Reply to Reviewer #1

We thank the Reviewer for carefully reviewing our manuscript and providing insightful comments. Below we address each comment point by point. For clarity we mark the reviewer comment in **blue**, our answers in **black**, and changes to the manuscript in **red**. Page and line numbers in our replies refer to the revised manuscript.

Secondary organic aerosol (SOA) is an important fraction of aerosol particles in the atmosphere all over the world. However, its formation via different chemical and/or physical processes remains largely unquantified, mostly due to incapacity of separating these pathways. In addition to the traditional measurement of SOA by aerosol mass spectrometry, in which the molecular fingerprint of SOA is seldomly preserved, the recent development of FIGAERO inlet does allow to explore the molecular information. A primary challenge for FIGAERO data analysis is that there are also several processes going on in parallel that is difficult to deconvolute. As also pointed out by the authors, vapor condensation and aerosol-phase (or aqueous-phase chemistry) are occurring simultaneously; the latter alone also contains many different pathways, such as oligomerization, hydrolysis, formation of organic salts, and etc. To address this major challenge in FIGAERO data analysis, the authors applied PMF analysis on such data sets for the first time, which convincibly shows that PMF is able to separate, to a big extent, different parallel processes. Thus, in general, I found this work containing enough new insights and recommend its acceptance in ACP. However, besides these insights, I have several comments to be addressed, as list below:

1. P2 L23-24, ". . .,thus reducing the mass transport limitation which hinders evaporation." This sentence reads ambiguous. It can mean that reducing the mass transport limitation hinders evaporation, which I believe the opposite of what the authors meant. Please rephrase.

The sentence has been rephrased as:

On the one hand, it will act as a plasticiser, reducing the particle viscosity (Renbaum-Wolff et al., 2013; Virtanen et al., 2010) and thus reducing the mass transport limitation in the particles. These transport limitations are responsible for the reduced evaporation under dry conditions.

2. P6 L24-26, Eq. 4-6. The Ratioexp seems to represent the explained fraction of the measured data by PMF. How does this differ from the traditional way of calculating the explained fraction (sum|Rij – Xij|)/(sum|Xij|)? What is the advantage of using this one?

The ratio of explained variance (variation) is a standard parameter used in the analysis of results when expressing measurement data with models. We decided to use this metric in addition to the examination of residuals between the reconstructed and measured data.

The explained, unexplained, and total variance (or variation) are normally calculated with the quadratic distance from the "expected" value (i.e., the average value for each ion i).

$$Var_{total} = \sum_{ij} (\boldsymbol{X_{ij}} - \bar{X}_{\imath})^{\mathbf{2}}$$

$$Var_{explained} = \sum_{ij} (\boldsymbol{R_{ij}} - \bar{X}_{\imath})^2$$

$$Var_{unexplained} = \sum_{ij} (\boldsymbol{X_{ij}} - \boldsymbol{R_{ij}})^2$$

$$Var_{total} = Var_{explained} + Var_{unexplained}$$

Then the ratio between $Var_{explained}$ and Var_{total} can be interpreted as R^2.

When using these equations with our data, the sum of $Var_{explained}$ and $Var_{unexplained}$ was not equal to Var_{total}, but much smaller for PMF solutions with low factor number and larger for solutions with higher factor numbers. The latter leads to ratios >1 which are not meaningful in this context. Also, if the calculation was performed in the other dimension, i.e. calculating the variance with respect to the average value for each observation j, the values for $Var_{explained}$ / Var_{total} changed.

When using the absolute distances instead of the quadratic this behaviour changed and $Var_{explained} + Var_{unexplained} \approx Var_{total}$. Thus, we decided to use this metric as a compromise.

3. P8 L18, Eq.8. Based on the observation of model residue, you decide to use CNerror instead of PLerror for uncertainty matrix. As shown in Figure S1, CNerror is about 1-2 orders of magnitude smaller than PLerror. However, with the CNerror, Q/Qexp got very close to 1, as shown in Figure S2, which seems to indicate that CNerror is the true error or close to that. Do you have any idea about the reason?

It may be that the overestimation of the error with the PLerror scheme has a stronger impact on the overall Q/Q_{exp} value than the underestimation in the CNerror case.

