

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 #2

Received and published: 22 January 2020

Summary:

The authors performed positive matrix factorisation on FIGAERO-CIMS data of SOA before and after isothermal evaporation, under both low and high humidity. They provide a detailed description of their methods including two ways of estimating PMF errors, which is useful and interesting. However, I found some of their interpretations to be a bit unconvincing or not completely evaluated. A lot of the analysis revolves around the highOC case under wet conditions, but I have several questions as to the quality of their PMF solutions for that case, and whether the aerosol in that case is even

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representative of anything that would be present in the atmosphere. The authors also haven't convinced me that PMF of thermograms could provide more information than one could get from single ion thermograms, so more discussion is needed to show how they're actually advancing the field. I think this work could be suitable for publication in ACP if these major revisions can be addressed. I include several major comments as general comments, followed by some more specific and technical comments.

General Comments:

1: Looking at Fig S7, what jumped out at me was that typically all of the factors are decreasing in absolute magnitude after 4 h compared to 0.25 h of evaporation. My first thought was that I would have expected the lower volatility factors to remain more constant, and just the higher volatility factors would evaporate. However, I think you could explain that all factors should lose at least some absolute mass because the total amount of OA will be decreasing, and that will change the equilibrium partitioning causing even the lower volatility compounds to evaporate. I think it could be really interesting if you would calculate how much of each factor you expect to evaporate, using their estimated volatility from the FIGAERO combined with the change in OA mass measured after evaporation, and compare this with how much you measured to evaporate. Do they match? This might be outside the scope of your manuscript, but it wouldn't take too much effort and would add value to the paper if you decide try it. It would give the reader more information with which to judge how well PMF actually is able to separate compounds of different volatilities.

2: Following up on my previous comment, one piece of information you've given the reader with which to judge the ability of PMF to separate compounds of different volatilities is table 2, the T_{\max} values for each factor for each experiment. In addition, you've described in the abstract page 1 line 29 how "Thus, the factors identified with PMF could be interpreted as volatility classes." However, I would expect that if PMF is truly separating compounds of similar volatilities into each factor, that the factor would maintain roughly constant T_{\max} (and roughly constant desorption shape) for each of

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the dry and wet experiments at both evaporation times. I would say that your factors for the lowOC and mediumOC cases maintain roughly the same T_{max} and shape across all wet/dry and 0.25,4 h cases. The only thing that changes is the magnitudes of the factors. This appears to be supporting evidence of the argument that PMF is separating compounds successfully by volatility. But for the highOC case, it doesn't appear to be successfully separating the volatility factors. The T_{max} for most of the factors changes substantially between dry and wet cases and after evaporation. This suggests to me that the factors are somewhat blended together. Another thing that leads me to that conclusion is that a lot of the mass gets shifted to the background HB1 factor during the wet,4h case, whereas the HB1 factor was much lower during other highOC cases. A background factor shouldn't change like that from case to case. I don't doubt that it is likely to be aqueous chemistry causing these changes in the PMF factors, but you haven't convinced me that PMF is giving you real and useful information about the process, particularly for the highOC/wet case which you're using as evidence of aqueous chemical changes. Maybe you need to revisit your PMF methods and see if you can find a 'better' solution, otherwise please explain your interpretation of the chosen factors in context of the points I've raised here.

3: You have demonstrated that PMF can be useful for pulling out background/contamination signals from thermograms, and also that higher volatility factors evaporate preferentially over lower volatility factors (though you could also say the same using just T_{max} of total signal). But, I'm not sure I see much discussion of which scientific insights you're gaining by doing PMF on thermograms. E.g., PMF on aerosol mass spectrometer (AMS) data can be used for general source apportionment. All of your aerosol comes from the same source in this particular experiment, but is there any information gained through PMF that could indicate anything about the aerosol formation/evaporation process? Are there factors that can be used as tracers for aqueous chemistry, that could be searched for in ambient datasets? Please expand on how you are making specific scientific advances using thermogram PMF that we can't get using other non-PMF methods.

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4: The highOC/wet case that you're using as evidence for aqueous chemistry is a particular case, in that the aerosol you're producing using the OFR is highly oxidized, and that oxidation happened much faster (and possibly through differing chemical pathways) than would happen in the real atmosphere. Thus, the specific molecules that comprise the aerosol are probably not representative of anything you'd get in the atmosphere. So, while the wet cases for lowOC and mediumOC illustrate that the diffusion limitation to evaporation is decreased in aqueous aerosol, you are suggesting that aqueous chemistry doesn't happen much except for the highOC aerosol, which may no longer be relevant for the atmosphere. Can you add some discussion of how your results relate to atmospheric aerosol?

Specific Comments:

Pg. 4 Ln. 9: Which size particles were you selecting in the nano-DMA? Also, it would be useful to mention to flow rates of your sheath and sample flows in the DMA, the ratio of which will determine just how quasi-monodisperse your selected particles become.

Pg. 4 Ln. 13: You have already assigned the acronym OFR, so you should avoid writing out the words oxidative flow reactor hereafter.

Pg. 4 Ln. 17: I assume the 0.25 h evap time for fresh particles is due to the collection time on the filter? Please make this clear, as it may confuse readers unfamiliar with FI-GAERO operation, and they may wonder why you didn't sample fresh particles without a 15 min delay.

Pg. 11 Ln. 20: Have you considered summing the LB1, LC1 and LC2 factors together? It could be that PMF is splitting up the background factor before pulling out the last of the V-type factors, so you could just recombine the split background factors.

Pg. 13 Ln. 1: How have you taken into account the effect of the stainless steel RTC walls on changes in VFR? Could there have been different wall effects during dry vs. wet conditions, i.e., different uptake coefficients to the wall surface? When it's humid

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enough to have one or several monolayers of water molecules on the walls, they could appear very different to a gas or particle than if it's bare metal.

Table 2: It would be informative if you present here and discuss elsewhere the estimated volatility of each of your V-type factors (by converting their T-max to volatility).

Figure 9: Could you subtract the background signals from the total, such that the V-type factors will add up to the light blue lines? It could be visually easier to understand then.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-926>, 2019.