrating the direct link between SV-OOA and primary combustion sources (mainly biomass burning) (Table ST.2). It can be seen in Figure ~~8~~SF.21, that increased concentrations of both BBOA and SV-OOA are linked to air masses originating from Northern and Eastern Europe. During wintertime, these flow categories are associated with the prevalence of synoptic-scale northern winds and a decline in temperature in the area, leading to the appearance of PM episodes due to local combustion for residential heating (Paschalidou et al., 2015). The input of local sources confined in the Athens basin and in the vicinity of the sampling site is indicated by results of the wind analysis presented in Figure SF.20. Markedly enhanced levels are associated with weak or stagnant conditions. Results are contrasted with those of Grivas et al. (2018) who at a moderately populated area in the eastern part of the basin found that local biomass burning emissions played a less important role than advections from the northern part of the area. In the present case, in the densely populated center of Athens this effect is less apparent. The locality of wood burning aerosols in dense residential areas in Athens has also been indicated by Argyropoulos et al. (2017).

Comparison of the HOA time series with BC and CO yields a good correlation (r^2=0.65 and r^2=0.65 respectively). The factor correlates consistently better with BC_{ff} than with BC_{wb} (e.g. for the 2016 – 2017 r^2 is 0.60 versus 0.52 respectively).~~HOA correlates very well with BC (R^2=0.53), CO (R^2=0.54) and with NO (R^2=0.55).~~ Correlation of COA with nss-K^+ and chloride (0.3<r^2<0.4) could indicate a minor influence from emissions derived from biomass burning in meat-cooking (Akagi et al. 2011; Kaltsonoudis et al., 2017). ~~correlates moderately poorly with nss-K^+ (R^2=0.32) and chloride (R^2=0.27) while low correlation with BC and CO (both R^2=0.22)~~. ~~has also been previously reported at the same site (Florou et al., 2017).~~ Finally, LV-OOA showed a good correlation with ammonium (r^2=0.~~62~~58), nitrate (r^2=0.61~~3~~), nss- K^+ (r^2=0.~~52~~4) and m/z 73 (r^2=0.51), demonstrating that part of the very oxidized OA during wintertime may also originate from combustion sources as well.

Therefore, during the cold period, the organic aerosol in the area linked to secondary organic aerosol formation contributes around 65% to the total organic fraction. In contrast to summer, the semi-volatile product seems ~~has a very clear origin,~~to be linked to the fast oxidation of primary combustion sources (e.g. BBOA~~ and HOA~~), which is also reflected on its diurnal variability ~~as will be discussed shortly~~ (Fig. 6) and also on the strong correlations with external tracers of primary combustion (see Table ST.2). Its affinity to biomass burning tracers points out that the largest part of it originates from the fast oxidation of BBOA. The low-volatility product is in this case likely of more local than long-range transport nature, as also highlighted by the almost two-fold higher values during night-time.

The diurnal cycles of the five factors are shown in Figure 6~~ (bottom left panel)~~. HOA, originating from fossil fuel combustion, exhibits maximum values during night, associated with combustion from central heating, and presents a secondary peak ~~during~~ at 09:00 coinciding with the early morning traffic rush hour. The association of the factor to local primary emissions is also corroborated by the wind analysis plots (Figure SF.20). The dependence of~~n~~ HOA on wind speed and direction is similar between cold and warm seasons. The concentration vs. wind speed distribution, displays a wind dilution effect and is characteristic for traffic-related fine particles in Athens (Chaloulakou et al., 2003; Kassomenos et al., 2012).

COA has similar winter and summer diurnal profiles ~~t~~ with a moderate hump, with concentrations rising form 30% to 60% of the daily average during lunch hours (12-15:00 LT) and a large night-time peak (approx. 22:00 LT), partly controlled by the decrease of the planetary boundary layer, but also owing to the expected increase in the activity of numerous restaurants in the area. A similar diurnal cycle for COA has been reported by Florou et al. (2017). BBOA is characterized by a pronounced diurnal cycle with peaking values during night-time, associated with the production of this component in the evening by combustion for heating purposes. SV-OOA exhibits the largest diurnal amplitude, with night-time values being almost 6-fold higher compared to daytime. A ~~moderate peak~~plateau, with concentrations of SVOOA being around 50% of the daily average value, following the sharp decline after midnight, is observed~~-~~ during the morning traffic rush hour,~~ (partly masked by the high night values)~~ before another decline occurs until the daily minimum is reached at 14:00, demonstrating~~es~~ ~~its ~~the possibility of the factor's provenance from the oxidation of freshly-emitted primary combustion organic aerosol~~ (both BBOA and HOA)~~. Finally, LV-OOA also exhibits 2-fold higher values during night compared to daytime. It has a, similar to the SV-OOA factor behavior, with a secondary peak at 10:00, followed by a 1 – hour lag the morning traffic rush hour, showing once more that part of the low volatility OA may also originate from the fast oxidation of primary combustion source, as also implied by its correlation with combustion tracers.

Table 2 sums up the contribution of each one of the 5 identified factors during the three studied winters. Overall, during wintertime BBOA constitutes around 10% of the total organic fraction. Based on the diurnal variability of this factor, its contribution is more pronounced during night-time, when concentrations are 4-fold or higher than the daytime ones, matching emissions from fossil fuel combustion ~~(~~represented by the HOA factor~~;~~ incorporating both traffic and heating oil combustion~~plus heating~~). ~~Taking into account~~Even though an exact mechanism has yet to be established, our assumption that the larger part of the semi-volatile OOA (SV-OOA) comes from the rapid oxidation of freshly emitted BBOA through processes which involve nitrate radicals and/or heterogeneous reactions, appears justified via the excellent correlations with biomass burning tracers as well when considering similar assessments found in other studies (Lathem et al., 2013; Cubison et al., 20011; Bougiatioti et al., 2014~~,~~). In this manner the overall contribution of biomass burning becomes even more significant. Given that SV-OOA contributes around 30% to the organic mass, it is evident that during wintertime, biomass burning may contribute almost half of the total organic aerosol, with this contribution maximizing during night-time. More specifically, for BBOA the lowest contribution during daytime is ~~2.6~~5.5% reaching a maximum of ~~19.4~~27.5% during night (Figure 6~~, bottom right panel~~). The same applies to SV-OOA with daytime minimum contribution of 13.~~5~~8% and night-time maximum of ~~35.7~~34.9%. What is also very important is the fact that even though the winter and summer mass spectra of SV-OOA have some similarities (~~R^2~~r^2=0.~~85~~83~~, θ=21.4°~~), there are also differences, especially in the origin of this component, as during winter the majority is linked to the oxidation of primary combustion sources, while during summer the absence of a significant correlation with BC or nss-K^+ implies the presence of different sources, both anthropogenic (but not biomass burning) and possibly biogenic.

4. Summary and conclusions

High temporal-resolution measurements were conducted for an entire year (plus two, two-month duration, intensive measurement campaigns during wintertime) at an urban background site in Athens, using an ACSM, a PILS-IC system and an aethalometer, in excess to routine pollution measurements. During the ~~16~~ 16 – month measurement period, several pollution events with PM_1 concentrations reaching as high as ~~240~~ 220 μg m^{-3} were recorded, all encountered during wintertime nights. In these cases, organics contributed the largest fraction to the submicron particulate mass, with overall contribution during wintertime reaching 50%, followed by sulfate (~20%) and BC (~14%). Within a typical winter day, organics, BC and nitrate double their concentrations during night-time~~, as a result of the additional primary combustion emissions for heating purposes~~. The increase of the first two can be attributed to emissions linked with domestic heating while nitrate exhibits higher concentrations due to the combined effect of decreased temperature and aerosol acidity, favoring partitioning in the aerosol phase. During summer, ~~all concentrations are significantly lower~~organics, BC and nitrate concentrations are significantly lower while sulfate and ammonium levels are increased. ~~, and o~~Organics are once more the main aerosol constituent contributing by ~~44~~46%, followed by sulfate (~~33~~30.5%), ammonium (~~13~~8.3%) and BC (8%). Within a typical summer day, ammonium and sulfate concentrations peak at about 14:00 LT (UTC+2), consistent with secondary aerosol formation.

