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 #3 and reviewer #4 for reviewing our manuscript and for the helpful 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*. We have numbered the specific comments of reviewer #4.

Reviewer #3

The authors have adequately addressed my concerns from the first iteration. I noticed some typographical errors in the added / revised text; hence the request for technical corrections.

We thank reviewer #3 for his/her comments. We have carefully read through the manuscript and corrected any typos found.

Reviewer #4

The authors present here an investigation of how FIGAERO-CIMS thermal desorption data can be used to understand volatility distributions and evaporation kinetics, specifically through comparison to isothermal evaporation experiments. Overall, I think this is useful work of interest to the ACP community, and I think the authors have explored and considered in detail many of the potential areas of uncertainty in the approach. My opinion is that is generally suitable for publication in this journal. I have two main comments below that I think need to be discussed and addressed prior to publication, and list a number of specific comments below (in some cases, specific comments may just be specific examples/cases of the general comments and can be responded to as such).

Major comments:

1) Presentation. The authors are very detailed, but I fear this may contributed to the fact that I find this paper and these figures hard to get through. With all the different comparisons and model paramters, it takes a lot of re-reading sentences and mentally refreshing myself on the modeling frameworks to keep on top of what I am looking at. This is particularly true in considering all the variables in the evapogram modeling. Unfortunately I'm not sure I have a lot of concrete suggestions for how to fix this issue, it may just stem out of all the modeling details. I think one clear thing that might help would be to make the "takehome points" of the figures more clear within the figures themselves instead of relying entirely on captions and legends, for example: in all figures, including in each subplot what data set (e.g. "Fresh, medium O:C SOA") is being shown, in Figure 2 move most of the legend into the plot by just labeling "VD_evap" in gray and "Factors" in colored text, etc. Other possible ways to increase clarity might be: refer to and label the volatility classes as "low", "semi-volatile", and "volatile" instead of 1, 2, and 3 so the read doesn't have to keep track; spend less time discussing (and labeling in figures) the issues around min, mean, and max evaporation

times since it doesn't really impact the conclusions and move most of that to the SI. A minor but still important issue is awkward phrasing and grammar - on top of general complexity of the presentation, there are a lots of grammatically questionable phrases and/or typos that should be fixed (some, but not all, are listed in the specific comments).

We thank reviewer #4 for these suggestions that helped to further clarify the presentation. We have made following changes to the figures in the main text:

- added the name of the data set to each subplot in Figures 1 – 8 in the manuscript
- added labels for each PMF factor in Figure 2 to make it easier to recognize the factors without looking the legends.
- Modified the legend texts in Figures 4 – 6 so that they are better in line with the main text and the captions
- Added text arrows to Figure 6 that explain what bar shows what data.

We have removed the mentions about min, mean and max evaporation times in lines 395, 401-402, 404-406, 424, 429-432, 436-439, 539-541 and in the figure captions in the highlighted version of the manuscript. Instead, we briefly describe the results concerning different evaporation times in the captions of the supplementary Figure S8

The simulations of the fresh samples that start at the mean or maximum evaporation time resemble the measured evaporation and the evaporation simulations calculated with the VD_{evap}*. The simulation of the fresh sample that starts from the minimun evaporation time does not produce evaporation curve similar to the measurements. The results highlight the fact that it is not likely that the fresh sample consists of particles that have just entered the residence time chamber.*

and Figure S9

The results of medium O:C SOA in high RH experiments show that the VD_{PMF} *best resembles the* $VD_{PMF,opt}$ *of the maximum evaporation time, although the difference to the mean evaporation time is not significant. For low O:C SOA in high RH experiments, the results show that the* VD_{PMF} *best resembles the* $VD_{PMF,opt}$ *of the mean evaporation time.*

We have corrected the typos and phrases pointed out in the specific comments as well as read through the manuscript carefully and corrected any typos / unclear sentences we found.

