Authors’ response to comments received to manuscript *“Comparing SOA volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO-CIMS measurements”*

We thank both reviewer #1 and reviewer #2 for reviewing our manuscript and for the insightful comments that helped to improve the manuscript. Below we address the comments presented by the reviewers. The comments of the reviewers are **shown in bold,** our answers are shown as normal text, and the changes made to the manuscript are *shown in italic*. To improve readability we have numbered the comments of reviewer #2. All the line numbers given refer to the revised version of the manuscript.

Please note that the parametrization used for calculating effective saturation mass concentration C^* from the desorption temperatures of each PMF factor is different in the revised version of the manuscript than in the ACPD version of the manuscript. The parameterization used in the ACPD version corresponded for a different type of FIGAERO and we have now revised the results using a parametrization applicable for the FIGAERO used in this study. The parametrization used in the revised version results in lower C^* than the parametrization used in the ACPD version with the same desorption temperature input. This correction did not change our main conclusions. However, the new parametrization affects the results discussed in the comments 10 and 15 by the reviewer #2.

Reviewer #1

In this manuscript, Tikkanen et al. compare SOA volatility derived from two different analyses: isothermal evaporation data and PMF applied to FIGAERO-CIMS data.Volatility is a critical property of organic aerosol, and I agree with the authors that the volatility data from FIGAERO-CIMS measurements have been under-utilized. This manuscript focuses on the comparison of the FIGAERO-CIMS PMF volatility data to isothermal evaporation data; the details of the FIGAERO-CIMS PMF volatility analysis are described in another manuscript currently under review (Buchholz et al., 2019 https://www.atmos-chem-phys-discuss.net/acp-2019-926/). It seems to me that this manuscript can only be accepted if Buchholz et al., 2019 is also accepted. I also request that my specific comments below be addressed before publication of this manuscript.

The companion manuscript Buchholz et al. (2019b) is now at the “Editor Final Decision” status after some further minor revisions.

1. The authors use data from previously conducted experiments in which SOA wasformed from alpha-pinene and ozone/OH. By varying experimental conditions, the SOA produced had low, medium or high O:C. Here, the authors only use experiments when the SOA formed had low or medium O:C. This choice is currently not explained or justified in the manuscript. In my opinion, the dataset utilized here is fairly limited,and the analysis would benefit from inclusion of these additional high O:C data. For

Example, overall the authors find that the agreement between the two volatility analysis better for intermediate O:C than for low O:C, and I am curious about the agreement at high O:C.

Answer: The detailed analysis of the high O:C evapogram and particle composition data presented in Buchholz et al., (2019a and 2019b) strongly suggests an important influence of particle phase chemistry for these particles in the wet cases. For example, Buchholz et al., (2019a) show that one of the PMF factors has a significant contribution to the total thermogram in the wet RTC sample (sample taken at the later stages of the evaporation) even though the same factor is virtually non-existing in the fresh sample. This means that compounds were being formed during the isothermal evaporation experiment.

Including the high O:C results in our manuscript would require particle phase chemical reactions to be included in the model. Not enough is known about such reactions and therefore assumptions would need to be made about properties of the reaction products and the extent of the particle phase chemistry happening during the evaporation of the particles. This would lead to considerable uncertainty in the results. In our manuscript we wanted to keep the analysis as simple as possible and therefore elected not to include the more complex high O:C cases to the manuscript. Instead we included only the low and medium O:C cases for which Buchholz et al., (2019a,b) did not observe signs of significant effects from particle phase chemical reactions We have added the following explanation to line 91:

The closer analysis of the high O:C experiments suggest particle phase reactions during the evaporation (Buchholz et al., 2019a,b). To avoid the uncertainty that would arise from unknown particle phase reactions, we chose not to include the high O:C data in our analysis.

2. The main takeaways from the manuscript should be clarified. The authors state in the abstract that "FIGAERO-CIMS measurements analyzed with the PMF method area promising method for inferring organic compounds' volatility distribution". The more detailed results point to the method working better under some conditions than others.It would be useful if the authors could make more concrete recommendations for future use of this method (PMF applied to FIGAERO-CIMS data) to obtain information on organic aerosol volatility.