Organics, nitrate, chloride and BC exhibited a clear seasonal cycle with maximum during winter and minimum during summer. Sulfate and ammonium exhibited the opposite cycle, as a result of enhanced photochemistry, limited precipitation and higher regional transport.

Based on the source apportionment of the organic aerosol, four factors were identified during summer, namely hydrocarbon-like OA (HOA), cooking-like OA (COA), semi-volatile oxygenated OA (SV-OOA) and low-volatility OA (LV-OOA), and five factors during winter, the same as in summer with the addition of primary biomass burning emissions (BBOA). During summer, HOA makes up ~~5.7~~4.3% of the total organic fraction, COA around ~~12~~10%, and the rest is linked to secondary organics (SV-OOA and LV-OOA). HOA has peaking values during the morning traffic rush hour, and COA mainly during night-time. SV-OOA exhibits two-fold higher concentrations during night-time while LV-OOA exhibits a peak during mid-day, consistent with photochemical processes. The semi-volatile product is clearly of mixed origin, linked to quick atmospheric processing within a few hours, of VOCs emitted from primary sources like vegetation, traffic and to some limited extent to processed regional biomass burning. The low-volatility product, on the other hand, is the result of more excessive oxidation, in the order of several days, having thus a more regional character.

Combining the results from the three different winter campaigns, HOA accounts for almost ~~16~~13% of the organic fraction, COA around ~~8~~10%, BBOA 10%, SV-OOA ~~31~~22% and LV-OOA ~~35~~45%. All constituents exhibit significantly higher concentrations during night-time, with HOA being also linked to primary emissions ~~affected~~ by heating oil combustion from central heating units and presenting a secondary peak during the morning traffic rush hour. COA has a similar diurnal profile to the one observed during summer. BBOA is also characterized by a pronounced diurnal cycle with peaking values during night from combustion for heating~~ purposes~~. SV-OOA has almost 6-fold higher concentrations during night, consistent with its link to the oxidation of primary combustion sources, while even LV-OOA exhibits almost 2-fold higher concentrations during night. In contrast to summer, the semi-volatile product during winter has a very clear origin, linked to the fast oxidation of primary combustion sources (HOA and BBOA) with BBOA being the major source, due to the affinity of SV-OOA with biomass burning tracers. Part of the LV-OOA, as well, could originate from the extensive oxidation of the local primary combustion sources, showing that LV-OOA during winter is of more local than regional character.

Concluding, it is clear that organic aerosol constitutes a large fraction of submicron aerosol throughout the year, in the urban environment of Athens. During wintertime, a large part of this OA, as high as 50%, originates from combustion sources for heating purposes, such as biomass burning and diesel oil fueled central heating ~~and biomass burning~~, causing significant air quality deterioration. Night-time contribution of BBOA is 7-fold higher than the one during day, while the respective contribution of SV-OOA is increased by a factor of 2.6. Given that during wintertime, fine PM concentrations reach up to ~~240~~ 220 μg m^{-3}, the significance of these sources

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contribution becomes even more striking, demonstrating the necessity for strategic, long-term mitigation actions.

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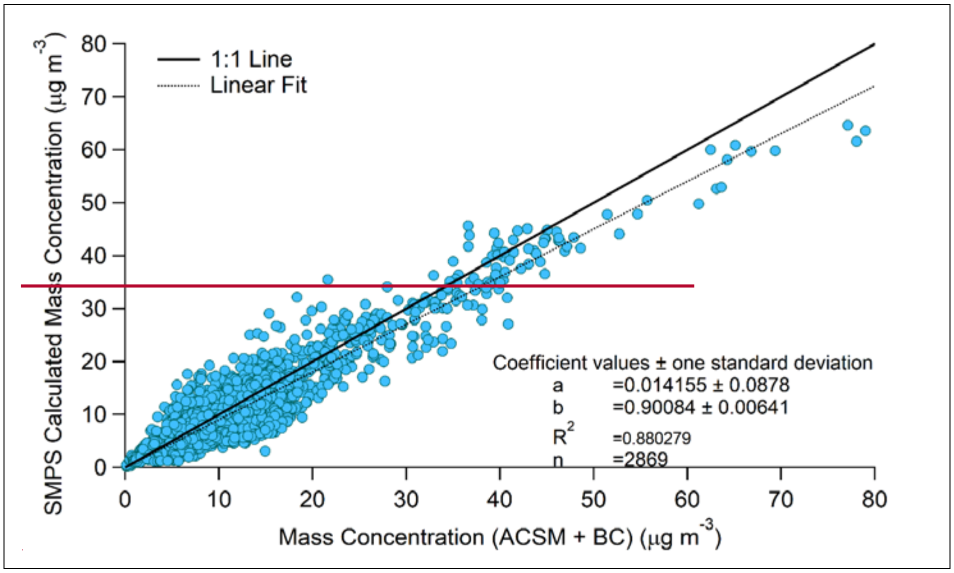
1:1 Line
Linear Fit
SMPS Calculated Mass Concentration (µg m^{-3})
Mass Concentration (ACSM + BC) (µg m^{-3})
Coefficient values ± one standard deviation
a =0.014155 ± 0.0878
b =0.90084 ± 0.00641
R^2 =0.880279
n =2869
0
10
20
30
40
50
60
70
80

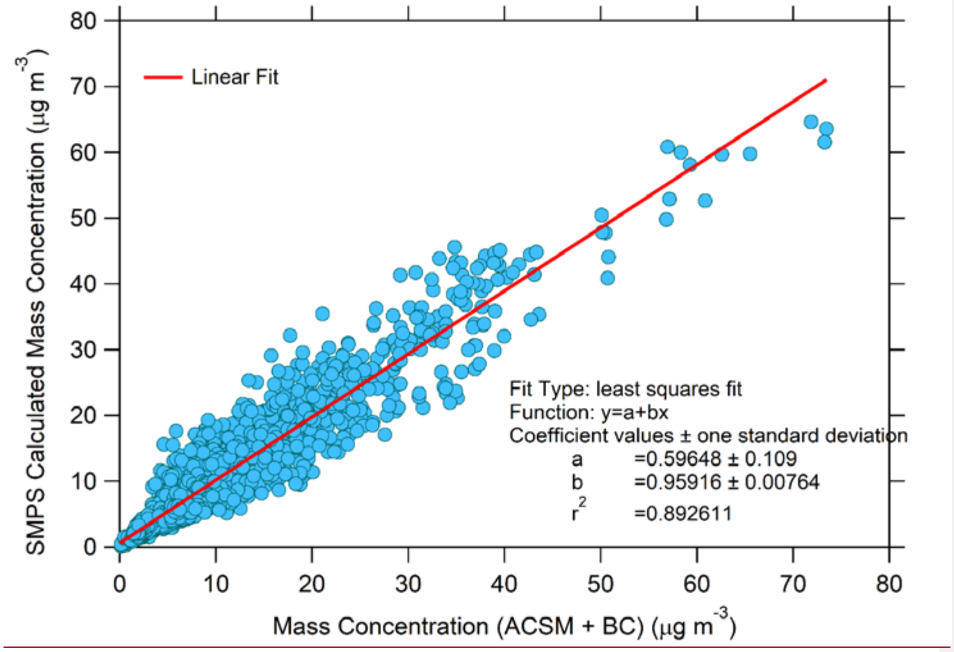
Linear Fit
SMPS Calculated Mass Concentration (µg m^{-3})
Mass Concentration (ACSM + BC) (µg m^{-3})
Fit Type: least squares fit
Function: y=a+bx
Coefficient values ± one standard deviation
a =0.59648 ± 0.109
b =0.95916 ± 0.00764
r^2 =0.892611
0
10
20
30
40
50
60
70
80

Figure 1: Correlation between ACSM+BC vs. SMPS-derived 1 – hour averaged mass concentrations for the 2016-17 measurement period.