In principle we agree that it would be useful to label volatility classes 1,2 and 3 into “low”, “semi-volatile” and “volatile” classes. In theory the volatility of a compound of course depends on the conditions where the volatility is studied and for our system it would be justified to name the three classes as “low-volatile”, “semi-volatile” and “volatile”. In practice we think that the terms “low-volatile”, “semi-volatile” and “volatile” have settled within the SOA community to mean specific C* ranges which are different from the C* ranges than what we use in our study for our volatility classes 1, 2 and 3. To avoid confusion, we label the volatility classes with numbers, even though it is not the most convenient labeling.

2) Benefit of PMF. A core component of this work is the PMF analysis of the FIGAERO data, and the authors do a detailed investigation to understand thermogram-derived volatility. A major conclusion of this work is that PMF factors can seemingly be used to describe the volatility/evaporation, but only if you optimize the T --> C* conversion by

fitting to evapogram data (i.e., account for the "uncertainty in the desorption temperature"). However, it's totally unclear to me that the PMF step is at all necessary, given the scale of that uncertainty, and the typical absence of evapogram data to provide that constraint. The C* that describes each factor is uncertain to around an order of magnitude, bounded by the desorption temperature range of the factor. Given this range of uncertainty (which is typical for C* estimates), what do you gain by having some specific T_max or T range associated with each factor? Why not just cut the thermogram into VBS bins based on temperatures (either by cutoff temperatures, or by fitting peaks constrained to the temperatures defining each bin)? Would this approach do any worse a job in comparison to the VD_evap or evaporation kinetics? This might even do better - M4, for instance, is very broad with T_max near T_25, so forcing all mass in the factor to this range might drive some bias. There are reasons beyond volatility you might want PMF, but this paper does not convince me that the effort of PMF provides any benefit in estimating volatility, and if not, why is it being used at all? Something needs to be added to this manuscript to provide support or context for this decision, e.g., a discussion of other peoples use of PMF for volatility; a discussion of why PMF might reasonably be expected to do a better job than a simple VBS approach; or a comparison of the present PMF approach to a VBS-only approach. Ideally, I'd love to see the VBS-only approach applied because if it works it informs how one can use the thermogram without the more complex need for PMF, but I would understand if the editor and/or authors feel that is beyond the scope. If it is beyond the scope, I do think it should be considered and discussed as a possibility - one major takehome for me is that it seems like it should work at least within similar unceratinty, so I think it would broaden the audience and potential impact of this paper to explore the possibility.

There can be two important issues with deriving VBS distributions directly from the sum thermograms:

1) There can be a considerable contribution of background and/or contamination distorting the sum thermogram. Especially, when the collected mass loading on the FIGAERO filter is low (few 10s of ng), it is important to separate the background from the real sample signal.

   As also described in our reply to specific comment 21, the low O:C, fresh, dry sample had a significant contamination. In Figure AR1, we depict the measured (black circles) and reconstructed sum thermogram (blue line). The red line shows the reconstructed sum thermogram using only the contribution of L1-L5 and LD1, omitting the background and contamination. It is clear that “binning” these two sum thermograms will lead to different VBS distributions.

The PMF approach identifies the instrument background (and contamination) and allowed us to omit it from further analysis.

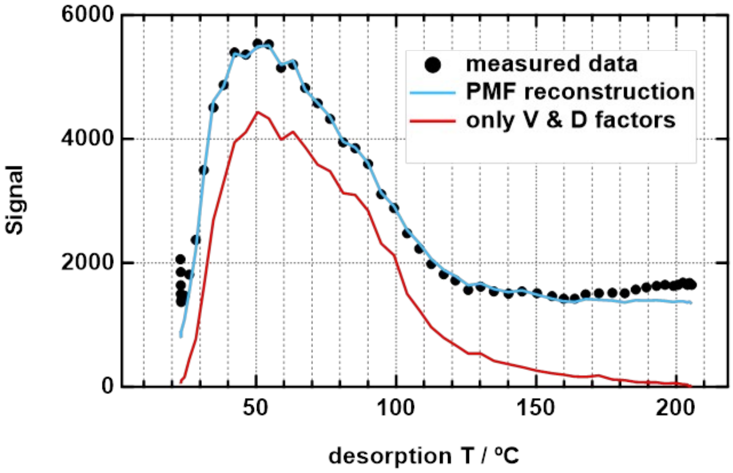

Figure AR1: Measured and reconstructed sum thermogram for the low O:C, fresh, dry sample.

