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# *Interactive comment on* "Deconvolution of FIGAERO-CIMS thermal desorption profiles using positive matrix factorisation to identify chemical and physical processes during particle evaporation" *by* Angela Buchholz et al.

**Anonymous Referee #3**

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In this work, Buchholz et al. demonstrated for the first time the application of positive matrix factorization (PMF) on high-resolution FIGAERO-CIMS data. They were able to identify distinct volatility classes, background, and decomposition products as PMF factors. Their results also offer additional confirmation of the effects of aerosol water on partitioning and particle-phase processes. Overall, the manuscript is well written and the approach described is novel. However, I have some concerns with the PMF design, experimental design, and data interpretation as described below. I would recommend the manuscript for publication in ACP if these comments are addressed.

PMF design and interpretation

2.3.1, page 7, line 19-22. The advantage of PMF is that it requires no a priori information. Pre-grouping thermograms based on knowledge about the SOA precursors, extent of aging, and aerosol water content defeats the purpose of using PMF, if not for laboratory sample then certainly for ambient samples. The advancement brought by the FIGAERO thermogram PMF in its current state is perhaps overstated. This limitation should be discussed in the manuscript. The analysis could also be carried out further to involve different SOA types all at once to validate its usefulness in a broader context.

3.1. Page 11, Line 10-13: Why is not a consistent factor identified across all SOA types (L, M, H, x dry, humid)? Is it expected that, for example, species that make up LV1 have negligible contributions to the overall SOA mass and evaporation behavior under the MediumOC ("M") conditions? It seems to me that there is significant factor blending here. Have the authors tried to combine the different SOA types (e.g. L and M) and see if the different factors (e.g. LV1, LV2, MV1, MV2) can be retrieved all the same?

Page 12. Line 3 to 7: Filter/instrument-related background should be consistent for low- and mediumOC samples. The direct evaporation ions after isothermal evaporation observed in lowOC samples should therefore be expected to appear in the mediumOC sample as well, but why do they not?

Experimental Design

SI 1.1: Some experimental designs are unclear. Did the collection of the 0.25 hr isothermal evaporation sample start immediately after filling up after size selection? Was the t_0.25hr aerosol collected directly at the outlet of the DMA column, or was the aerosol drawn through the RTC first?

Evaporation of aerosol already collected on the filter during the 15 minute collection period is likely to be significant for t_0.25hr samples, and should therefore be taken

into account. It would be good to show, at least qualitatively, how much effects this has for different evaporation timescales.

Considering the potential artifacts introduced by the use of a stainless RTC (as mentioned by the other referee), I was surprised that the authors did not attempt (or mention) isothermal evaporation directly over the FIGAERO filter, as has been done in some previous studies (e.g. Schobesberger et al. 2018). It seems to me a lost opportunity to monitor gas-phase changes that can corroborate particle-phase observations. I would like to see a comparison between isothermal evaporation RTC vs. FIGAERO filter results, at least under dry condition, that shows if there is any systematic biases introduced by the use of RTC.

Minor comments

Figure S5: Were the labels for MV1 and MV2 switched? It is also surprising that the Tmax increases going from ELVOC, LVOC, to SVOC categories, if the labels are indeed correct.

Page 2. Line 5: The application of this technique to ambient data is not shown or discussed in the manuscript. This sentence should be removed.

Page 2. Line 6: What is meant by "physical source"?

Page 4. Line 7-9: Operational details of the DMA column should be mentioned here.

Page 4. Line 9-11: Potential artifacts related to the use of stateliness steel chamber, e.g. peroxide decomposition, should be mentioned.

Page 7. Line 2-3: What is the reason for using the absolute value instead of the squared value?

Page 9, Line 27-29: Please remove the "great"s.

Page 10, Line 4: Ulbrich et al., 2009 has already shown that the change in Q/Qexp with respect to the number of factor is a more reliable indicator than Q/Qexp. This is

mentioned later in this manuscript, but should perhaps be moved up to this section here.

Page 10, Line 13-16: Maybe a quotient could be defined here, such as the incremental increase in ion behaviors well-captured (what is the criteria for "well-captured"?) vs. number of factors chosen. What is correlation of the two for the PMF solutions obtained here?

Page 11, Line 17-19: Table 1 would suggest that background ions were dominated by organic residues instead of fluorinated compounds. Which is the case here?

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