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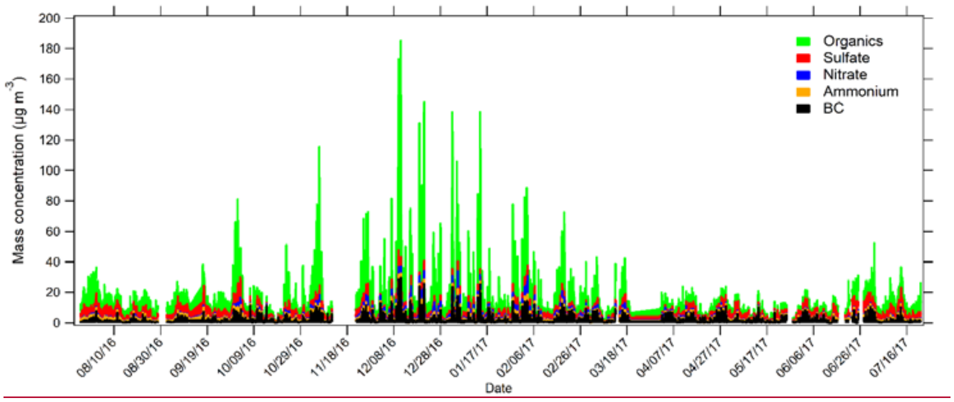
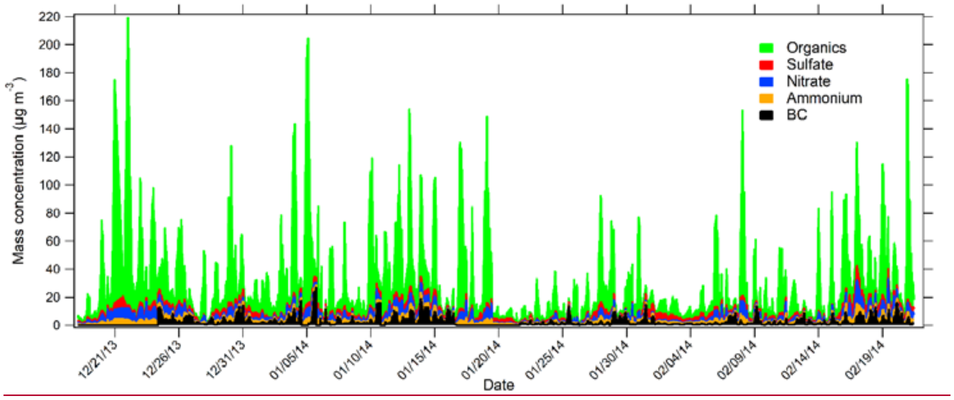
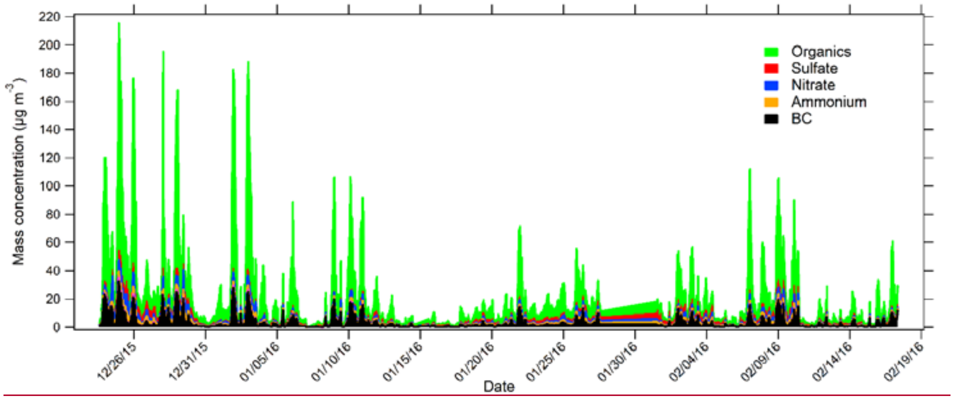
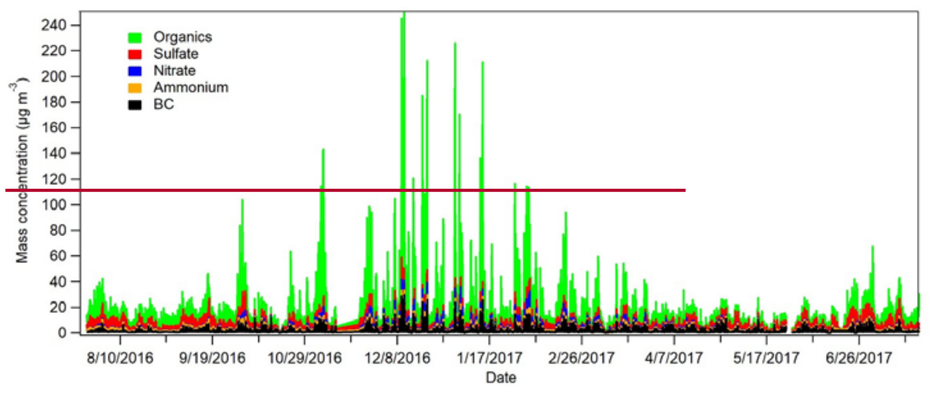
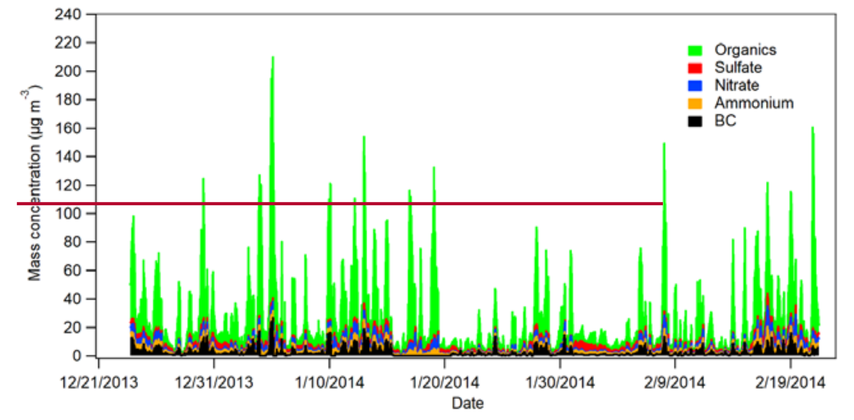

Mass concentration (μg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
08/10/16
08/30/16
09/19/16
10/09/16
10/29/16
11/18/16
12/08/16
12/28/16
01/17/17
02/06/17
02/26/17
03/18/17
04/07/17
04/27/17
05/17/17
06/06/17
06/26/17
07/16/17
Date
Organics
Sulfate
Nitrate
Ammonium
BC


Mass concentration (μg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
220
12/21/13
12/26/13
12/31/13
01/05/14
01/10/14
01/15/14
01/20/14
01/25/14
01/30/14
02/04/14
02/09/14
02/14/14
02/19/14
Date
Organics
Sulfate
Nitrate
Ammonium
BC


Mass concentration (μg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
220
12/26/15
12/31/15
01/05/16
01/10/16
01/15/16
01/20/16
01/25/16
01/30/16
02/04/16
02/09/16
02/14/16
02/19/16
Date
Organics
Sulfate
Nitrate
Ammonium
BC