2) The T_{max} → C* conversion is derived for single compounds relating their T_{max} values to their volatility. The area or the shape of the thermogram is not considered. Without further studies, it is not clear if this discrete calibration can be applied to the continuum of the sum thermogram.
   A compromise could be to determine the T_{max} value for each single ion thermogram and then use this as the volatility measure. However, there are multiple ions with multimodal or broad single ion thermograms in our data set. A single T_{max} value per ion again ignores the shape of the single ion thermogram, and thus possibly overestimates the volatility.

The PMF analysis can be understood as “binning” the sum thermogram by using the information from the desorption of all ions. The calculation time is clearly longer than for a simpler approach. But the amount of information and the solution of the issues mentioned above more than justifies that.

As the reviewer states, there are also reasons beyond volatility why one might want to use the PMF method. For example, one such reason might be understanding the particle phase chemistry during SOA evolution as was done in our group in Buchholz et al., (2019).

Because the PMF method might be important for interpreting the properties of the SOA constituents on a different level than calculating physicochemical properties from the mass spectrometer data, we feel that it is important to study that the method can also represent the volatility, which is perhaps the most important property for SOA formation and evolution, correctly.

Comparing the PMF method to VBS-only approach is an intriguing idea, but we feel that it is out of the scope of this paper. We have added the following to the discussion part (lines 507-512) in the revised version of the manuscript about the different methods to estimate the volatility

In addition to the PMF method used here, also other ways of characterizing SOA compound volatilities or VBS from FIGAERO-CIMS thermograms have been suggested (e.g. Stark et al., 2017). These include, for example, the more straightforward method of calculating the C of each detected ion based on their T_{max}, using Eq. (3) and lumping them into a traditional VBS. While such other methods may capture the volatility distributions sufficiently, the benefit of PMF method is that it offers a new way to understand what happens inside the particles, e.g.*

during the heating in FIGAERO. Here we have evaluated this method with respect to its ability to capture the volatilities of SOA.

Specific comments:

1. Line 40-41. This whole sentence is awkward English and difficult to understand, re-phrase

We have rephrased the sentence to:

There exist gaps in the knowledge especially on formation and deposition of SOA as well as how the processes are affected by changing physicochemical properties such as volatility (Glasius and Goldstein, 2016).

2. Line 41. Should be phrased "the phase state...has also..."

We have moved the word ‘also’ as suggested.

3. Line 45. Mass Spectrometer should be capitalized

We have capitalized Mass Spectrometer.

4. Line 77. "conduction a" is a typo

We have changed *“conduction”* to *“conducting”*

5. Line 82. For "How to interpret..." is not a grammatically correct question, should be "How shoud....be interpreted?"

We have modified the sentence as:

How should the PMF results of FIGAERO-CIMS data be interpreted in terms of volatility?

6. Line 104-107. Do I understand correctly that these 80 nm particles sit in the 100 L chamber for 4-10 hours? Even a monodisperse population will have some size distribution - how do you account for particle-dependent wall losses that might change the apparent size distribution? These might be negligible, but if so, the authors should provide evidence to support such an assumption.

The selected monodisperse distribution is narrow. We fitted the measured size distributions with an asymmetric log-normal function from which we get the half-width of the distributions and the peak position. For the low O:C, wet experiment (which exhibited the strongest evaporation) the half-width was 9-10 nm for the 75 – 80 nm particles at the start of the experiment. After 10 h, the particle size may decrease to as low as 55 nm with a half-width of 6-7nm. We do not expect significant size dependence of the particle wall loss for such narrow size distributions in the range of 80 - 50 nm.

