

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.

Anonymous Referee #3

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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)

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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 $\leq 10\%$ 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 Grippa et 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 is worth publishing. However, major changes need to be done before this paper merits publication in ACP. I recommend

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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.

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.
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.
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.
4. Page 12; affinity between spectra by 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.
5. Meteorological parameters; meteorological parameters are not given in the paper. Please provide at least temperature, radiation and boundary layer height that are im-

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portant regarding the concentrations and the sources of aerosol

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.
7. Page 3, line 82; "non-refractory part"; you also measured BC, why it is not included in main objectives (BC is refractory component)?
8. Page 4, line 101-102; "s/n 140-139" not needed here
9. Page 4, line 102; Aerodyne Research Inc.
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.
11. Page 4, line 118-120; give RIE values
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.
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)?
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?
15. Page 5, line 144; remove "Necessary"
16. Page 5, line 145; remove "historic"
17. Page 6, line 160; on the organic mass spectra obtained

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18. Page 7, line 185; "following section"; give the number of sections
19. Page 7, line 194-196; describe PM2.5 filter collection and thermal-optical method in experimental section
20. Page 8, line 223; add time base for averages e.g. 1-hour average
21. Page 8, line 244, change "to the levels" to "on the levels"
22. Page 8-9, line 244-247; "These observations are in accordance..." this sentence is unclear and needs to be modified
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.
24. Page 9, line 273; what are increased local sources for nitrate in winter?
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?
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.
27. Page 13, line 383-385; "OA precursors are maximum during night similar to SV-OOA". Please give reference or results.
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?
29. Page 13, line 3963-397; "COA shown moderate correlation with nitrate". Explain why.

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30. Page 14, line 403; Is figure number here really 8? Double-check figure numbers.
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.
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.
33. Page 16, line 463; How did you calculate Nss-K?
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 associated with BBOA and SV-OOA (and other factors)?
35. Page 16, line 477-478; why COA correlates with potassium and chloride?
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.
37. Page 17, line 494-495; "moderately hump for COA during lunchtime". This cannot be seen in Figure 6.
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.
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

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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).

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.

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.

42. Figure 1; Add “1-hour averaged” mass concentrations

43. Figure 4; in upper figure you use “organic aerosol” but in lower figure “Organics”. Please be consistent with the names.

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?

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

Technical comments:

46. Page 6, line 163; time series

References

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, et al. Organic aerosol components derived from 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy. *Atmos. Chem. Phys.* 14, 6159–6176, 2014.

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Mohr, C., DeCarlo, P.F., Heringa, M. F., Chirico, R., Slowik, J. G. et al. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmos. Chem. Phys.*, 12, 1649–1665, 2012.

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