Organics
Sulfate
Nitrate
Ammonium
BC
Mass concentration (µg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
220
240
8/10/2016
9/19/2016
10/29/2016
12/8/2016
1/17/2017
2/26/2017
4/7/2017
5/17/2017
6/26/2017
Date


Organics
Sulfate
Nitrate
Ammonium
BC
Mass concentration (µg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
220
240
12/21/2013
12/31/2013
1/10/2014
1/20/2014
1/30/2014
2/9/2014
2/19/2014
Date

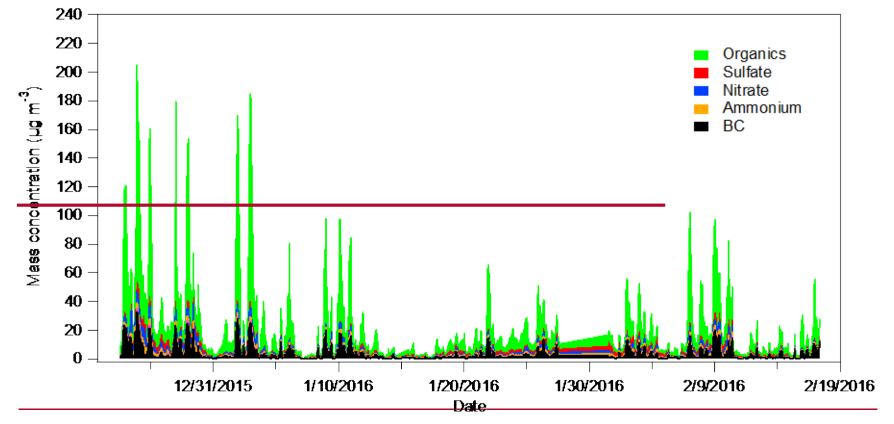
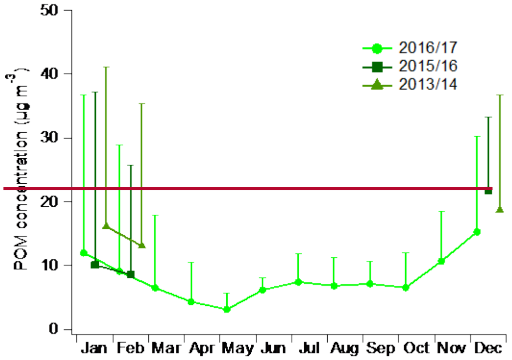
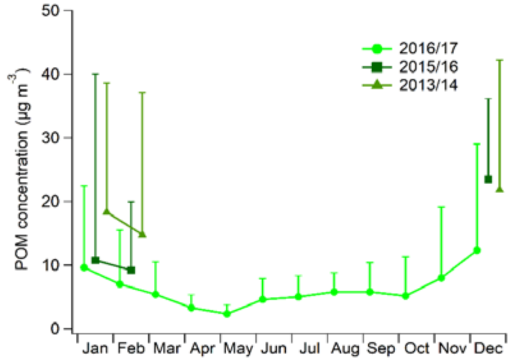
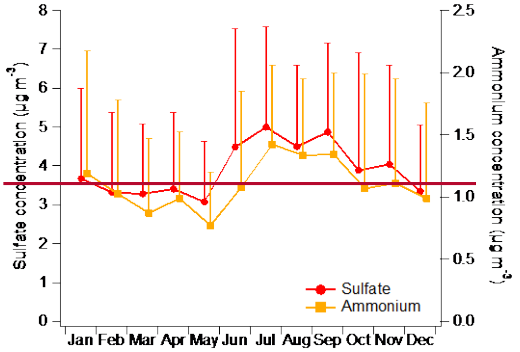
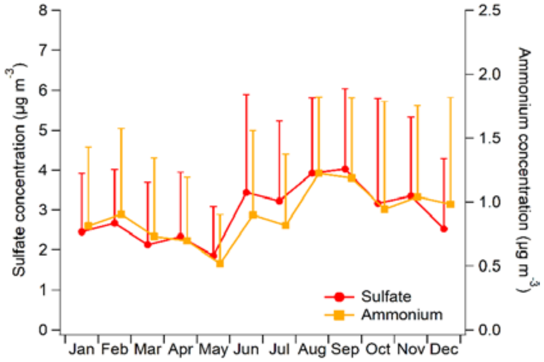

Organics
Sulfate
Nitrate
Ammonium
BC
Mass concentration (µg m^{-3})
0
20
40
60
80
100
120
140
160
180
200
220
240
12/31/2015
1/10/2016
1/20/2016
1/30/2016
2/9/2016
2/19/2016
Date

Figure 2: Time series of the main submicron aerosol components. On the top panel the one-year period starting on 26 July 2016 and ending on 31 July 2017, on the middle panel the 2013-2014 winter campaign (18 December-21 February), and on the bottom panel, the 2015-2016 winter campaign (23 December-17 February).


POM concentration (µg m^{-3})
0
10
20
30
40
50
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2016/17
2015/16
2013/14


POM concentration (µg m^{-3})
0
10
20
30
40
50
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2016/17
2015/16
2013/14


Sulfate concentration (µg m^{-3})
Ammonium concentration (µg m^{-3})
0
1
2
3
4
5
6
7
8
0.0
0.5
1.0
1.5
2.0
2.5
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Sulfate
Ammonium


Sulfate concentration (µg m^{-3})
Ammonium concentration (µg m^{-3})
0
1
2
3
4
5
6
7
8
0.0
0.5
1.0
1.5
2.0
2.5
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Sulfate
Ammonium

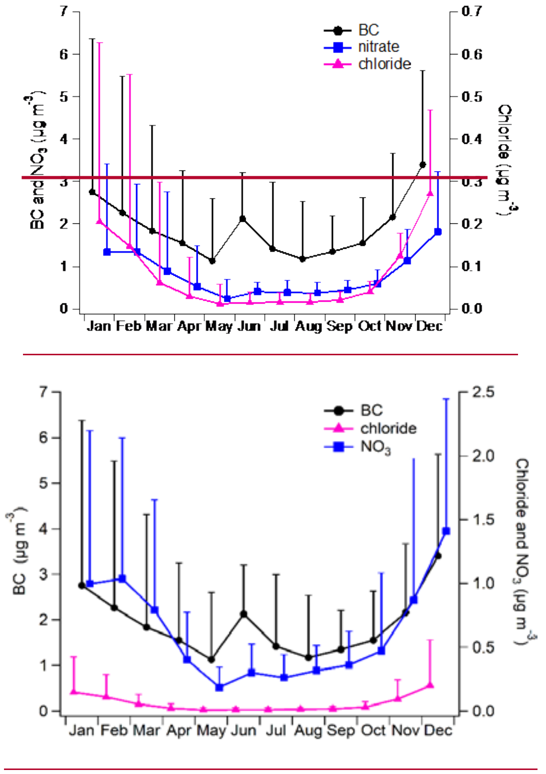
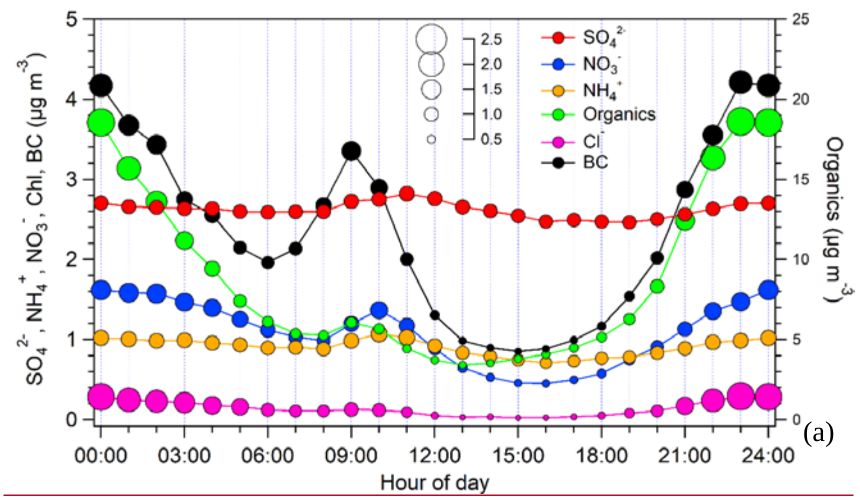
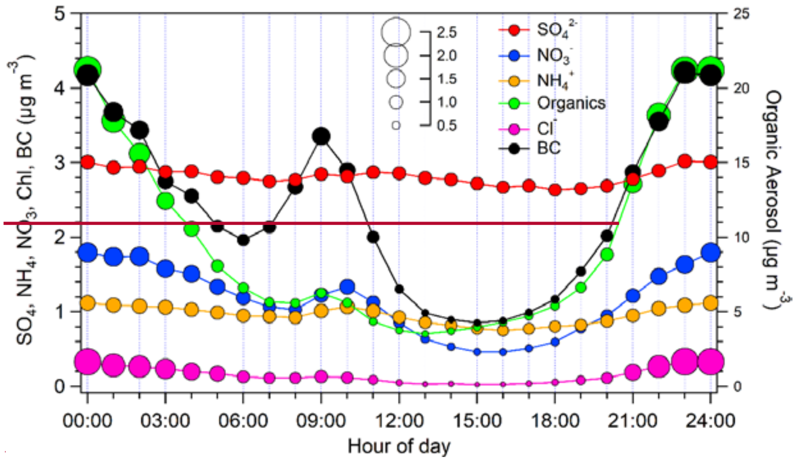


