

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

Anonymous Referee #1

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The manuscript presents aerosol concentration, chemical speciation and source apportionment data for 2 one-year periods separated in time. This potentially allows for analysis of an interannual variability of aerosol sources in the urban background site of Barcelona. The secondary aerosol dominance was revealed in both periods with some differences in oxidation levels between the two. Seasonal and diurnal changes were also discussed. The manuscript presents invaluable data and information and has a great potential to advance our knowledge in secondary aerosol formation, composition as well as transformation. While authors claim the observation of trends over the years, sufficient evidence that this is indeed a trend rather than year to year variation has not been provided in this version of the manuscript. Therefore, I recommend accepting this publication subject to major revisions listed above and below.

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While the manuscript is easy to read, it would still benefit significantly from better proof-reading and improving the English language. I have indicated few points in the specific comment, but they are by far not a complete list of required language corrections. The proper tense should be used throughout the manuscript, e.g. use past tense when talking about observations for the past periods (concentrations were, not are, line 167 – ‘BC are’ . . .) if referred to specific period in the past and are not recurring properties, etc.). Correct this consistently throughout the manuscript.

The main concern, however, is with the aforementioned claim of the observed trends in concentrations and atmosphere’s oxidative potential, while the proof of that is missing from the current version of the manuscript. The ‘reduction’ claimed on line 168 and elsewhere might as well be an interannual variation due to differences in meteorology. Like LO-OOA formation in B is explained by ozone potential mostly (Lines 281-283), which can really be just interannual variability of ozone without any additional information or discussion that are lacking here.

Introduction requires more information that is relevant to this paper rather than just presenting general aerosol studies. Provide more info on MO-OOA/LO-OOA and secondary in general, discuss the atmosphere’s oxidative state and its changes as these are important for this manuscript. Provide the state-of-the-art that is relevant to this paper.

There are several references to other studies (line 57 and elsewhere) performed with similar instruments at similar location, like Minguillón et al., 2016 and others, but details on how this study is different from the cited ones are missing. This could be highlighted in the introduction with while the study by Minguillón et al. (2016) found such and such, they did not show this and this, therefore, in this study we . . . or something along these lines. Do it for all studies performed with an ACSM in Barcelona.

A flow of the method section can also be improved. Currently, information on PMF is scattered all over the place. E.g., if you haven’t changed or modified the code, the

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information on lines 104-116, related to the PMF, is redundant, just provide a citation and add more details on the PMF version that is relevant to this paper. Paatero ME-2 was not used here, so combine the information on SoFi that is provided later with the Paatero citation. Also, the citation to (Canonaco et al., 2013) for SoFi might be more appropriate? Or have both, Canonaco and Crippa (line 124).

Similarly, for the a-value approach, there is some info on lines 117-119 and then again later on lines 130-131 as well as the description of factor selection, which first appear on lines ~125, but has no appropriate details that are presented later. Be consistent and provide all related information in one place. Moreover, do not just refer to a table or figure without describing it, a reader is not supposed to make his/her own observations/conclusions, this paper is about what you see from these tables and graphs (one example would be the statement that in similar forms appears several times in the manuscript: 'Differences between solutions of different number of factors for each season are shown in Table S1, Fig. S 2 and chosen seasonal profiles in Fig. S3.' – so what are these differences? Reference to Table S1 (lines 132-136) does not provide details of what we are supposed to see either. Provide details, do not expect a reader to analyze the table by him/herself.

Lines 165-166: discuss all tables and graphs that are included, there is no point of providing them otherwise.

Lines 162-163: it does not seem that OM RIE is the only problem, all compounds are overestimated, can this, thus, be IE problem instead? Similarly, the statement in the conclusions (line 350) refers to OM RIE problem, but there is no discussion why other compounds are systematically overestimated? Instrument or location dependent RIE is a huge drawback for the technique, so you should be certain that this is really the case (problems with OM only and other compounds agree very well, etc.) when adding such a statement to the conclusions.

Finally, if significant environmental policies were implemented that influenced HOA

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concentrations (Line 320), more information with references is required to base this statement on.