Answer: This comment is also linked to the first and third comment made by reviewer #2 about the discussion part of our manuscript. We have edited the discussion to better frame our findings. Please see our response to Reviewer 2.

Editorial comments: There are several typographical and grammatical errors in the manuscript. I include a list of examples below:

Line 19: “volatility distributions derived the two ways are comparable within reasonable assumption”

Line 233: “and only evaporated th at different conditions”

Line 311: “To investigate the observed discrepancy more detailed”

Line 376: “In this section we compare VDPMF,opt of the fresh samples to VDPMF ofthe RTC sample to study are the two VD comparable.”

Line 521-522: “thermogram data is good estimating the volatility distribution of organic aerosols”

We thank reviewer #1 for pointing out these errors. We have corrected the ones presented here and also other typographical errors we found in the manuscript.

Reviewer #2

Review of acp-2019-927 ”Comparing SOA volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO-CIMS measurements” by Olli-PekkaTikkanen, Angela Buchholz, Arttu Ylisirniö, Siegfried Schobesberger, Annele Virtanen,and Taina Yli-Juuti

This paper describes a study that compared volatility distributions derived from direct evaporation measurements to estimates derived from measurements made using a FIGAERO-CIMS. Given the central role gas-particle partitioning plays in determining the amount of organic aerosol, this is an important topic. The FIGAERO-CIMS provides information on composition as a function of evaporation temperature but it has not been widely evaluated in the context of figuring out volatility distribution of complex aerosols.The paper describes a detailed analysis of previously published, relatively limited set of data – SOA formed from alpha-pinene formed in a oxidation flow reactor at two differentO:C levels (low and medium). They consider low and high relative humidity and two different residence times. The very limited amount of the data is a real limitation to the paper.

1. Major comments/issues that broadly apply to the manuscript –I found the paper to be a super detailed methods paper. It was not clear why it was submitted to ACP and not a journal like AMTD or AST. Based on the way the paper is written now, those journals are a better fit for the manuscript. My feeling is that while the topic of organic aerosol volatility is relevant to ACP this paper seemed is a very narrow and specialized for that journal (to me it read like a physical chemistry methods papers).

Answer: In our manuscript we show that volatility information derived from FIGAERO-CIMS data is in agreement with the volatility information derived from isothermal evaporation experiments. Considering the recent popularity of the FIGAERO-CIMS instrument in laboratory and atmospheric studies, we feel that this finding is of general interest to the ACP audience.

We agree that the presentation of our manuscript is somewhat more technical than the ACP audience may expect. We have edited the discussion part of our manuscript to better frame our findings and balance the text against the technical details of our study.

2. I had a hard time interpreting some the figures (e.g. Figure 2), which were often very detailed and contained many comparisons. For example, do you really need to show the three different VDevap results on Figures 2, 3 and 7 3 given they are basically the same – seems like an SI detail to help the focus the figure on what is important. This results in the paper have a bit of kitchen sink feel.

Answer: Thank you for this suggestion which helped as to clarify the presentation. We have edited the figures and tables the following way:

- We moved the old figures 2, 3, 4, 5, 6 and 7 and tables 2 and 3, which show the VD_{PMF} derived assuming different sample evaporation times to the supplementary material.
    - The new figures 2, 3, 4, 5, 6 and 7 and table 2 show the analysis only at the mean PMF sample evaporation time for the fresh samples (and at minimum PMF sample evaporation time of the RTC samples in figures 4 and 5 and table 2).
    - The old table 2 has been moved entirely to the supplement
    - The captions of the figures 2, 3, 4, 5, 6 and 7 have been edited to describe the new figures better

Due to these changes in the presentation of the figures and tables we have also edited the main text where the figures are described in the results section.

3. A closely related comment to the previous one, while the text described the figures and the results, I found it lacking in discussion of the results were telling us, specifically around this technique. There was too much focus on describing the data versus what the data are telling us about the technique and aerosol volatility. If it is to

be accepted in ACP, I think the paper should be extensively rewritten to make it more accessible and understandable to the ACP audience.