Figure 3: Monthly average concentrations of the main aerosol constituents. Organics are shown on the top panel for the one year 2016-2017 period as well as the 2013-2014 and 2015-2016 winter periods, while sulfate and ammonium on the middle panel, and BC, nitrate and chloride on the bottom panel shown for the one year 2016-2017 period. Standard deviation is also depicted (error bars; only the positive part is shown for plot's clarity issues).


SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, Chl, BC (µg m^{-3})
Organics (µg m^{-3})
Hour of day
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
0
1
2
3
4
5
0
5
10
15
20
25
2.5
2.0
1.5
1.0
0.5
SO$_4^{2-}$
NO$_3^-$
NH$_4^+$
Organics
Cl$^-$
BC
(a)


SO$_4$, NH$_4$, NO$_3$, Chl, BC (µg m^{-3})
Organic Aerosol (µg m^{-3})
Hour of day
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
0
1
2
3
4
5
0
5
10
15
20
25
2.5
2.0
1.5
1.0
0.5
SO$_4^{2-}$
NO$_3^-$
NH$_4^+$
Organics
Cl$^-$
BC

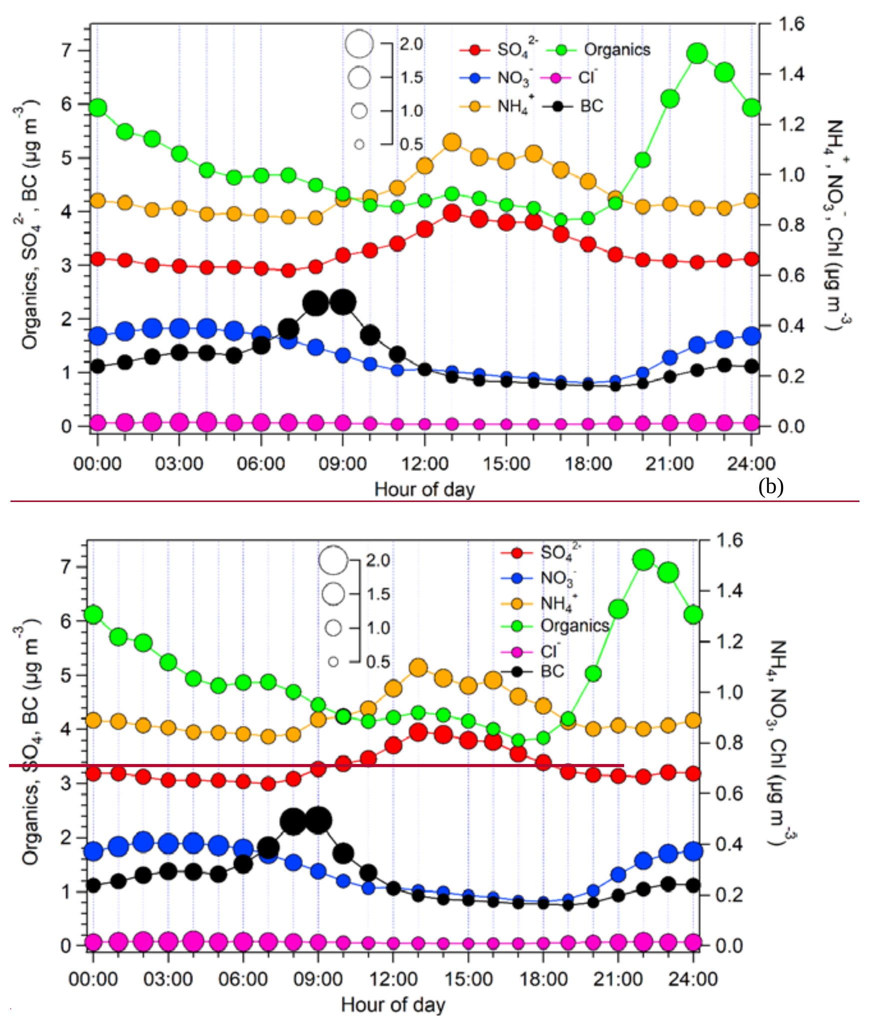
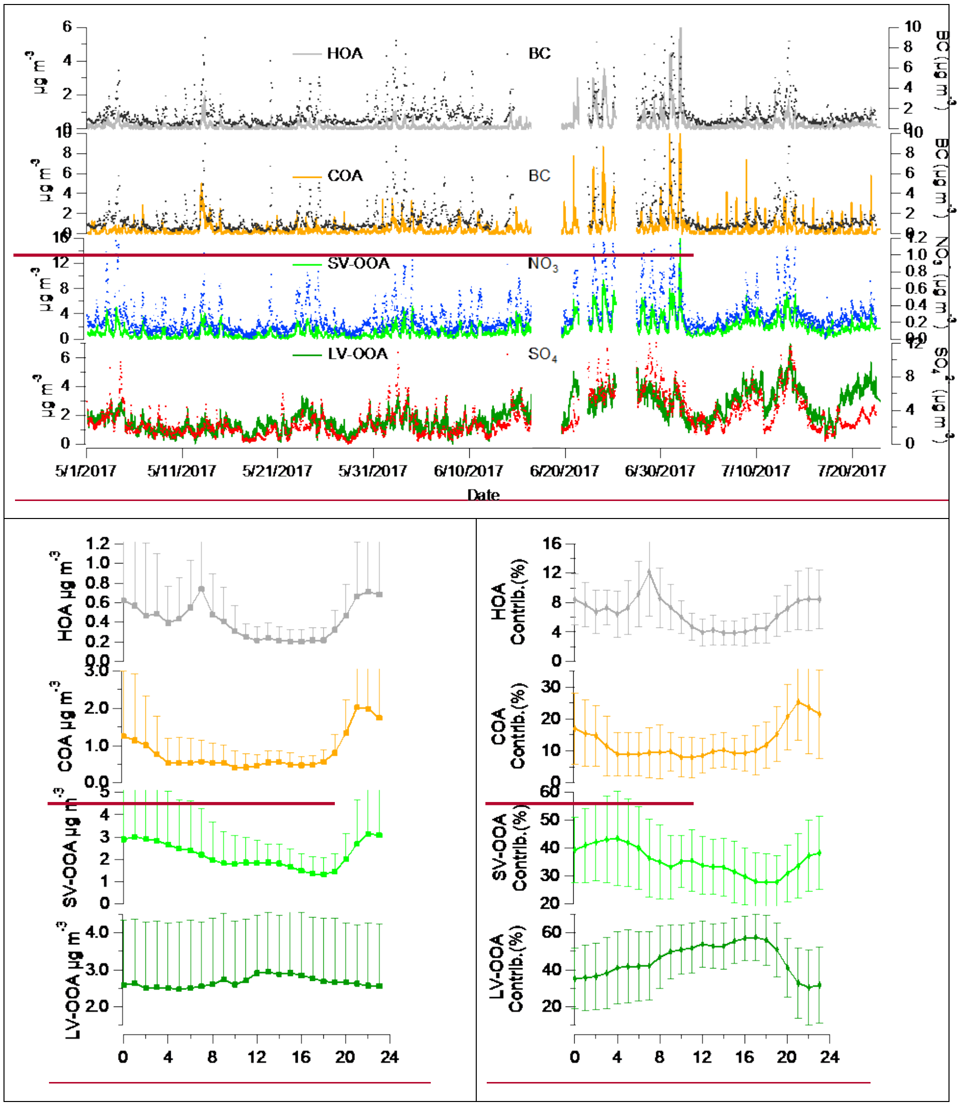