7. Line 111. I don't think you need to include Aerodyne Research Inc. here, you already reference it in the paranthetical at the end of the sentence.

In line 111 we reference the Aerodyne Research Inc. first for the FIGAERO and later for the CIMS in the parenthesis. There are custom-build FIGAERO units thus it is necessary to indicate that the used unit was the model from Aerodyne Research Inc.

8. Line 114. It might be worth noting that in Isaacman-VanWertz et al. cited here, the volatility distribution of the FIGAERO-CIMS based on thermograms was similar to that of a TD-AMS. This suggests that any overall conclusions from the present work likely extend to other thermal desorption based estimates of volatility.

We would at least hope so. On the other hand, in Isaacman-VanWertz the authors test only one SOA system (α-pinene oxidized by OH). In general it might be that depending on which system is being investigated, different experimental methods may perform better or worse in producing accurate volatility distributions. For this reason, we feel that it is perhaps better not to draw conclusions from the present work to other thermal desorption based estimates of volatility.

9. Line 115. "a-" instead of "alpha-"

We have changed “a-” to “α” in line 115 in the old version of the manuscript.

10. Line 143. Why not just call them "VD bins" in all cases, and avoid the confusion with "compounds"? Having read the paper in detail, it's not clear to me that the use of the term VD compound is at all necessary - each bin has average properties (e.g., T_max) and I don't see any need to refer to them explicitly as psuedo-individual compounds.

Thank you for this suggestion. We have changed all occurrences of “VD compound” to “VD bin”.

11. Line 144. Are these really the properties of each VD compound? It looks like just basic assumptions about the properties of all (not each) bin. This sentence makes me think the Table is going to contain a list of many different properties for each of the bins.

To avoid confusion we have changed the sentence in line 144 of the old version of the manuscript from

The physicochemical properties of each VD bin are listed in Table 1 as well as the ambient conditions of each evaporation experiment.

to

The physicochemical properties of each VD bin are assumed to be the same. These properties and the ambient conditions of each evaporation experiment are listed in Table 1.

12. Table 1. Use column and row dividers to make clear that the rows with only one value are for all columns

We have added column dividers to Table 1.

13. Line 219. "and conducting a" should read "and conduct a"

We have changed this as suggested.

14. Line 223-224. I don't understand the purpose of this interpolation. Isn't the mass loading profile basically a represenation of mass as a function of time/temperature? What do the authors mean a temperature "step". Usually, the CIMS collects data at ~1 Hz - how large a step in temperature occurs in one second? Do the authors mean they

interpolate 100 spectra per degree C? Or 100 spectra per Hz? I would guess that if you are just interpolating from your existing data, this would not actually increase your statistical power, since the amount of "real" information is not increasing, but I'm not a statistician so I'm not sure.

The raw CIMS data had indeed a time resolution of 1 Hz. But because the raw signals of many ions were so low (and noisy), it was necessary to average the raw signals over a longer time period before the high-resolution analysis could be conducted. We used 20 s as averaging intervals which leads to an average ΔT between two adjacent data points of ~4 °C during the linear phase of the heating ramp.

While the overall shape of the thermograms is still visible, this T grid is to coarse to determine T_{max} and the 25th/75th percentiles directly. One option would be to fit the thermograms with a function, assuming a peak shape (e.g. gaussian or log-normal). Instead we chose to apply a linear interpolation assuming a continuous, linear distribution between two adjacent data points.

We have modified the paragraph in lines 225-229 in the revised version of the manuscript to:

Once the PMF algorithm was applied to the FIGAERO-CIMS data we calculated the VD from the mass loading matrix ***G****.* Due to the very low signal strength of many ions, the CIMS data had been averaged over 20 s leading to enhance the reliability of the high-resolution analysis. This leads to an average desorption temperature difference $\Delta T_{desorp} \approx 4°C$ between two adjacent data points. To overcome this coarse T_{desorp} grid, w*e interpolated each factor's mass loading profile with a resolution of 100 sample points between two temperature steps to gain sufficient statistics for further analysis.*

15. Line 243. Missing close parenthesis

We have added a closing parenthesis.