Answer: We have expanded the discussion and conclusion parts of the manuscript to make it more accessible to the general ACP audience and to highlight the main findings. The changes are on lines 505-507, 515-517, 519-523, 540-543, 548-550, 554-557, 562-563.

4. I spent a fair bit of time on the paper and got repeatedly bogged down. E.g. essentially all the tables can easily be moved to SI(maybe keep a very collapsed version of Table 1) because they are likely not of interest to a general ACP reader.

Answer: Please see our answer to comment 2

5. The very limited data set (a handful of conditions) seems like a pretty large limitation.Even for this limited set of data the method appears to not work so well for some conditions (e.g. low O:C in Figure 4b). There was also no discussion of experimental repeatability. There is probably enough data to justifying publication but this limitation of applying to a very narrow set of systems (and potentially overinterpreting the results) needs to be explicitly stated.

Answer: In figure 4 we compare the PMF VD with C* calculated from peak temperature value (T_{max}) of each factor to VD_{evap}. As noted in the results section, the T_{max} value is not adequate for calculating C* when detailed particle dynamics (i.e. evaporation) is modelled. The $VD_{PMF,opt}$ whose C* values are optimized to match the evaporation data is able to capture the evaporation dynamics. The optimization fails only when we assume that the PMF sample represents the evaporating aerosol particles at the start of the fresh sample collection interval Overall the volatilities from FIGAERO-CIMS and isothermal evaporation agree for all our cases as long as the uncertainties in C* are taken into account.

We agree that the data sets available is a narrow one and we have added a note about this limitation in Section 5 lines 540-543

We compared the two methods for obtaining the volatility distribution data for two different particle compositions and two evaporation conditions. The results are promising and suggest that the methods provide volatility distributions that are in agreement. We note that the data set available here is limited and additional investigations on comparing the methods are desirable in the future.

The base case (low O:C a-pinene) has been studied in our lab in five separate measurement campaigns and the isothermal evaporation is the same within measurement error in all cases.

Also in a later campaign, which is not part of this study as the detailed design and settings of the FIGAERO-CIMS were different, we did repeat FIGAERO-CIMS measurements of the same type of aerosol on multiple days. The behavior of the identified PMF factors is the same between the different samples – only the contribution of background and contamination factors changed significantly as the circumstances changed on different days (e.g. switching to a new filter in FIGAERO). We therefore have a good reason to expect that the results presented here were repeatable even though repeated experiments were not included in this study.

6. FIGAERO-CIMS – Given that it uses chemical ionization with iodide as the reagent ion as opposed to electron impact ionization, there are always concerns about mass closure. What fraction of the SOA mass is being detected by the instrument? If a large fraction of the aerosol mass that is not, then that seems like a big problem. This issue needs to be explicitly discussed, including its implications for measuring volatility. More Molecular ions is a big advantage, but not measuring a large fraction of the material seems like a huge limitation as you are trying to draw inferences about the bulk aerosol based on characterizing only a limited fraction of the aerosol.