Figure 4: Average daily cycle of the main submicron aerosol constituents for the cold period 2016-17 on the top panel and the warm period of 2017 on the bottom panel. The size of the markers indicates the normalized values relative to each species' daily mean value.


HOA
BC
COA
BC
SV-OOA
NO_3
LV-OOA
SO_4
µg m^{-3}
BC (µg m^{-3})
NO_3 (µg m^{-3})
SO_4^{2-} (µg m^{-3})
5/1/2017
5/11/2017
5/21/2017
5/31/2017
6/10/2017
6/20/2017
6/30/2017
7/10/2017
7/20/2017
Date
HOA µg m^{-3}
COA µg m^{-3}
SV-OOA µg m^{-3}
LV-OOA µg m^{-3}
HOA Contrib.(%)
COA Contrib.(%)
SV-OOA Contrib.(%)
LV-OOA Contrib.(%)
0
4
8
12
16
20
24

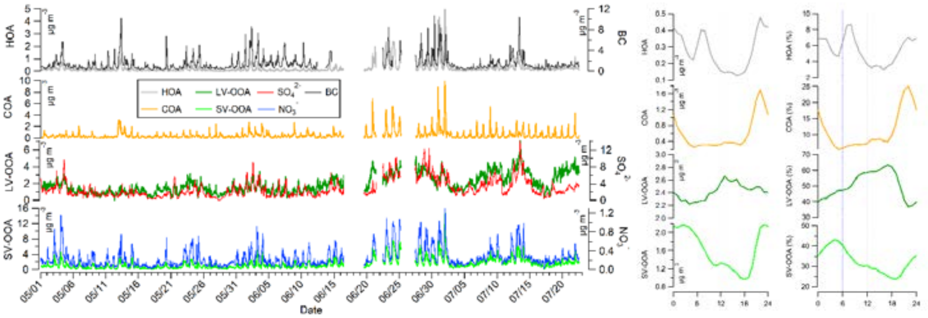
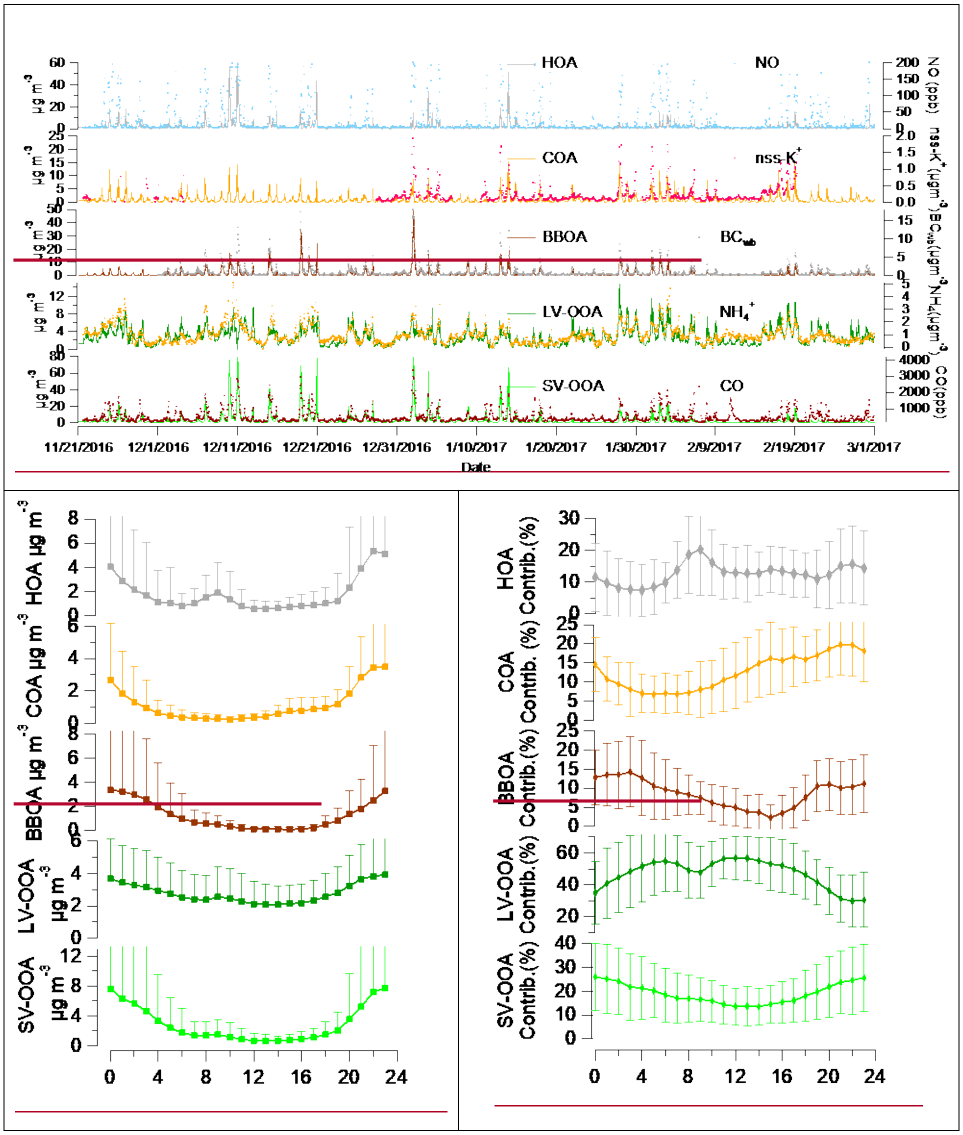


Figure 5: Time series of the contribution of the different factors identified by PMF between 1 May – 31 July 2017 (~~top~~left) along with their average diurnal cycles (~~bottom left~~middle) and the respective hourly average contributions (~~bottom~~ right).