16. Line 251. Out of curiosity, how was 0.3 nm chosen? This is approximately the length of 2 carbon-carbon bonds, so effectively a monolayer or thinner.

The 0.3 nm was chosen to be close to one monolayer in the particle. In practice, we wanted to choose as small a value as possible for computational reasons that still makes physically sense.

17. Line 256-258. This assertion is made a few times, but it's not clear to me if this is simply an assertion, or if it is also observed that the VD_evap model suggests this to be true as well. This should be clarified/discussed

The fact that the particles are produced in the same conditions and only evaporate in different conditions is an important aspect for interpreting these data and for modelling the evaporation. It means that when we determine VD_{evap} at t = 0 s from experiment in one relative humidity, we can use the same VD as the initial VD (at t = 0 s) for modelling the evaporation at different relative humidity.

The experiment set-up was specifically designed to assure that the starting composition of the particles were the same. We monitored the output from the OFR continuously with an AMS. FIGAERO-CIMS samples of the polydisperse Aerosol were taken on different experiment days. Both instruments showed very little variety in the particle composition with time. The monodisperse sample is then selected from this polydisperse distribution. The only difference will be the water content in the particles. But as we compare the organic mole fractions the assumption still holds. The results from our VD_{evap} modelling do not contradict this aspect from the experimental set-up.

18. Line 271. The mass spectra contains ions, not compounds. In any case, do I understand correctly that DeRieux et al provide a way to estimate Tg as a function of molecular formula? This isn't quite clear.

The reviewer is correct here. We have clarified this in line 278 in the revised version of the manuscript.

This parametrization requires the number of carbon, oxygen and hydrogen atoms to calculate the T_g*.*

19. Line 285. What is the difference between Figures 1 and S2? I see that the contaminant and blank factors have been removed, and MD1 and has been split, but this is not all of the differences. For instance, in Figure S2 factor M1 coes to ~5000 signal, but only 2000 signal in Figure 1. The caption seem to imply these are the same data, but they don't look like it. Also, the desorption temperatures in Figure 1 go down to 0 C, which I don't think is correct.

Thank you for noticing this! The figure S2 wrongly shows the PMF factors for the experiments done in dry conditions. We have corrected the figure S2 to show all the PMF factors for the experiments done in high RH. The difference between Fig. 1 and Fig. S2 is that the latter shows the full 7- or 9- factor PMF results including also factors from filter background and from contamination (in the low O:C case). In Fig. 1, these background and contamination factors are removed and the decomposition factor (factors M/LD1 in Fig. S2) is split into two parts (factors M/LD1a/b in Fig. 1).

We have corrected also the issue where the desorption temperatures went down to 0 °C. In the plots where the desorption temperature went down to 0 °C, we had by accident included a data point below 23 °C that should not have been there.

20. Line 288. I think it's fine to point the reader to Buchholz for details, but a one or two sentence summary explanation is still necessary, I think, so the reader does not have to go to Buchholz unless they want the details. In other words, its fine to have a companion paper, but to be a separate paper, this paper still needs to be readable and understandable on its own.

The arguments for favoring a PMF solution over another need quite a bit of background information in this specific case. The details are explained in the companion paper. But to improve readability we added the following brief explanation in lines 294-297 in the revised version of the manuscript

We carefully investigated the Q/Q_{exp}*, time series of scaled and unscaled residuals, and the ability of a PMF solution to capture the characteristic behavior of as many single ion thermograms as possible (see Buchholz 2019b for details). Based on this analysis, a 7-factor solution was chosen for the medium O:C cases and a 9-factor solution for the low O:C ones.*