The I^- anion in an iodide CIMS preferably clusters with molecules which contain hydroxyl-, hydroperoxyl-, carboxyl- or peroxycarboxyl- groups in their structure. Most products of the reaction of a-pinene with OH or O_3 contain two or more of these functional groups. Thus, the majority of them will be detectable with iodide CIMS even though it is more selective than EI. Mass closure studies for a-pinene SOA generated in a smog chamber have been conducted by Isaacman-VanWertz et al., (2017, 2018) comparing FIGAERO-CIMS to measurements with an SMPS (non-mass spectrometry technique) and a High-Resolution time of flight Aerosol Mass Spectrometer (AMS, Aerodyne research Inc., EI ionisation). They observed very good agreement for the detected particle phase carbon if FIGAERO-CIMS was calibrated as they laid out in the Supplement Material to Isaacman-VanWertz et al., (2018). The compounds produced in our study are comparable and thus a similarly good mass closure could be expected if similar sensitivity calibrations had been conducted for our FIGAERO system. However, such calibration is onerous and not available for the datasets at hand. So, by using uncalibrated FIGAERO-CIMS data here, we are implicitly assuming that the sensitivity towards individual compounds is uncorrelated to the compounds' volatility. We are not aware of published research against which to clearly test that assumption, but it appears plausible that less volatile compounds tend to be detected at higher sensitivity (Iyer et al., 2016; Lee et al., 2014). To our aid comes the maximum sensitivity (corresponding to ionization at the kinetic limit), which is obtained, e.g., for most di-carboxylic acids (#C>3). But it is likely that a bias is introduced that shifts FIGAERO-derived SOA compositions towards lower volatility. Indeed, if such a bias was accounted for, it could bring the evapograms modelled using VD_{PMF} closer to the observations, as in particular the initial (fast) evaporation of relatively volatile material may be systematically underestimated when relying on (uncalibrated) FIGAERO data [Note that such bias would less clearly apply to observed desorption signals that are due to thermal decomposition, so, e.g., PMF factors associated with decomposition would still lead to high estimates when their T_{max} is translated to C* (i.e. opposite bias, towards higher volatility), as discussed in Section 3.1.]

We have added the following to the revised version of the manuscript to lines 113-116 to clarify:

Previous studies using FIGAERO-CIMS with iodide as the reagent ion found 50% or better mass closure compared to more established methods of quantifying OA mass (albeit with high uncertainties; (Isaacman-VanWertz et al., 2017; Lopez-Hilfiker et al., 2016). Therefore, it appears that the bulk of reaction products expected from a-pinene oxidation contains the functional groups required for detection by our FIGAERO-CIMS.

And to lines 197-202:

One more potential source of bias is our implicit assumption of a constant sensitivity of the CIMS towards all compounds, which follows from the lack of calibration measurements for our datasets (which indeed is a challenging endeavour; e.g., Isaacman-VanWertz et al., (2018)). It is plausible that less volatile compounds tend to be detected at higher sensitivity (Iyer et al., 2016; Lee et al., 2014), up to a kinetic limit sensitivity. Consequently, a volatility distribution derived from FIGAERO-CIMS thermograms may be biased towards lower volatility (C^* bins), at least for compositions not associated with thermal decomposition.

7. A closely related FIGAERO-CIMS concern – The FIGAERO only ramps to 200 oC (line200). This is likely much too low to evaporate all of the SOA. Can the authors estimate what fraction of mass is evaporated? Do they account for that in any way? This issue needs to explicitly addressed in manuscript.

Answer: As described in the reply to the previous comments, with appropriate sensitivity calibrations, the FIGAERO instrument ramping up to 200 °C gave mass closure with other instruments.

Our (as well as other's, e.g. Mohr et al., 2018) C* calibration suggests that at 200 °C the corresponding C* value is ~10^{-14} µg m^{-3}, meaning compounds with this C* value will desorb at that temperature. This means that the recently defined class of ultra low volatility compounds (ULVOC, Schervish and Donahue, 2020) starting from C* values of $10^{-8.5}$ µg m^{-3} would still be detected. Additionally, one has to keep in mind that many of these E/ULVOC, especially dimers, will decompose at temperatures below their theoretical desorption temperature. The thermal decomposition products will have a much higher volatility and are detected as such. Most of the compounds assigned to the D-type factors are products of such decomposition. This is discussed in section 3.1.

8. Uniqueness of fit – The paper takes a very empirical approach of fitting data to extract volatility distributions. That is fine and expected given the complexity of the aerosols. However, the number of data points is often quite small, comparable to the

number of free parameters. For example, Figure 4 shows~7 data points that are fit to determine VDevap. How many free parameters are in the VDevap model?

Line 516 indicates that you are fitting both C* and viscosity parameters – that is a lot of free parameters given the amount of data. The fit is clearly very underconstrained. The result is that there are likely many other solutions are close to the nominally best solution. This is an optimization problem and I suspect that the optimization function looks more like a plateau then a sharp peak therefore (within experimental uncertainty) there are likely many good solutions.

