

Interactive comment on “Positive Matrix Factorization of Organic Aerosol: Insights from a Chemical Transport Model” by Anthoula D. Drosatou et al.

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Received and published: 19 November 2018

(1) *This paper summarizes PMF analysis conducted on OA simulated from a chemical transport model and compared with AMS PMF factors for a single summer month. The authors find similar number and categorization of PMF factors as AMS, and provides further insight for the modeled factors. First, the primary (HOA-like) factor often contains some SOA and biomass OA. Second, two OOA components found are likely more oxygenated and less oxygenated, but are not always separated in volatility space. Finally (among other conclusions), SOA from various sources can be lumped into a single PMF factor. The manuscript is well-written and easy-to-read. Many of the technical*

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decisions (e.g., regarding the PMF error matrix for simulations) seem well justified, and there are additional insights regarding errors in source apportionment (mixing of sources or not extracting the source altogether) during periods of minor contributions. These results are of great interest to the atmospheric chemistry community and is therefore recommended for publication with minor revisions.

We appreciate the positive assessment of our work. Our responses and corresponding changes in the manuscript (in regular font) can be found below after each comment (in italics).

General comments:

(2) *The authors do not seem to explicitly mention this, but PMF appears to have been conducted separately at each site. One reason for applying site-specific PMF to measurements is that anthropogenic or biogenic SOA can be different at each site, but in these simulations they are effectively the same (e.g., a lumped species with C* belonging to anthropogenic POA is chemically the same across sites). However, the site-specific PMF is still desirable here for capturing site-specific proportion of source classes in each factor, and for comparison with site-specific AMS PMF?*

This is a good point also made by the first reviewer (Comment 3). Indeed, the PMF analysis presented in the original paper was performed for each site separately similarly to the standard analysis of field campaign measurements. This is now clarified in the manuscript. We have complemented this site-by-site analysis with analysis of the combined data in all sites. The application of PMF to this comprehensive set resulted in four factors: fresh biomass burning, other primary OA and two secondary OA factors (fresh and aged SOA). These could explain well the overall dataset. The number and character of the factors were similar with the site by site analysis, but there were differences in the composition and contribution of the factors. The results of this test are now discussed in a new section in the revised paper.

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(3) *The assumption that the components are "chemically different" is mentioned a couple of times, but it is not further discussed. For instance, the lumped species differ in C^* or reactivity with OH (depending on source class) so in many cases they are already treated as being chemically different. For the remaining lumped species, it's not unlikely that species from different source classes grouped in the same bin C^* are likely structurally different. However, a real chemical difference with respect to gross properties should not necessarily be required by PMF either, as it is possible to use isotope-labeled compounds in the analysis (which source-tagging effectively does here).*

This is an important aspect of our analysis that needs further clarification because it is the most important difference of our CTM-based approach and the AMS/PMF analysis of field data. As we provide PMF with the concentrations of 27 different predicted OA surrogate components, we implicitly assume that the corresponding measurement technique or techniques can separate and quantify these components. For the AMS, this may not be the case as two OA components (e.g., processed bbOA and aged SOA) may have quite similar AMS spectra. Of course, other measurement techniques, like the one mentioned by the reviewer, have different capabilities. We now provide a little more discussion about this assumption underlying our work.

(4) *Is the simulated OA size fraction used for PMF analysis equivalent to PM2.5 or what might be more directly comparable to the submicron fraction measured by AMS?*

We have used PM1 for our analysis for consistency with the AMS measurements. However, the difference in predicted OA in the PM2.5 and PM1 range is small in PMCAMx so our conclusions are also valid for PM2.5. This point is now explained in the revised paper.

(5) *Can the authors remark on the fact that the model, which does not include aqueous phase or condensed-phase chemistry, generates factors which agree on a "high-level"*

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with AMS factors? Is it that condensed-phase processes do not provide sufficient differentiation from covariations fixed by vapor-phase processes? Or could it a limitation of the sites/period studied?

This is a very interesting question also posed by the first reviewer (Comment 16). One could speculate that it may grouped by PMF together with the other aged OA. Unfortunately, we cannot test this hypothesis with the results of the current version of the model that does not include aqueous-phase production of SOA. It is clearly a good topic for future work.

(6) *The authors have previously published work integrating 2D-VBS into PMCAMx in the European domain; the model used here is apparently different and referred to as PMCAMx-SR - but the citation refers to a manuscript in preparation so it is hard to understand some of the details. How is this model different and why was the 1-D VBS selected? For this comparison with AMS, comparison of O/C ratios would have been useful to show further correspondence (or differences) between simulated and measured PMF factors (e.g., Aiken et al. 2008, Canagarathna et al. 2015); the authors may wish to add justification for the decision they made here.*

The reviewer is correct, the version of the model used here (PMCAMx-SR) is based on the 1D-VBS, similarly to the regular PMCAMx. Its major difference from its sister model is its ability to simulate separately the primary and secondary OA from different sources. Therefore, one can use different volatility distributions and aging schemes for organic compounds from different sources. This allows us in this work to use more up-to-date information about the bbOA properties. Use of the OA from the 2D-VBS in a similar exercise is in an excellent idea and could allow one to include the O:C in the analysis. This is the topic of ongoing work.

(7) *Others have found instances where the low/high volatility designation of PMF OOA do apply (e.g., Cappa and Jimenez 2010), so the conclusion (line. 512) that the nomen-*

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clature is misleading seems to broad - it may be rephrased that statistical separation of OOA by volatility cannot always be assumed?

The use of the volatility-based terminology suggests that there is a volatility threshold and OA components that are more volatile than this are grouped by PMF in one factor (e.g., SV-OOA) and the less volatile compounds in the second (LV-OOA). Our results both from this theoretical analysis but also from direct volatility measurements of AMS factors (Paciga et al., 2016; Louvaris et al., 2017) suggest that this is not the case. The so-called semivolatile factor may include very low volatility OA and vice versa the so-called low-volatility factor may include semivolatile material. We have rephrased the statement to indicate that it may be misleading in at least some cases.

Minor comments

(8) *Should the acronym PMCAMx be defined? For instance, CMAQ (Community Multiscale Air Quality Modeling System) is typically spelled out when first introduced in a paper.*

We have added the definition of the acronym PMCAMx (Particulate Matter Comprehensive Air Quality Model with extensions).

(9) *Regarding terminology, line 141: "primary organic compounds are all considered to be semi-volatile with C^* ranging from 10^{-2} to 10^6 $\mu\text{g}/\text{m}^3$ whereas Donahue, Robinson, and Pandis (2009) define SVOCs to have C^* ranging between 10^0 and 10^2 $\mu\text{g}/\text{m}^3$.*

We have rephrased this sentence that may confuse some readers about the definition of the term "semi-volatile".

(10) *Figure 7: Is this not more a reflection of the deviation in source apportionment for both measurements and simulation when the source contribution becomes small, rather than error that can be purely attributed to the apportionment from the simu-*

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lation side (as reflected by normalization to observed values)? Section 3.4 should correspondingly be renamed since "PMF error" can imply many things (error matrix, residual matrix, etc.).

The reviewer is right in general, however in our case the "measurement" error is zero as we use predicted values as inputs to the PMF algorithm. So this error is all due to the source apportionment algorithm. Our analysis suggests that this can be quite significant (a factor of 2 or more) for the smaller OA sources, so the corresponding estimates should be used with caution. We have changed the title of Section 3.4 to "PMF source apportionment error".

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-802>, 2018.

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