21. Line 291. How was it determined that they were "clearly an artifact"?

The dominant ions in these two factors were formic and lactic acid. Their signals in this sample were 10 times higher than in any other sample in the data set. While these two compounds do occur in SOA particles, they are also the most common contaminants for FIGAERO-CIMS measurements. Our lab exhibits quite high gas-phase concentrations of formic acid due to e.g. using it as a calibrant. Filters exposed to room air will take up some formic acid from the gas phase. An elevated lactic acid signal typically stems from touching the FIGAERO inlet with bare hands during maintenance (which is not standard procedure but can happen). Normally, such contaminations on the filter or inlet would have been removed by the cleaning cycles performed each day. But clearly something must have gone wrong on that specific day.

The second piece of evidence can be derived from additional samples that were collected during the measurement campaign. We could not use that data due to malfunctions of the temperature sensors, i.e. no reliable T_{desorp} values were available. However, the total composition measurements (integrating over the full desorption cycle) are still valid and did not show such high formic and lactic acid values for low O:C, fresh, dry particles.
Thus, we can conclude that the elevated values in the sample presented in the paper were indeed caused by a singular contamination of the filter or inlet. Normally, such a contaminated sample would be disregarded as “bad”. But with the PMF analysis, we could identify the part of the signal affected by the contamination and remove it, thus salvaging the information from this sample.

22. Line 295. This is a run-on sentence and should be split apart, probably at the first comma.

We have split the sentence at the first comma.

23. Line 299-301. I see why the authors split M/LD into two peaks, but this is a somewhat false dichomomty between the M/L peaks and the M/LD peaks - in reality they probably all contain some decomposition, it's just that for the other peaks it is a smooth enough transition as to appear monomodal.

The key difference between the V- and D-type factors is that V-type factors exhibit 1 single peak (i.e. all compounds in it fall into a narrow volatility range), while the D-type factors have a flat or dual peak thermogram shape. This means that, yes, a V-type factor may contain thermal decomposition products. But then it will not contain the direct desorption part for that same ion. For the D-type factor, this is exactly what happens.

An example is shown below the factors M1 -M5 and MD1 for the ions $[C_8H_{12}O_5 \cdot I]^-$ and $[C_4H_2O_4 \cdot I]^-$. The colored background indicates the direct desorption (grey) and thermal decomposition (red) temperature range that we applied for the splitting of MD1. Note how the first part of MD1 falls in the same T_{desorp} range as the V-type factors M1-M3. M5 falls in the thermal decomposition range where we also find the second part of MD1. So, factors M1-M3 are dominated by directly desorbing isomers of this composition. M5 is most likely dominated by thermal decomposition products. M4 may have contributions of both. This means that for all but 1 V-type factor the splitting of the integration area will have no effect as they are either almost completely in one or the other.