Specific comments: Line 21: ...SOA was found to be sensitive ... Line 26: ...SOA factors seem to be linked... Line 29: what do you mean by 'air-cleaning' episodes? Lines 37-38: correct the reference format for 'in Millán, 2014; Millán et al., 1997.' Lines 75-76: the difference between IEs for two periods is very large, explain why this is reasonable (major changes in the instrument or different instrument?); Line 81: provide CE ranges for the two periods; Line 88: 5-minute Lines 97-98: provide a link or a proper reference to the quality control document. It is not possible to retrieve it from the information provided. Line 131: sensitivity analysis? Line 154: I'm confused about the reference to different size ranges for the measurements in periods A and B ('...to differences in the particle size range measured...'), was that really the case? Which instrument? Or is this just a theoretical possibility that is not applicable to this study? Provide details if not. Line 157: provide slopes for specific compounds as well, not just R2 Lines 176-178: rewrite this sentence in proper English Line 205: supposed to be reference to figure 6 rather than 5 here? Line 215: R2 values in the brackets belong to BC or NOx? Line 216: provide information, refer to graph/table on where we can see these differences in ratios. Line 226: states that SOA was freely resolved, provide information that POA factors were constrained with specific a-values, where appropriate, when discussing primary factors then. Lines 271-272: rewrite to: Therefore, the higher the difference is between MSY and PR, the more ozone... Lines 277: I'd say decrease and then increase? Line 307: Fig 9 not S9b, maybe? Line 308: 'due to major occurrence in an aforementioned anomalously cold, wet summer' - double-check if it is really mentioned as I don't recall reading this. Also, can this be the explanation for differences between A and B rather than a consistent trend? Line 319: is this a reduction by 18 and 4%? And why the HOA shows a higher reduction? Discuss it.

Line 324: 'at the expense of', rewrite the whole sentence on lines 323-325 ('Digging into SOA composition, it is more aged in period B, as shown by the increase of MO-

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OOA component at expenses of the LO-OOA reduction, becoming the main OA constituent 325 in period B.)

Lines 325-326: provide more details, increased potential due to what? Or the years were just different as you have referred before to the exceptional summer of A?

Line 337: Very strange that strong winds contributed to the accumulation of local pollution? Usually, these contribute to dilution of local emissions, not increase in concentration. Provide an explanation.

Lines 339-342: this is just repeating the results, without any further contribution to discussion. Add an appropriate discussion.

Lines 353-354: the reasons of 'BBOA was only present in the subperiod November-March and only one OOA factor was apportioned in the cold subperiod in 2014-2015' were never explained in the manuscript. This needs better discussion in discussion section, not just a statement.

Lines 357-359: do you refer to gradual increase or just year to year variation? as there is not enough evidence for the former yet.

Figure 2: I think there is a mistake in average concentrations number at the centre of the pies, table indicates 4.2 and 4 for A and B respectively? Figure 3: bars are shifted to the right in B? e.g. 55, 57, 60 and other m/zs do not appear at their marks on x-axis. Explain the lack of error bars on BBOA, do not expect a reader to guess. Rename LOOA and MOOA to be consistent with the text (LO-OOA and MO-OOA).

Figure 4: this figure can be moved to supplementary.

Figure 6: very strange representation of diurnal trends. It is quite confusing without any information provided in the caption. I suggest replotting this with only one day on the x-axis and playing with different colours or different panels to represent different years and seasons. Moreover, sharp rise in BBOA and consequent drop in LO-OOA looks very artificial. Figure s8 is so much more reasonable. Finally, COA patterns in Fig 6

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and Fig S8 seem to be different, there is no such strong morning peak in S8 as in Fig 6. I would suggest replacing Figure 6 with S8. It only adds to the confusion, especially, that you do not discuss anything that is there in addition to S8. E.g., no discussion on seasonal and period differences that would refer to this figure is provided. Otherwise discuss it (different diurnal cycles between years and seasons for the same factor).

Figure 7: explain the values in the brackets.

Table S1: what is the Anchor number? Is it a-value? so should it be 0.3 not 03 for May 2014? No bold line for Jun-Aug 2014, no factor was selected?

Table S3: the correlation with SMPS looks strangely poor, atypical for such type of measurements. Double check if everything was in order (instrument performance, analysis, if there is no shift in time between the instruments, etc.).

Table S3: ACSM nitrate being larger than the offline concentration is quite strange. Usually, offline instruments have larger cut-offs, even if both are PM1, and sample higher nitrate concentrations than an ACSM. Could that be IE problem? This also relates to the comment on OM RIE, is there only OM problem or other compounds as well, like NO₃, which would rather point to IE, not RIE?

Figure S10: you could get rid of points that are below detection limit for this graph, this would make it clearer.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: 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, 10.5194/amt-6-3649-2013, 2013.

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

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