While I gave one example where this occurs, this is a general issue with the paper. For example, I am concerned about the same problem for the FIGAERO PMF approach, because that also have many free parameters. Presumably all of these solutions are reasonably close across the data, but I suspect with diverge as one extrapolates away from the data. This is a major issue with these sorts of empirical approaches. The paper needs to explicitly address this issue.

Answer: Here we address only the optimization done to high RH data. The comment refers also to low RH data which we will address in comment 16 where the optimization to low RH data is brought up again.

In an optimization run the amount of data point is small compared to the number of free parameters. When VD mole fractions are optimized based on only the evapogram data (VD_{evap}) the number of free parameters is equal to the number of VD bins minus 1 as the mole fractions must sum to one. When the C^* values are estimated from the high RH data the number of free parameters is equal to the number of PMF factors. However, in the latter case we are not optimizing a completely unconstrained model to the measurements. The C* values are given constraints from the PMF analysis and our goal is to inspect if it is possible to explain the observed evaporation with these values.

Figure AR1 show how the estimated C^* values are distributed among the 50 independent optimization runs performed for each fresh sample and mean sample evaporation time. The figure show that when the C^* of a factor affects the evaporation dynamics i.e. the minimum and/or maximum value of a factor is inside the red dashed lines the C^* values do not change much between different optimization runs. Note that the spread of values can become wider for a factor when its contribution to the total signal is close to zero (e.g. factor MD1a Fig AR1a or LD1a in Fig AR1b).