HOA
NO
μg m^{-3}
NO (ppb)
COA
nss-K$^+$
nss-K$^+$ (μg m^{-3})
BBOA
BC$_{wb}$
BC$_{wb}$ (μg m^{-3})
LV-OOA
NH$_4^+$
NH$_4^+$ (μg m^{-3})
SV-OOA
CO
CO (ppb)
11/21/2016
12/1/2016
12/11/2016
12/21/2016
12/31/2016
1/10/2017
1/20/2017
1/30/2017
2/9/2017
2/19/2017
3/1/2017
Date
HOA μg m^{-3}
COA μg m^{-3}
BBOA μg m^{-3}
LV-OOA μg m^{-3}
SV-OOA μg m^{-3}
HOA Contrib.(%)
COA Contrib. (%)
BBOA Contrib.(%)
LV-OOA Contrib.(%)
SV-OOA Contrib.(%)
0
4
8
12
16
20
24

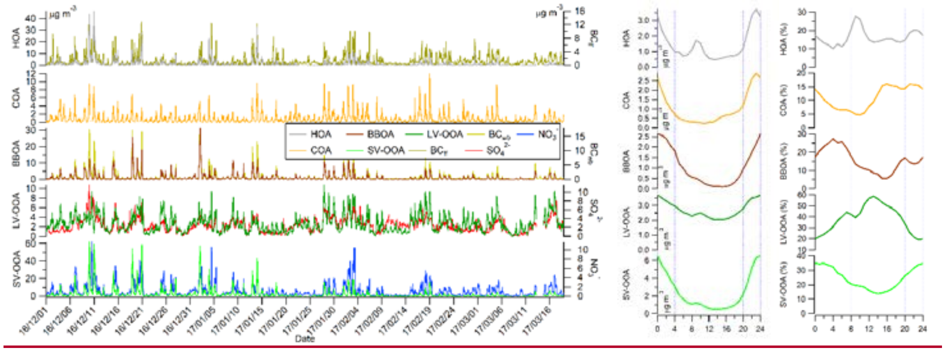


Figure 6: Time series of the contribution of the different factors identified by PMF between 21 Nov. 2016 – 1 March 2017 (~~top~~left) along with their average diurnal cycle (~~bottom left~~middle) and respective hourly contribution (~~bottom ~~right).

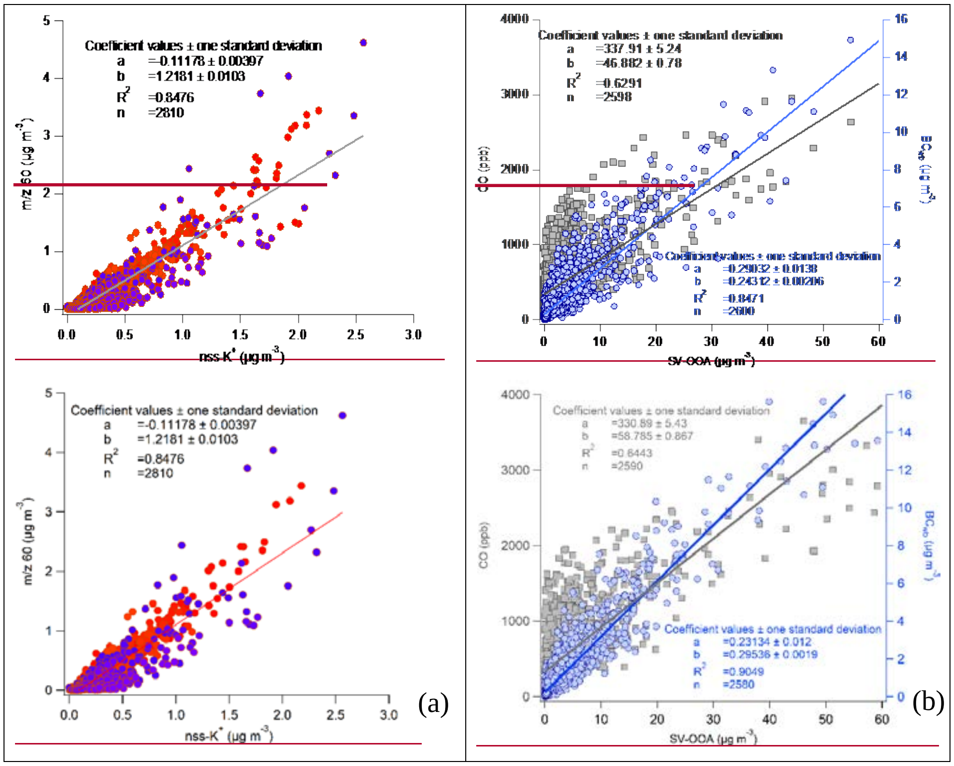
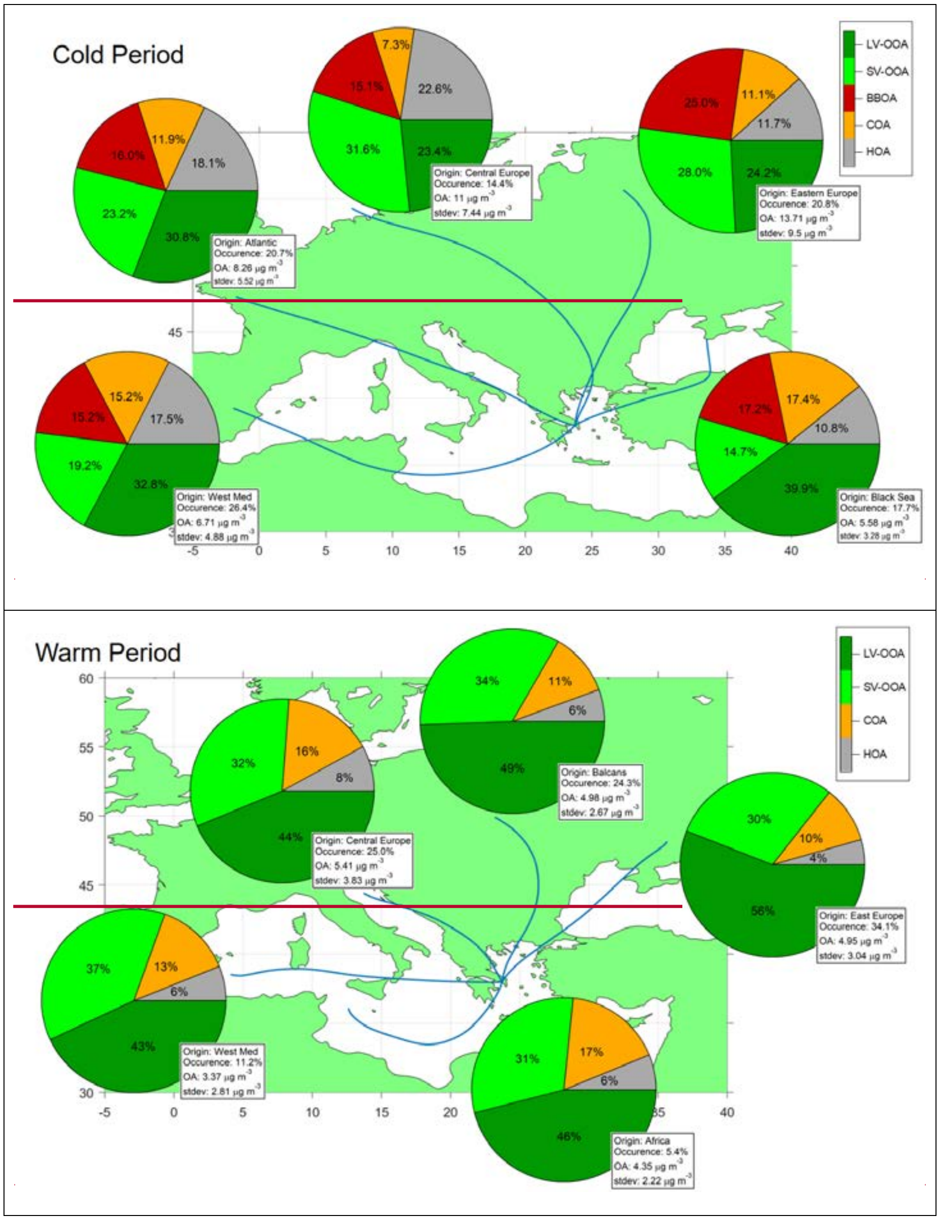


Figure 7: (a) Correlation of m/z 60 with nss-K$^+$ for 2013-14 (red) and 2016-17 (blue), and (b) Correlation of SV-OOA with CO (grey) and BC (blue) for 2016-17.


