

Interactive comment on “Primary and secondary organic aerosol origin by combined gas-particle phase source apportionment” by M. Crippa et al.

Anonymous Referee #1

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This paper presents the combined PMF analysis of AMS and PTR-MS data from the MEGAPOLI campaign, following the previous work of Slowik et al. This is an interesting and largely well-written piece, with probably the two most interesting results being the apparent improvement in primary apportionments and the splitting of the SV-OOA in the summer.

While I do not disagree with the methodology or the results, I do have some serious misgivings about how the data is interpreted, relating mainly to the applicability of the data model and the interpretation of correlations as being causal when other explanations are possible. That is not to say that the hypotheses presented are necessarily incorrect, but they remain untested within this paper and should therefore be presented as speculative. However, these criticisms, while fundamental to the nature of the paper,

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only necessitate the expansion of discussions, the insertion of caveats and the toning down of conclusions.

General comments:

There is a very fundamental problem with the entire technique relating to the data model that is employed when combining the two instruments. The standard receptor model employed with PMF requires fixed-profile factors, therefore any combined AMS-PTRMS factors must strictly covary for them to be derived as factors. While this will not be an issue for most primary factors (providing the respective lifetimes of the particle and gas phase markers are both long enough that the receptor measurement is representative of the source), one would not expect explicit covariance for secondary aerosol and gas-phase oxidation products in general. Firstly, the different oxidation products in both the gas and particle phase are likely to be produced and consumed on different timescales, which will mean their time series will not necessarily match up. Even if the AMS and PTR-MS simultaneously measure SV-OOA component that is in dynamic equilibrium with the gas and particle phases, the exact proportion that exists within the two phases will vary with ambient temperature, which will remove covariance between the two instruments whenever the temperature changes (e.g. between day and night). This is not to say the technique of combining the two instruments is not of use (this paper shows it clearly is), but it is fundamentally limited and the authors should include more discussion of the data model when introducing the technique. This is particularly important given the prominence SV-OOA is given when discussing the motivation for the work. This also has implications for the interpretation of the relationships found; see specific comments for more detail.

Specific comments:

P8533, L5: I note that the error model for the PTRMS does not include a ‘minimum error’ term. This means that a signal with a low background could have been assigned unrealistically low errors in the low signal regime, which can in turn cause problems for

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PMF. The AMS gets around this with the use of 'electronic noise' or 'single ion error' terms in its error model (Ulbrich et al., 2009). While I am not saying that this has caused problems here, the authors should comment on what the lowest values the errors are estimated to be.

P8547, L16: There is a fundamental difference in how delta-E is calculated and the more conventional Q/Qexp parameter, in that with Q, the weighted residuals are squared before being summed. This will have the effect of delta-E placing greater emphasis on the variables with the lower weighted residuals. Given that Q/Qexp is the more commonly used parameter within the AMS community, the authors need to justify why they used delta-E instead of the difference between the two Q/Qexp for the different instruments (after removing the effect of C on the PTR data).

P8552: Another reason for the lack of PTRMS tracers for COA may be that there is a mismatch between the lifetimes of the particulate and gas phase tracers, perhaps caused by the COA being semivolatile. See general comments.

P8557, L22: The difference between LV-OOA and SO4 is initially stated to be because of differences in regional sources, so there is no need to invoke local sources to explain the differences in the diurnal profile. The diurnal trend for LV-OOA is quite subtle compared to the others, so is probably not statistically significant compared to the changes in airmass. The comment about local sources should probably be removed. Additionally, when showing diurnal profiles, the authors should specify whether they are using medians or means.

P8558, L27: I would tone down the comment regarding the source of MOA, as this is currently a contentious topic and would require further proof before it can be stated as fact (although this work will undoubtedly contribute to overall understanding). Recommend rewording "due to" to "possibly due to"

P8560, L3: I would argue that the separation of the two SV-OOA factors is more or less expected, given that the temperature will cause the profile to change with respect to

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the two phases (see general comments). This being the case, it cannot be argued that this is solely due to different formation mechanisms; the two factors derived could just be two endpoints within the continuum of the temperature-dependent partitioning of the same collective 'SV-OOA' existing in both night and day. This SV-OOA could have been produced from a single source and the two factors are merely a manifestation of the effect of temperature on the partitioning (note that in this context, SV-OOA represents an ensemble of species with different volatilities, so changes in the mass spectra with partitioning are also expected). While there is a relationship between the daytime SV-OOA and biogenic emissions, this is not necessarily causal; both the repartitioning of SV-OOA and biogenic emissions are directly linked to temperature, so the correlation in itself does not prove the daytime SV-OOA is produced from biogenics. I should stress that I do not want to devalue the importance of the observations presented, but that there could be a range of explanations beyond those offered by the authors, so they should be more cautious when discussing them.

P8563, L11: I do not agree with presenting the data in figure 9 as 'source apportionment' of VOCs, due to the lifetime issue given the general comments. For example, benzene is emitted by pollution sources, but it also has a very long atmospheric lifetime (probably longer than HOA), so it is not surprising that there is covariance with factors such as LV-OOA as well as HOA. However, this does not mean that LV-OOA is a 'source' of benzene, this is merely how it is manifested in this particular receptor analysis. As such, I fail to see the value of this figure.

Figures: It is odd that the authors should use a combination of stacked bar charts and pie charts when presenting data. Recommend using bars for the sake of consistency and ease of reading.

Technical corrections:

P8539, L2: "a predominant" makes no sense. Revise to either "a prominent" or "the predominant"

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P8544, L5: The authors use an uppercase delta for standard error here, but a lower-case s in equations 5 and 6. They should make this more consistent.

P8545, L7: Contrary to what is implied here, the PMF2 algorithm natively supports 'robust' mode. While the authors explain what they mean on page 8547, they should clarify the statement here.

P8546, L5: The mismatch between the instruments is not just to do with SNR; this is already accounted for by the respective error models. This is more likely to do with the relative abundance of covariances (mentioned later) and 'strong' variables within the two datasets.

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