



EGUsphere, author comment AC3
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Reply on RC3

Marta Via et al.

Author comment on "*Rolling vs. seasonal* PMF: real-world multi-site and synthetic dataset comparison" by Marta Via et al., EGU sphere,
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Reply to Anonymous Referee #3 (Egusphere-2022-269)

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The authors would like to thank this reviewer for the comments and suggestions, which helped improving the quality of this work. A new version of the manuscript has been prepared following the suggestions from the reviewers. We provide below detailed replies to each of the comments in a point-by-point manner. Figures and tables cited in this document can be found in the supplementary annex.

COMMENTS FROM THE REVIEWER

The manuscript presents a comparison between two different approaches of PM₁ organic aerosol (OA) source apportionment through the Positive Matrix Factorization (PMF) source-receptor model applied on mass spectra by Aerosol Chemical Speciation Monitor (ACSM): the widely used "seasonal" PMF against the emerging "rolling" PMF. The two approaches are systematically applied on both real-world ACSM datasets (from 9 European sites) and on a synthetic dataset. The comparison shows that the two approaches lead to similar apportionment results, both addressing the quality standards required by the source apportionment protocol. Overall "Rolling" PMF can be considered more accurate, especially in "transition" periods between seasons because it is able to better adapt to the changes in OA sources along the time. Interestingly the application of PMF on the synthetic dataset performed not so well for both the methodologies. This result shows the strong influence of using and selecting anchor profiles to constrain the PMF solutions and encourages the development of local reference profiles to minimize this impact on OA source apportionment.

This is a well-written paper that clearly describes methodologies, analyses and results. Even if the subject looks quite methodological and possibly suitable for more technical journals, actually the manuscript clarifies important and debated advantages/disadvantages of the approaches and can have a large impact on a wide audience of the atmospheric organic aerosol community.

For this reason, I recommend its publication after consideration of some major/minor comments/changes detailed below.

MAJOR COMMENTS:

- **The discrepancies between original synthetic values and the PMF outputs on the same synthetic dataset are important and not negligible. For what I understand they originate by the choice of the anchor profiles used to constrain PMF solutions. Considering that it is now very common (and indeed strongly recommended by the AMS-data Source Apportionment protocols) to use constraints to apportion OA primary components, I also believe that this result is somewhat worrying. In particular the fact that POA are underestimated and SOA overestimated with respect to the original synthetic values might indicate that using constrains cannot be always the best option. Although I recognize this alone can be the topic of a specific publication, in my opinion the Authors in Section 3.1 should try to assess the general implications also with respect to previous/future studies applying OA source apportionment protocols. Specifically, the Authors should explain better the reasons for the choice of specific anchor profiles used in the different PMF solutions and possibly show (or at least comment) the results of the unconstrained PMF solutions on the synthetic dataset. More specific comments are below.**

One of the unexpected outcomes of this paper is the acknowledgement of the constraint influence on the solution. The PMF outcoming factors are biased by the a priori information introduced to initialise the **F** matrix. This finding then could represent a major reason to overhaul the source apportionment protocols to prevent introducing too much subjectivity.

The multi-site comparison profiles were chosen by the participating PMF runners according to previous knowledge of site-specific OA sources' profiles. In some cases, the cited studies of each individual source apportionment mention a-value and reference profile testing. The most used reference profiles were HOA from Crippa et al., (2013) and BBOA from Ng et al., (2011), and for this reason these were those selected for the synthetic dataset approach.

In the following graph, the seasonal unconstrained and constrained experiments are compared to the truth. The rolling results are not shown here because these must point to a similar direction as seasonal ones as has been demonstrated multiple times in this paper.

The Figure R.3.1, now included in SI as Figure S2, presents how these key ions are in all cases better described by the constrained experiment. HOA truth profile is the same as the anchor one, so the proximity of the points to truth was expected. Contrarily, in the BBOA and SOA profiles cases, the proximity of the constrained runs is greater even though: i. the constrained profile was different to the truth one in the case of BBOA; ii. No constraints were applied in the case of SOA. This figure proves that the application of constraints is still positive even though they are shown in this study that they significantly influence the solution. Furthermore, it can be seen how even if a factor is not constrained (like SOA in the current situation), it is better defined if other factors are constrained.

The current study does not intend to comprehensively determine the role of the anchors on the continuously-evolving source apportionment guidelines, but to raise the suspicions on the effect they might have once these are come across. However, these anchoring still provides more benefit than unconstrained runs, therefore the inclusion of these procedures in source apportionment protocols should be maintained. Future research should be promoted in this direction in order to generate consensus towards profile anchoring relying on solid evidence.

- **I find the term “truth” to describe the synthetic dataset quite pretentious and misleading. I would suggest to change the name, especially in Figures, using for instance “original synthetic” or something else.**

The choice of “truth” as the word to refer to the original factors was already justified in Comment #5 of the Anonymous Referee #1.

SPECIFIC COMMENTS

- **P1-P2, L40-46: too general statements, not easy to really understand the importance of the findings and “quantify” them. Sentences like “although the rolling PMF profile adaptability feature has been proven advantageous” or “these results highlighted the impact of profile anchor on the solution” are quite hasty and vague: what this impact is? And the advantages? Although I acknowledge that it is not easy to find a quantitative and synthetic way (suitable for an abstract) to evaluate these advantages/impacts, I would recommend trying to do it by elaborating more (using also some numbers if possible) and/ or removing too general sentences.**

These two sentences were rephrased as follows:

This approach revealed similar apportionment results amongst methods, although the rolling PMF profile adaptability feature has been proven advantageous as it generated output profiles moving nearer to the truth points. Nevertheless, these results highlighted the impact of the profile anchor on the solution, as the use of a different anchor with respect to the truth led to significantly different results in both methods.

