Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-1244-RC2, 2021

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Increase of secondary organic aerosol over four years in an urban environment" *by* Marta Via et al.

Anonymous Referee #2

Received and published: 9 February 2021

Review

The Marta Via et al. manuscript aims to compare the aerosol chemical composition measured by a Quadrupole ACSM at the urban background station of Palau Reial (Spain) during 2 periods of one year each (May 2014 – 2015 and Sept. 2017 – Oct 2018). The organic aerosol mass concentration is further described using source apportionment analysis (ME-2) allowing the identification of 5 factors (HOA, COA, BBOA, LO-OOA, and MO-OOA). Based on these results, the authors investigate the seasonal change in the aerosol chemical composition as well as the variation between the two sampled years. Although the present work follows a classical approach regarding the analysis of the Q-ACSM dataset, the comparison of the 2 sampling periods, as well as the influence of the wind direction and trajectory analysis, represents an important

Printer-friendly version

Discussion paper

added value of the manuscript. Therefore, the present work is fully suitable for the focus of ACP. However, this work is suffering from some conceptual issues on the comparison between the two years to properly support the conclusions and major revisions are needed before a potential publication on ACP.

Major comments - The paper is focused on the change of the aerosol chemical composition (included organic aerosol sources) over 4 years. However, the dataset itself covers only the years 1 and 4 of these 4 years. So in reality, the authors compared the mass fraction and chemical composition only between two years and can therefore hardly conclude on a possible trend since no information on the variation of the aerosol chemical composition and masses between the 2 periods. The strong limitation for such an approach is to properly quantify the influence of the interannual variability of the meteorological conditions and its impact on the aerosol chemical composition. How did the authors consider this variability? Can their conclusion be bias by the fact that the summer of period A was colder and wetter than a typical summer? Consequently, it is difficult to consider it as an absolute evolution trend over the 4 years. - Another critical issue is related to the estimation of the chemical composition change between the 2 years itself. The conclusions are based on a direct comparison of the average mass concentration values obtained during periods A and B. For example, the authors did not convince me concerning a possible decrease of the organic mass concentration by 5 % between periods A and B when the respective average concentration at 4.0 (+/- 2.8) and 4.2 (+/- 2.8) $\mu g/m^3$ (line178) but at the same time this difference is considered as “similar” (line 317). I agree that there is a difference of 5 % between the two values but is this difference significant enough? Could it be rather considered to be inside the instrumental uncertainties or the resulting of the interannual variability? The same comments can be made for all chemical species as well as for the factor analysis. Here a summary table including all average mass concentrations of each species and factors as well as their estimated change including a proper discussion is necessary. Again, in absence of continuous measurement over the 4 years, it is difficult to conclude about a significant change without any statistical analysis for comparing the 2 years. Maybe

a seasonal approach could also be considered to affine the conclusion of the authors. Moreover, the discussion on the spatial origin of the OA is weakening the argumentation on a possible change in the SOA mass concentration between periods A and B. Line 308, the authors mentioned that the summer of period A was anomalously cold and wet. Could it be that the reported difference of SOA mass concentration between the two periods, been influence by this untypical summer leading to lower SOA formation due to bad weather conditions for period A compare to more typical summer? This is also supported in Figure 8, which shows that LO-OOA and MO-OOA were not coming from the same area during periods A and B. - Off-line filter analysis: I would expect more details regarding the off-line measurements. What was the sampling time (24h, midnight to midnight)? On the manuscript, only the ICP-AES is mentioned, while the SI referred to ICE-AES and ICP-MS. Could you please clarify? Please also provide the type of the instrument, the manufacturer, and under which condition the analysis was made? A similar comment can be made for the Ion chromatography analysis and the selective electrode. Last but not least, it is known that the value of the OC and EC strongly depend on the reference method used (Chiappini et al., 2014, Cavalli et al., 2010), it is important to provide also the reference of the instrument used for the analysis as well as the applied method (NIOSH-like, EUSAAR-2, IMPROVE_A). - The description and the discussion of the source apportionment analysis need to be improved and to be combined in a single place in the manuscript. Moreover, the authors included a lot of figures and tables on the supplementary information that are not described at all. In a more general comment, all figures and tables present in a manuscript have to be properly discussed by the authors. This is quite a pity and the description of the factor analysis will certainly gain clarity if the authors described the results of the intermediate factor solution and why they were satisfied by their final factor solution as well as factor identification. For example, the authors considered the presence of a biomass burning factor based on the monthly average of the ratio f60 and f73, what about the ratio of f44 vs f60? Could this average mask some biomass burning events? Did the authors also investigate the presence of BBOA for the other