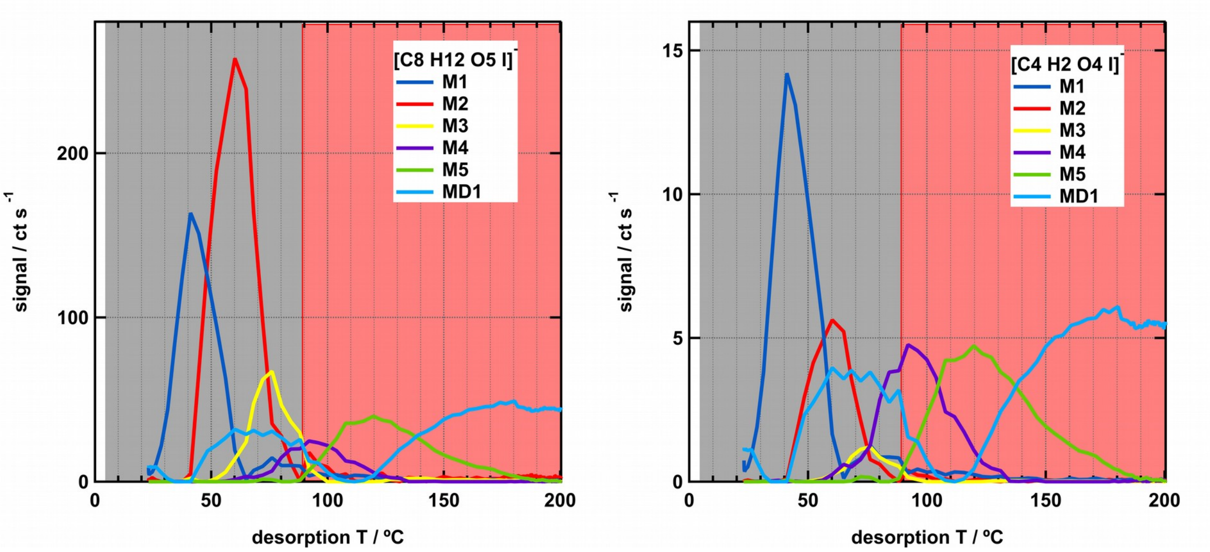

Figure AR2: Factor thermograms for the ion $[C_8H_{12}O_5 \cdot I]^-$ *(left) and* $[C_4H_2O_4 \cdot I]^-$ *(right). The grey background indicates the direct desorption range and the red background the thermal decomposition range used for splitting MD1.*

24. Line 323. It would helpful to note here (based on the SI) that the selection of min, mean, or max evap time does not significantly impact the conclusions of this work.

We have added the following to line 332 in the revised version of the manuscript.

The choice of sample evaporation time does not affect the conclusions we draw about the analysis presented in this section.

25. Figure 3. It might be helpful to include error bars. Sources of uncertainty on VD_evap presumabely include min, mean, max evap time, and possible uncertainties in the LLEVAP model. Sources of uncertainty in VD_PMF are harder to assess - definitely uncertainty in the T --> C* conversion as discussed below, also theoretically PMF uncertainties but those are harder to understand in this context, and maybe other things?
Similarly, what is the benefit of grouping VD_PMF in this way? It requires all the mass in one factor to be assigned into a bin based on T_max. Why note just slice the thermogram by the relevant temperatures, and bin mass just based on evaporation temperature (without the need for PMF)? I guess that's actually an overall question - does PMF really improve modeling or understanding of volatility, or would slicing the thermogram into C* bins just based on temperature yield basically the same conclusions?

We show the uncertainty associated with VD_{evap} in Figure S6. In our opinion the benefit of grouping the volatility distributions like we do in Figure 3 is that it allows us to compare VD_{evap} and VD_{PMF} on a qualitative level (answering for example questions like "which VD contains more non-volatile material"). This kind of analysis is hard to make solely from Figure 2 where the two distributions are plotted in a C^*-$X_{mole,dry}$ plot. We mention the reasoning for this kind of analysis in lines 287-290.

Regarding the remark about the usefulness of PMF see our response to the second major comment.

26. Lines 391-392. It is reassuring that the desorption profile is usable in this way, but it is notable that uncertainty in the C* of each factor seems to be on the order of 1 log unit based on Table 2. Such issues are typical in volatility experiments, but really suggest that this assumption of using T_max to describe a PMF factor is highly uncertain. Unless the operator has some evapogram data to validate against (which is of course uncommon), it is not clear that such an assumption should be used, nor is it clear that uncertainty in the desorption temperature can feasibily be considered. This does not mean the present work is not valuable, because the assumptions being tested are being used by the community, but I think it actually should present more doubt or caution in applying the assumptions being tested.

We do put doubt on the ability of the PMF results to represent volatility when the volatility is calculated from the T_{max} in the discussion part of the manuscript (lines 514-517 in the revised version of the manuscript).

We have the added following also to the conclusions to lines 562-563 in the revised version of the manuscript.

[...]and it should be noted that deriving the volatilities based on only the T_{max} of PMF factors may not be sufficient for representing detailed SOA dynamics.