Cold Period
LV-OOA
SV-OOA
BBOA
COA
HOA
16.0%
11.9%
18.1%
23.2%
30.8%
Origin: Atlantic
Occurence: 20.7%
OA: 8.26 μg m^{-3}
stdev: 5.52 μg m^{-3}
7.3%
15.1%
22.6%
31.6%
23.4%
Origin: Central Europe
Occurence: 14.4%
OA: 11 μg m^{-3}
stdev: 7.44 μg m^{-3}
25.0%
11.1%
11.7%
28.0%
24.2%
Origin: Eastern Europe
Occurence: 20.8%
OA: 13.71 μg m^{-3}
stdev: 9.5 μg m^{-3}
45
15.2%
15.2%
17.5%
19.2%
32.8%
Origin: West Med
Occurence: 26.4%
OA: 6.71 μg m^{-3}
stdev: 4.88 μg m^{-3}
17.2%
17.4%
10.8%
14.7%
39.9%
Origin: Black Sea
Occurence: 17.7%
OA: 5.58 μg m^{-3}
stdev: 3.28 μg m^{-3}
-5
0
5
10
15
20
25
30
35
40
Warm Period
60
55
50
45
30
LV-OOA
SV-OOA
COA
HOA
32%
16%
8%
44%
Origin: Central Europe
Occurence: 25.0%
OA: 5.41 μg m^{-3}
stdev: 3.83 μg m^{-3}
34%
11%
6%
49%
Origin: Balcans
Occurence: 24.3%
OA: 4.98 μg m^{-3}
stdev: 2.67 μg m^{-3}
30%
10%
4%
56%
Origin: East Europe
Occurence: 34.1%
OA: 4.95 μg m^{-3}
stdev: 3.04 μg m^{-3}
37%
13%
6%
43%
Origin: West Med
Occurence: 11.2%
OA: 3.37 μg m^{-3}
stdev: 2.81 μg m^{-3}
31%
17%
6%
46%
Origin: Africa
Occurence: 5.4%
OA: 4.35 μg m^{-3}
stdev: 2.22 μg m^{-3}
-5
0
5
10
15
20
35
40

~~**Figure 8:** Average compositional pie charts of OA fractions for each trajectory cluster, separately for cold (November 2016 – March 2017) and warm (Aug-Sep 2016 and May-Jul 2017) periods on the top and bottom panel respectively. Displaying also frequency of occurrence and average OA concentrations for each cluster.~~

	Mar – Apr – May 2017	**Jul-Aug 2016 & Jun- Jul 2017**	**Sep – Oct – Nov 2016**	**Dec – Jan – Feb 2016-2017**	**Dec – Jan – Feb 2013-2014**	**Dec – Jan – Feb 2015-2016**
Organics	3.~~5~~3 ± 3.~~3~~0 (0.3-3~~5.9~~1.3)	5.~~3~~4 ± 3.4 (0.~~4~~3-4~~4.8~~1.9)	6.~~3~~1 ± 7.~~9~~5 (0.~~3~~1-98.~~6~~2)	9.~~9~~0 ± 1~~6.1~~3.4 (0.2-~~200.5~~153.9)	~~15.7~~18 ± ~~21~~24.~~8~~4 (0.4~~5~~-~~189.4~~212.2)	1~~1.5~~2.4 ± 1~~8.4~~9.9 (0.7-1~~51.4~~150.5)
Ammonium	0.6 ± 0.5 (0.4-~~2.9~~3.1)	1.0 ± 0.6 (0.2-~~3.9~~4.1)	1.~~1~~0 ± 0.7 (0.4-5.~~1~~7)	~~1.0~~0.9 ± 0.7 (0.2-5.~~1~~7)	1.8~~9~~ ± 1.2~~3~~ (0.2-9.1~~9~~)	1.~~0~~1 ± ~~0.9~~1 (0.3-6.~~2~~7)
Sulfate	2.~~8~~1 ± 1.~~4~~5 (0.2-~~9.7~~10.1)	3.6 ± 2.~~0~~1 (0.~~2~~3-14.~~5~~9)	3.5 ± 2.~~2~~3 (0.~~2~~1-1~~5.4~~7.1)	2.~~7~~5 ± 1.~~7~~5 (0.~~2~~1-1~~4.8~~1.7)	2.6~~3~~ ± 1.4~~3~~ (0.4~~3~~-13~~2~~.~~3~~9)	2.2 ± 1.~~5~~7 (0.4-~~9~~10.3)
Nitrate	0.4 ± 0.5 (0.05-~~4.8~~5.4)	0.3 ± 0.2 (0.01-1.~~4~~5)	0.~~6~~5 ± 0.~~8~~7 (0.1-6.~~5~~9)	1.2 ± 1.5 (0.05-1~~1.1~~2.1)	2.6~~1~~ ± 2.4~~0~~ (0.09-18~~5~~.~~4~~3)	1.~~4~~5 ± 1.~~8~~4 (0.07-~~9.9~~16)
Chloride	0.~~03~~02 ± 0.05 (0-0.~~9~~8)	0.02 ± 0.02 (0.04-0.2)	0.~~05~~04 ± 0.~~1~~09 (0.~~08~~07-2.0)	0.~~17~~15 ± 0.~~33~~3 (0-3.~~7~~5)	0.16~~4~~ ± 0.24~~2~~ (0.09~~8~~-~~6.8~~8.1)	0.~~11~~12 ± 0.24 (0-2.~~5~~6)
BC	1.5 ± 1.4 (0.1-14.6)	1.2 ± 0.8 (0.2-10.5)	1.7 ± 1.6 (0.1-12.4)	2.4 ± 3.4 (0.1-29.6)	2.7 ± 3.2 (0.2-26.8)	3.4 ± 4.6 (0.2-32.3)
PM1	~~10.2~~8.9 ± ~~7~~6.1 (0.6-~~115.6~~42.4)	~~9.6~~10.3 ± ~~6.2~~5.6 (0.5-~~67.4~~52.2)	1~~5.8~~3 ± 1~~3.2~~1.1 (0.9-1~~43.9~~15.5)	~~20.7~~16.1 ± ~~26.4~~19.5 (0.8-~~251.8~~185.8)	2~~5.1~~4.5 ± ~~29.9~~ 24.7(1.4-~~213.1~~227.2)	~~19.5~~21.2 ± ~~25.3~~27.4 (1.7-~~202.5~~215.3)

Table 1: Seasonal average concentrations ± standard deviation (range) and total mass of the main submicron aerosol components for the one-year study period and the two winter campaigns.

	Winter 2013-14 18/12/13 – 21/02/14	**Winter 2015-16** 23/12/15 – 17/02/16	**Cold 2016-17** 01/11/16-18/03/17
BBOA	~~8.3~~12.4%	~~9~~8.9%	~~10.3~~11.9%
HOA	~~16~~12.2%	~~12.5~~9.7%	~~16.5~~16.4%
COA	~~7.4~~10.4%	~~7.2~~8.1%	~~11.4~~11.7%
SV-OOA	~~33.1~~19.8%	~~27.5%~~17.7%	~~30.8~~28%
LV-OOA	~~35.2~~45.2%	~~43.8%~~55.6%	~~31~~32%

Table 2: Contribution of the five organic aerosol components to the total organic fraction during the three individual winter campaigns.