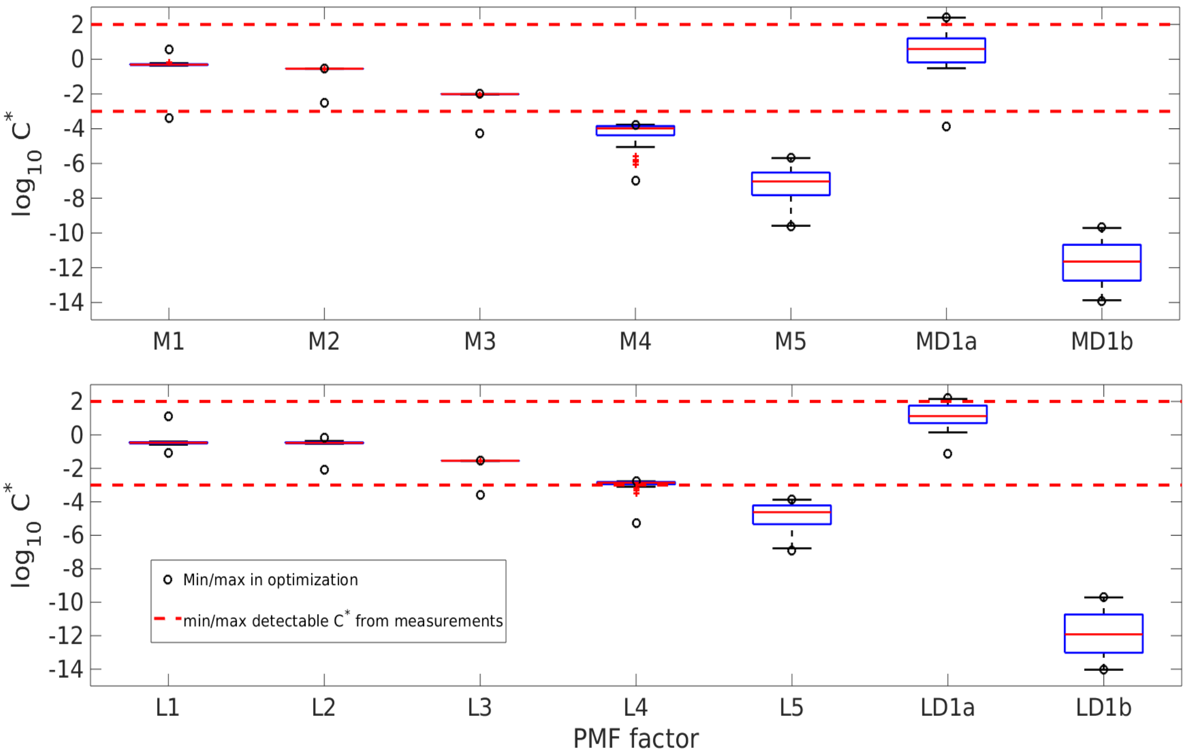

Figure AR1: Box plots showing how the estimated C* of PMF factors are distributed in 50 independent optimization runs of high RH fresh samples. a) medium O:C mean sample evaporation time b) low O:C mean sample evaporation time Black circles show the minimum and maximum possible value allowed in the optimization (based on the thermograms of the PMF factors) and red dashed lines show the minimum and maximum C* value that can be estimated from the isothermal evaporation measurements.

9. Here are some specific (but not exhaustive) comments (I spent several hours on this review but was unable to sort through all the details, even though I have published a fair bit on the topic of organic aerosol partitioning).

Line 65 – The paper highlights inconsistency between growth and evaporation experiments. Ultimately C* is a thermodynamic property (certainly at the molecular level) so these inconsistencies point to changing aerosol composition or other properties. Some of this sort of framing may be useful. I.e. if the volatility distribution of the aerosol is really changing, then presumably this reflects some other changes in composition that alters the underlying C* values. Alternatively there could be issues with the kinetics of evaporation. The authors are familiar with all these issues but the introduction might be improved with this framing. To me the issue seems more fundamental then measuring a volatility distribution.

Answer: In line 65 we brought up the difference between SOA evaporation and growth measurements to point out that the volatility information derived from experiments depends on the experiment setup. The limitations of the methods raise a need to develop new tools for extracting the volatility information of SOA constituents.

We have modified the text in line 68-73 in the revised version of the manuscript to

However, the experimental setup also defines the range of C^* values that can be estimated from the data. Vaden et al., (2011) and Yli-Juuti et al., (2017) have both shown that the volatility basis sets derived from SOA growth experiments results in too fast SOA evaporation compared to measured evaporation rates when used as input for process models. Possible reasons for such discrepancies include the different C^* ranges to which the SOA growth and SOA evaporation experiments are sensitive and the role of vapor wall losses in SOA growth experiments.

10. Line 327 – "matches better" Based on what quantitative metric? This is one example of a broader issue of providing quantitative metrics of goodness of fit.

Answer: Note that the simulated evapogram curves in Fig. 4 have changed as we corrected the error in the T_{max}-C^* calibration. The evapograms calculated with the VD_{PMF} of the medium O:C RTC sample produce almost equal evapogram as the one calculated with VD_{evap}. We have adjusted the text accordingly. Also, we increased the readability of the figure by showing only the simulations with medium evaporation time for the FIGAERO samples.

The reviewer is correct, that this is a purely qualitative term and whenever suitable one should use objective and mathematically based parameters for such comparisons. But for this specific example we decided to use a qualitative description rather than goodness of fit statistics. We are comparing the overall shape of the simulated and measured evapograms, but for the evapogram curves simulated with RTC VD_{PMF} we have only 1 or 2 measurement points to directly compare to. It is very clear that the evapograms simulated with the fresh VD_{PMF} underestimate the evaporation (too slow evaporation) for medium O:C particles while those using the RTC VD_{PMF} create curves that display a very similar shape as those simulated with VD_{evap} and estimated from the measured points. In the low O:C case, we now see a slight underestimation of evaporation rate using the fresh VD_{PMF} and overestimation of evaporation rate with the RTC VD_{PMF}. A simple goodness of fit parameter like the mean squared error would not reflect the direction of this discrepancy as a qualitative description can. Looking at the revised Fig. 4a where we show only one brown line we feel that "matches well" describes well what we want to say.

11. Table 1 – The analysis appears to have used an accommodation coefficient of 1 to interpret the evaporation data (alpha in Table 1 versus the alpha in equation (3)). This was not discussed or justified (none of the values were in Table 1 were justified). There are papers that report smaller values for this system (e.g. Saleh et al. Env. Sci.