We observed that adding the blank measurements to the dataset decreased the Q/Q_{exp} values in the CN case. Note that in the low- and medium O:C case (where we had 4 blank measurements) approx. half of the datapoints are dominated by noise as no significant signal was detected.

4. P11, L1-4. It seems that the criterion of justify the type V factors is its little change in Tmax with aerosol age or water content. As the authors stated "But this method can be applied to e.g. ambient FIGAERO-CIMS measurements as well" In the abstract (P2 L5), it is important to suggest how to determine the type V factors when applying PMF on ambient data sets, where aerosol oxidation degree (O:C), aerosol age and water content are often correlated.

The main criterion for V-type factors is indeed the shape and small change in T_{max} in comparison to the B- and D-type factors. This characteristic persists when looking at ambient data. We have just started applying this new method to an ambient dataset which will be the topic of a future publication.

5. P11 L10-14. I have difficulty in understanding why V factors in different experiments with similar Tmax may have significantly different compounds. For example, LV5, MV4, and HV4 seem to have similar Tmax but very different average elemental composition. Can you give more explanations?

Volatility (or vapour pressure) is primarily controlled by the detailed molecular structure (i.e. functionality) of a compound. There are many different compounds that have similar vapour pressures so they would fall into the same VBS bin or here V-type factor. Assume different compounds A, B, C, D which all have the same order of magnitude C*. If one SOA type contains A and B but no C and D while the other SOA type contains only C and D, a PMF analysis of the thermal desorption data of these two aerosol types will yield two factors with the same T_{max}. One will contain A and B while the other has C and D. What we find a bit surprising is that changing the oxidation field for a single precursor has such a strong effect on the composition. One possible explanation is that the HO_2/RO_2 chemistry may be strongly affected by increasing the OH exposure by an order of magnitude.

Also prompted by the request of Reviewer #3 we decided to add two section in the SI material (1.3 and 1.4) elaborating on the effect of different SOA types on our PMF analysis.

6. P13 L20-23. Likewise, same molecules (e.g., C8H10O5) can be separated into different V factors. Together with Point 5, do these observations suggest that the degree of thermos-decomposition may play an important (even a major) role in the final detected FIGAERO spectra?

For our dataset there are two main reasons why a single detected composition (e.g. C8H10O5) is split over several factor: 1) there is a direct desorption and thermal decomposition part (possibly from a range of different low volatility precursors). 2) there are several conceivable isomers of that composition. Please remember that any 1D mass spectrometer can only provide information on the sum formula of a molecule but not the functionality within the molecule (i.e., the connections between the atoms). This is why we avoid speaking of molecule or compounds in the manuscript.

As we state in the conclusions, thermal decomposition plays an important role for desorption temperatures above ~120 C. This should definitively be considered when analysing integrated FIGAERO-CIMS mass spectra and e.g. using the detected sum formulas in parameterisation to calculate vapour pressure. This has been pointed out also in earlier FIGAERO publications (e.g. Lopez-Hilfiker et al., 2014; Stark et al., 2017). With PMF we can now separate the contribution of direct desorption and thermal decomposition for each detected ion/sum formula.

7. P14 L3-4. Do you have any hint to explain why highOC SOA seems to be more influenced by aqueous-phase chemistry?

We elaborated on possible chemical reactions in our previous publication (Buchholz et al., 2019). Briefly, there we speculate that in the highOC case a larger fraction of organic (hydroxy-)peroxides is present. Those are sensitive to hydrolysis which will initiate a range of reactions in the aqueous phase. As peroxides are also thermally unstable, they are most likely detected as their non-peroxy analogues in FIGAERO-CIMS which complicates interpretations. We now mention this at the start of section 3.3:

As discussed by Buchholz et al. (2019), the different behaviour of the highOC SOA is most likely due to higher fractions of (hydro-)peroxides in the particles caused by the much higher HO_2 concentrations in the OFR at the highOC oxidation conditions. Most peroxides are sensitive to hydrolysis which will initiate a range of reactions in the aqueous phase. The low volatility products of these reactions thermally decompose to similar fragments as did the peroxide precursor. Thus, the same groups of ions are detected but at a higher T_{desorp}.

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