Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-356-AC4, 2018

Atmospheric Chemistry and Physics Discussions

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.

Iasonas Stavroulas et al.

kbougiatioti@gmail.com

Received and published: 23 August 2018

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

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

Printer-friendly version

Discussion paper

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 (R2=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).

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 f55,OOAsub and f57,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 f55,OOAsub vs f57,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 attached).

Figure 1. f55, OOAsub plotted against f57, 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).

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

Printer-friendly version

Discussion paper

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.

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.

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.

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.

References

Bressi, M., Cavalli, F., Belis, C. A., Putaud, J.-P., Fröhlich, R., Martins dos Santos, S., Petralia, E., Prévôt, A. S. H., Berico, M., Malaguti, A., and Canonaco, F.: Variations in the chemical composition of the submicron aerosol and in the sources of the organic fraction at a regional background site of the Po Valley (Italy), Atmos. Chem. Phys., 16, 12875-12896, https://doi.org/10.5194/acp-16-12875-2016, 2016.

Budisulistiorini, S. H., Baumann, K., Edgerton, E. S., Bairai, S. T., Mueller, S., Shaw, S.

L., Knipping, E. M., Gold, A., and Surratt, J. D.: Seasonal characterization of submicron aerosol chemical composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia,and Look Rock, Tennessee, Atmos. Chem. Phys., 16, 5171-5189, https://doi.org/10.5194/acp-16-5171-2016, 2016.

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.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159-6176, https://doi.org/10.5194/acp-14-6159-2014, 2014.

Florou, K., Papanastasiou, D. K., Pikridas, M., Kaltsonoudis, C., Louvaris, E., Gkatzelis, G. I., Patoulias, D., Mihalopoulos, N., and Pandis, S. N.: The contribution of wood burning and other pollution sources to wintertime organic aerosol levels in two Greek cities, Atmos. Chem. Phys., 17, 3145-3163, https://doi.org/10.5194/acp-17-3145-2017, 2017.

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priest-

man, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévôt, A. S. H.: ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, Atmos. Meas. Tech., 8, 2555-2576, https://doi.org/10.5194/amt-8-2555-2015, 2015.

Minguillón, M. C., Ripoll, A., Pérez, N., Prévôt, A. S. H., Canonaco, F., Querol, X., and Alastuey, A.: Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor, Atmos. Chem. Phys., 15, 6379-6391, https://doi.org/10.5194/acp-15-6379-2015, 2015.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prévôt, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, Atmos. Chem. Phys., 12, 1649-1665, https://doi.org/10.5194/acp-12-1649-2012, 2012.

Kassomenos, P., Flocas, H.A., Lykoudis, S., and Petrakis, M.: Analysis of mesoscale patterns in relation to synoptic conditions over an urban Mediterranean basin, Theor. Appl. Climatol., 59, 215-229, 1998.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-356/acp-2018-356-AC4-supplement.pdf

---

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

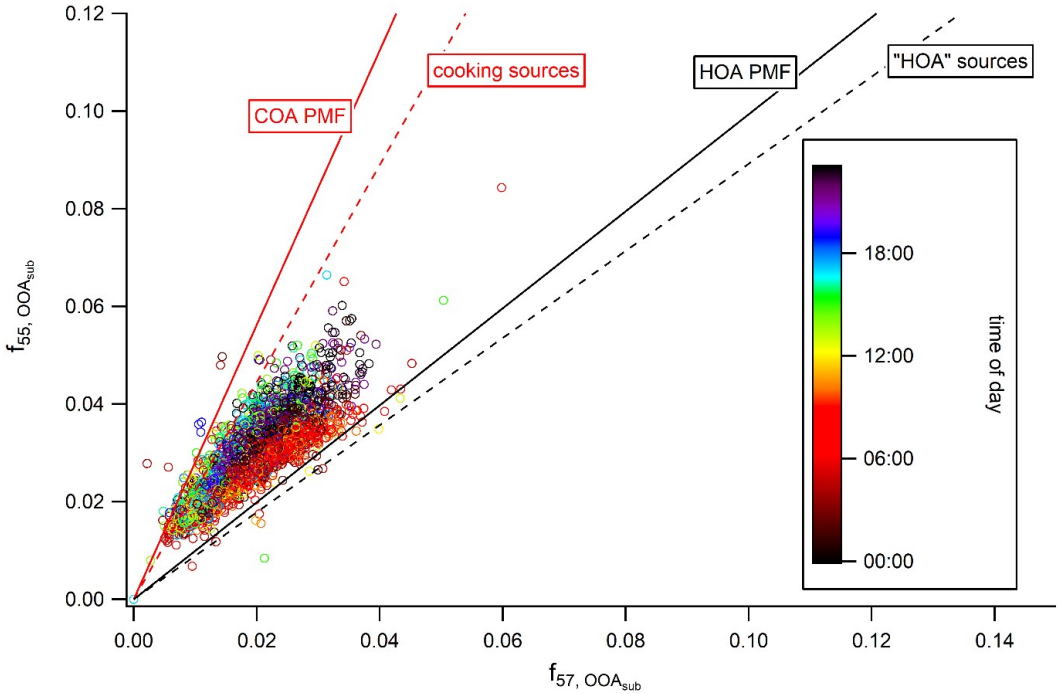

Fig. 1. f55, OOAsub plotted against f57, OOAsub. Data points are colored according to time of day. Lines correspond to linear fit results conducted using COA and HOA results both from PMF and laboratory stand

Printer-friendly version

Discussion paper