Tech.2013). How would reducing this value alter the results from the analysis? This should be discussed in the paper.

Answer: The theoretical framework used by Saleh et al., (2013) assumes that the mass-accommodation coefficient includes any mass transfer limitations caused by high viscosity of the particle phase. In Saleh et al., (2013) SOA growth and evaporation experiments were performed with α-pinene ozonolysis SOA at 10% RH. Based on the work of Li et al., (2019) it is likely that there are significant mass transfer limitations associated with this type of SOA and RH. Those mass transfer limitations likely decrease the mass-accommodation coefficient in Saleh et al., (2013).

In our work, we model the mass transfer limitations explicitly with the KM-GAP model and thus the mass-accommodation coefficient in our work consists of effects due to e.g. surface sticking which we neglect. Additionally, the work of Julin et al., (2014) reports near-unity mass-accommodation coefficients for various organic molecules based on molecular dynamic simulations and experiments.

We have added justification for the properties of the organic compounds presented in Table 1 as a footnote to the table

[b)] values are chosen to represent a generic organic compound with values similar to other α-pinene SOA studies (e.g. Pathak et al., 2007; Vaden et al., 2011; Yli-Juuti et al., 2017).

12. Figure 2 indicates little agreement in the “raw” volatility distributions between the PMF and evaporation approach. This is mentioned but not discussed in the text. The figure is also very confusing since there are overlaps in the volatility of the different PMFfactors (i.e. one you don’t show a volatility distribution of the PMF factors). I think it would be much clear if you lumped the factors together into a volatility distribution,using the colors to indicate the contribution of each factor to each bin (i.e. the volatility distribution would have stacked colored bars). Compared to Figure 2, there is better agreement in Figure 3 when the offers have lumped in the material into larger bins wider than one order of magnitude. That seems encouraging, but this lumping process and its justification was not\discussed in the text.

Answer: In Figure 2 we show the information from PMF analysis that we utilized in the model simulations. Therefore, the range of C* values for each factor is an important piece of information and we find that combining the factors in stacked bars would not convey this information as directly. Our motivation for the lumping process was that when we examine the “raw” volatility distribution of Figure 2, it is not evident if the two VD are similar as the reviewer also points out. One issue complicating the comparison is that the PMF analysis does not set uni-distant C^* values for the factors. The second point is that the FIGAERO samples can differentiate compounds with C^* values below -2. These compounds do not evaporate under the investigated isothermal evaporation conditions and are thus already grouped into the lowest volatility bin in VD_{evap}. We lumped both volatility distributions to volatility classes to study the similarities between the distributions on a qualitative level. The justification for the choice of these volatility classes is given in lines 325-328 of the manuscript. Finally, as a quantitative comparison we study what kind of evapograms the “raw” (i.e. “non-lumped”) VD would produce. We have clarified our reasoning in the beginning of the results section on line 280-283:

We investigate the VD both on a qualitative and quantitative level. On a qualitative level we compare the amount of matter of different C^* *intervals. On a quantitative level we study what is the evaporation behavior of the particles based on the determined VD and how they compare to the measured evaporation.*

13. How different are the evapograms (Figure 4) when you use these different representations? A key issue is what level of information is there in the data. As I have discussed in earlier comment this problem seems very under constrained given the amount of data they have collected.

Answer: We do not use the three lumped volatility classes VD in the model simulations. The evapograms are always calculated with the “raw” VD (the one shown in Fig. 2). We hope that the modifications of the text mentioned above in comment 12 clarifies this.

14. Line 109 – What compounds were used to calibrate Tmax? The paper should provide a calibration curve showing these results.

Answer: We used polyethylene glycols (PEG) solutions in acetonitrile with 5 to 8 glycol units. As requested, we added the calibration curve and a brief description to the SI material.

