

# ***Interactive comment on “Sources and processes that control the submicron organic aerosol in an urban Mediterranean environment (Athens) using high temporal resolution chemical composition measurements” by Iasonas Stavroulas et al.***

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Received and published: 23 August 2018

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

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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 measure-

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ments 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 from 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 from 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.

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

Response: The IE for NO<sub>3</sub> and RIEs for NH<sub>4</sub> and SO<sub>4</sub> are now reported in the revised Supplementary material. The ACSM was calibrated just before its deployment to the

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site and successfully participated in the ACSM intercomparison exercise.

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.

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  $\mu\text{m}$  fraction?

Response: We believe that the slopes for  $\text{NO}_3^-$ , which are 0.99 for 2016 – 2017 versus 1.02 for the winter of 2015 – 2016, the slopes for regression of  $\text{NH}_4^+$  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  $\text{SO}_4=$ . 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  $\text{PM}_{2.5}$  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

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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.

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.

Lines 290 293: Is nitrate primary emitted? Do you mean that nitrate is quickly formed from primary NO<sub>x</sub>? 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

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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.

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.

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 BCff than with BCwb.

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  $0.1 \mu\text{g m}^{-3}$  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

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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.

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.

## References

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Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-356/acp-2018-356-AC5-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-356>, 2018.

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