As the reviewer mentioned, the summary of this technical paper into an abstract is a difficult matter, and more quantifications or numbers could not be added here.

- **P2, L46-47: “The results of this comparison.... were scarce.”, it is redundant, please remove the sentence and/or integrate with the rest.**

This sentence referred to the multi-site comparison, whose results point to the same direction than those from the synthetic result. In order to promote this intention, the sentence was rephrased as follows:

The results of this multi-site comparison coincide with the synthetic dataset in terms of rolling-seasonal similarity and rolling PMF reporting moderate improvements.

- **P3, L104: what is “o their” meaning? is it a spelling mistake? In general, this sentence is hard to follow, consider to re-phrase it.**

This sentence was removed as it was confusing and did not add information. Here it is reproduced the paragraph without it:

(...) Some of them contain site-specific sources related to instrument artefacts or proximity to pollution hotspots. The factors identified at all sites are Hydrocarbon-like OA (HOA), (...)

- **P3, L114: I am not a native English speaker but the use of "concerning" as a comparative clause sounds strange to me. Please check here and also in other parts of the text.**

This word was replaced here as follows:

It works at a lower mass-to-charge resolution but it is more robust compared to the Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc, Billerica, MA, USA) allowing for long-term deployment.

It was also replaced along the document to ensure a better readability.

- **P4, L118: again, the term "granularity" sounds quite strange to me associated with timestamps, consider to replace with "size" or other.**

This word was removed from the text and that sentence is modified as follows:

The resolution of ToF-ACSM datasets (10 minutes) was averaged to 30 minutes (resolution of the Q-ACSM) to have a harmonised of timestamps.

- **P4, L146-148: the last two sentences of the paragraph appear redundant or not clear. Please, consider to re-phrase.**

The whole paragraph was rephrased for the sake of clarity:

The first step for the synthetic dataset creation was to select p (number of factors), POA and SOA spectral profiles from the High-Resolution AMS Spectral database (Crippa et al., 2013; Ng et al., 2010; Ulbrich et al., 2009) and multiply them by the time series of the same sources from the model output. The error matrix was generated following the same steps as for real-world data and real-world parameters were used as detailed in SI. For this purpose, the dataset used is that from the Zurich site which ranges from February 2011 until December 2011. Hence, the same CAMx outcoming time series period was used to generate the concentration matrix. Gaussian noise was subsequently added to the outcoming matrix.

- **P5, L168-171: the verb of the main clause seems to be missing. Please add it or rephrase.**

The missing verb was introduced as follows:

In order to reach an environmentally-reasonable local Q minimum, the implementation of constraints on Primary Organic Aerosol factors (POA), has been performed according to the COLOSSAL guidelines for source apportionment (COLOSSAL, COST Action CA16109, 2019) and the protocol from Chen et al. (2022).

- **P8, L265-266: what about the unconstrained application of PMF? Did you try? How unconstrained solutions perform in comparison with original synthetic values?**

This issue is extensively tackled in the first major comment. As a summary, the unconstrained solutions are less accurate than the constrained ones even though the latter also contain significant differences with respect to *truth*. For this reason, one should be aware that anchors do bias results but still reproduce better the *truth* than setting PMF runs free, so that anchoring should still be yet advised in source apportionment protocols.

- **P8, L275-280: As already mentioned, the discrepancies reported in this section of the paper are a major issue that deserves more emphasis and possibly more elaborations. The risk is that, considering that the ability to reconstruct even a synthetic dataset is low, someone could question the OA source apportionment protocols and argue that PMF results are in general not robust in apportioning real-world sources, at least the ones using a *priori* POA chemical features. I'm not saying this is true, but in my opinion the Authors should not underestimate the importance of these findings and spend more words to explain what their implications are in applying the OA source apportionment protocols in other studies (past and future). For instance, the analysis of the unconstrained-PMF runs and a comparison with the "best" solutions identified following the protocol could be worth of an assessment or at least comments.**

The comments required in this comment are shown in the following question.

- **P9, L303-305: here (or somewhere else in this section) a comparison with unconstrained PMF would be very welcome.**

The text was enriched by adding some more discussion as follows:

The influence of reference profile constraints might have enhanced the misattribution of the profiles, for example, imposing m/z44-to-m/z43 ratios has led to a significant difference in the degree of oxidation solution with respect to truth. Nevertheless, constraining profiles has provided more accurate solutions than unconstrained set-ups, as shown in Figure S2. These plots show how seasonal constrained PMF launches always present higher similarity to truth in terms of key ions ratios. Moreover, OA sources of unanchored runs were less robust due to lower reproducibility along accumulation of runs. By extension, rolling results are expected to reproduce the same results as it has been proven that both techniques' outcomes converge sufficiently.

And the conclusions:

(...) , as it differed significantly from the truth results when the anchor was significantly different to the truth profile. However, the use of profile constraints still provided solution closer to the truth than unconstrained PMF. Besides, the rolling method has been proven to give a more sensitive representation (...)

- **P9, L308: "m/z" is repeated.**

This change was already addressed in Anonymous Referee #1 minor comment number one.

References

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Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys.*, 11(13), 6465–6474, doi:10.5194/acp-11-6465-2011, 2011.

Please also note the supplement to this comment:

<https://egusphere.copernicus.org/preprints/2022/egusphere-2022-269/egusphere-2022-269-AC3-supplement.pdf>