Printer-friendly version

Discussion paper

seasons in an early stage of their source apportionment analysis? I also have a small concern regarding the averaged values of the BBOA contribution (6% for period A and 4% for period B, figure 2). When comparing the different average values (figures 2, 5, 7, and 9), I got the impression that the BBOA contribution is slightly overestimated compare to what can be expected from figure 5 (it could also be an averaging effect). This is also the case when regarding the BBOA contribution between periods A and B in figure 7, the overall BBOA mass faction seems to be always higher than 10% (especially for period B). Did the authors consider the BBOA mass concentration as 0 μg/m3 or as no value for seasons when BBOA was not identified? Also, a discussion will help to understand the choice of the single OOA factor for period A during the Nov.-March period. How the two mass spectra of this MO-OOA compared to the 3 other MO-OOA of period A? - The discussion on the special origin of the aerosol is very interesting but it would be extremely helpful to include a map showing the surrounding of the station when describing for example the presence of roads, or residential areas. Similarly, the different air mass trajectories analysis is poorly described in the current version of the manuscript. Here again, it would be helpful for the reader to know which method was used to classified the trajectory, to characterize each of them by their frequency of occurrence, their meteorological characterization (main period of occurrence, average temperature, wind speed...), and to include a figure with the different class of trajectories. Last but not least, it is damageable that the inorganics species and BC are not included in the trajectory analysis. It would certainly provide added values to support the discussion. - The statements of the authors must be systematically supported by numbers. Only mentioning “highest”, “higher”, “lower”, “high proportion”, “lowest” is hard to understand if there are no clear references.

Minor comments: - Abstract: line 13: is the different between 10.1 and 9,6 μg m-3 statistically significant? - Line 15: please support the term “significant” decrease and “higher” by numbers. - Line 21: how the authors defined SOA based on their PMF results? - Line 37: please check the uniformity of the referenced labeling. - Line 65 and rest of the manuscript: please choose between Q-ACSM or ACSM. - Line 70: 70

eV - Line 75: Could the authors please precise how often the ACSM was calibrated during each period? Are the IE and RIE a single calibration or an average value? - Line 86: Could the authors precise the range of the OPC measurements and how is it comparing to the SMPS? - Line 93: is the SIR S-5012 NOx monitor equipped or not with a blue-light converter? - Line 93-96: Were all the additional measurements performed at the same place or not? - Line 100: Could the authors refer her to section 3.1. At this stage, it is not clear that the comparison will be discussed later on. - Line 116 and follow: only ME-2 allows to constrain a factor and the use of the a-value, PMF cannot do that. - Line 125: Please also include here reference to Canonaco, F., Crippa, M., Slowik, J. G., Prévôt, A. S. H., and Baltensperger, U.: SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6, 3649-3661, doi:10.5194/amt-6-3649-2013, 2013. - Lines 121, 128: The authors should define their acronym the first time they use them in the manuscript (here BBOA, HOA, COA), not a few lines later (here line 138-140). - Line 153: The results of the comparison between ACSM and co-located measurements will gain an understanding by also including the plots on the SI and not only a table. - Line 153 and Table S3: please check the homogeneity of the fitting parameters. The authors used either one or three digits for the same analysis. Only, 2 digits are necessary here. - Line 157: The authors should not only look at the R^2 to consider that the agreement is “very good” but also on the slopes and intercepts. For example, nitrate and sulfate correlation have both high R^2 (0.84 to 0.93, respectively) but their slopes (1.9 for the nitrate in period A and 1.32 for sulfate in period B) show a large overestimation by the ACSM. This must be discussed too before concluding on a “good agreement”. - Line 160: I do not fully agree with the conclusion of the authors. The comparison between the organic mass measured by the ACSM and the OC from the filter can also be impacted by the reference method used for the OC estimation. Did the authors try to convert their organic mass into OC directly compared to the offline OC? - Line 165: why not including the time series of the ACSM measurements directly in the main

manuscript. - Line 262: Is the number of “high”, not a bit too “high” in this sentence? - Line 291: reference to Fig. 8 is missing? - Line 297: could you please add a reference here? -line 319: Please refer to the corresponding figure. - Figure 2: Should the total mass of organic not be 4.2 μg/m3 for period B? - Figure 8: The legend of the color code is missing. - Figures 3,4,6, S1, S2, S3, S4, S5, S9, S12: legend of the x-axis is missing. - Figure S8: The legend of the y-axis is missing. - Diurnal figures: It is hard to identify the different seasons as well as the hours on the present figures. I would strongly suggest separating each diurnal profiles. - Supplementary section 1: please provide more details regarding the sampling regime, the analytical instrumentation, and methods used. - Tables on the supplementary information: Please reorganize the tables to have a complete table on one page.

References: Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79-89, DOI 10.5194/amt-3-79-2010, 2010. Chiappini, L., Verlhac, S., Aujay, R., Maenhaut, W., Putaud, J. P., Sciare, J., Jaffrezo, J. L., Liousse, C., Galy-Lacaux, C., Alleman, L. Y., Panteliadis, P., Leoz, E., and Favez, O.: Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter, Atmos. Meas. Tech., 7, 1649-1661, 10.5194/amt-7-1649-2014, 2014.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-1244, 2020.

Printer-friendly version

Discussion paper