15. Figure 4 – It is interesting that the PMF approach performs better for the mediumO:C aerosol compared to the low O:C aerosol. The PMF approach overestimates the evaporation of the This is mentioned on line 327, but only briefly discussed (~line500). The authors speculate it may be due to viscosity or particle phase chemistry. It Would be good to think about whether this indicates a shortcoming of the approach. For example, could this be due to the CIMS not detected a larger fraction of the less oxygenated aerosol? (This is related to some earlier comments).

Answer: The Figure 4 has changed in the revised version of the manuscript as we corrected the error in the T_{max}-C^* calibration. With the new parametrization it looks like the PMF approach (VD_{PMF}) performs better for the low O:C aerosol compared to medium O:C aerosol. In both oxidation conditions the evapogram calculated with VD_{PMF} of the fresh samples shows less evaporation than the measurements or the evapograms calculated with VD_{evap}.

The point raised by the reviewer is a valid one. The PMF method lumps all the organic compounds detected by the CIMS into preset number of factors. These factors are then treated as surrogate compounds when the evapograms are calculated with the LLEVAP model in Fig. 4. Given that in VD_{PMF} only one value is assigned to C^* of every PMF factor, it is not surprising that the VD_{PMF} does not produce an evapogram similar to the measurements.

Because the VD_{PMF} underestimates the evaporation, it seems possible that the iodide CIMS does not detect some fraction of the less oxygenated organic compounds, as we mentioned in our answer to comment 6. In our work, we expect that majority of the compounds are detected in the CIMS and the disagreement between measured and simulated evapograms in Fig. 4 comes from lumping the organic compounds into surrogate compounds in the PMF analysis or from the uncertainty in the conversion of desorption temperature to C*.

16. Figure 8. Optimized results (around line 440). The agreement seems impressive,but I suspect this is a just the result of fitting a model with lots of free parameters toa small set of data. Therefore, I am not surprised that the fit is great. If the fit is under constrained is this telling us anything about the technique? It was not clear if the authors had tested the applicability of the extracted values from this optimization against data the model had not been fit to? If this optimization is to be presented these issues must be discussed and some sort of cross-validation presented.

Answer: We agree that in the case of optimizing simultaneously C* and viscosity parameters there are a lot of free parameters (although neither C* or b_i are completely free parameters as they are restricted with minimum and maximum values) and therefore the estimates of parameter values from such optimizations should be interpreted with caution. However, our motivation with the low RH case was not to derive a universal parameterization. Our interest with the low RH data was to perform a cross-validation using a parametrization developed previously based on measurements of glass transition temperature of various organic compounds (DeRieux et al., 2018). Such validations of parameterizations against SOA dynamics are of importance if the parameterizations are to be used in the future e.g. for interpreting ambient or laboratory measurements or in large-scale model simulations of SOA formation. Our results show that the viscosity of SOA can be captured with this parametrization given the uncertainty in the parametrization and the C* values that we estimated using the same approach as with the high RH data. We have clarified our intent with the low RH experiments by adding following to lines 426-430

Our aim is to test if the slower evaporation, presumably due to higher viscosity of the SOA can be captured with a recently developed viscosity parametrization based on glass transition temperatures of various organic compounds (DeRieux et al., 2018). We also compare the results using the viscosity parametrization to an approach where we fit both the viscosity and VD to the evapogram.

17. Figure 8 –I interpret the dashed lines as the range of predications for the FIGAERO based approach (i.e., using the "theory" to predict viscosity). Is that correct? It is hard to tell what comparisons are based on truly independent comparison just using the FIGAERO versus fits of the data.

Answer: The reviewer is correct. We have added following clarification to the caption of Fig. 8

Grey lines show the minimum and maximum possible evaporation calculated with $VD_{PMF,dry}$ *(*C^* *of PMF factors calculated from* T_{max}*) and the highest (the original parametrization of DeRieux et al., (2018), grey dashed lines) or the lowest (30 K substracted from the* T_g *of every ion, grey solid line) studied viscosity.*

18. Figure 8. Can't differentiate between grey and black dashed lines.

Answer: We have changed the color of both lines to grey and changed one line to be solid and the other dashed.

References

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