27. Line 506-507. Qualitatively I agree, but it's not clear that is quantitatively true - attempting to model evaporation using the PMF results alone (without optimization by comparison to an evapogram) yields moderately but not wholely successful results (Fig. 4). This is addressed below, but I think maybe this starting sentence needs to be tempered.

We agree and have added the following to lines 497-498 in the revised version of the manuscript to mark that the VD_{PMF} and $VD_{PMF,dry}$ do not capture the evaporation dynamics quantitatively

Qualitatively, VD_{PMF} and $VD_{PMF,dry}$ capture the evaporation dynamics well in all studied cases, although quantitatively there were discrepancies

Comparing SOA volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO-CIMS measurements

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Abstract.

The volatility distribution of the organic compounds present in secondary organic aerosol (SOA) at different conditions is a key quantity that has to be captured in order to describe SOA dynamics accurately. The development of the filter inlet for gases and aerosols (FIGAERO) and its coupling to a chemical ionization mass spectrometer (CIMS) has enabled near simultaneous sampling of gas and particle phases of ~~secondary organic aerosol (~~SOA~~)~~ through thermal desorption of the particles. The thermal desorption data has been recently ~~been~~ shown to be interpretable as a volatility distribution with the use of the positive matrix factorization (PMF) method. Similarly, volatility distributions can be inferred from isothermal particle evaporation experiments, when the particle size change measurements are analyzed with process modelling techniques. In this study, we compare the volatility distributions that are retrieved from FIGAERO-CIMS and particle size change measurements during isothermal particle evaporation with process modelling techniques. We compare the volatility distributions at two different relative humidity (RH) and two oxidation condition. In~~At~~ high RH conditions, where particles are in a liquid state, we show that the volatility distributions derived via the two ways are similar within reasonable assumption of uncertainty in the effective saturation mass concentrations that are derived from FIGAERO-CIMS data. In~~At~~ dry conditions, we demonstrate that the volatility distributions are comparable in one oxidation condition, and in the other oxidation condition the volatility distribution derived from the PMF analysis shows considerably more high volatility matter than the volatility distribution inferred from particle size change measurements. We also show that the Vogel-Tammann-Fulcher equation together with a recent glass transition temperature parametrization for organic compounds and PMF derived volatility distribution estimate are consistent with the observed isothermal evaporation under dry conditions within the reported uncertainties. We conclude that the FIGAERO-CIMS measurements analyzed with the PMF method are a promising method for inferring the ~~organic compounds'~~ volatility distribution of organic compounds, but care has to be taken when the PMF factors are analyzed~~interpreted~~. Future process modelling studies about SOA dynamics and properties could benefit from simultaneous FIGAERO-CIMS measurements.

1 Introduction

Aerosol particles have varying effects on health, visibility and climate (Stocker et al., 2013). Organic compounds comprise a substantial amount of atmospheric particulate matter (Jimenez et al., 2009; Zhang et al., 2007) of which a major fraction is of secondary origin, i.e., low-volatility organic compounds formed from oxidation reactions between volatile organic compounds (VOCs) and ozone, hydroxyl radicals and nitrate radicals (Hallquist et al., 2009). The aerosol particles containing these kind of oxidation products are called secondary organic aerosols (SOA) as opposed to primary organic aerosols i.e., organic particles emitted directly to the atmosphere. VOC oxidation reactions result in thousands of different organic compounds (Goldstein and Galbally, 2007)~~ .~~.~~ A recent review by~~ There exist gaps in the knowledge especially on formation and deposition of SOA as well as how the processes are affected by changing physicochemical properties such as volatility(~~ ~~Glasius and Goldstein, ~~(~~2016)~~ ~~.~~pointed out that our understanding of SOA is still lacking especially on formation and deposition, and their response to different physicochemical properties of the organic compounds such as volatility.~~ In addition, ~~also ~~the phase state of the organic compounds has also been shown to play a role in~~ the~~ SOA dynamics (Reid et al., 2018; Shiraiwa et al., 2017; Yli-Juuti et al., 2017; Renbaum-Wolff et al., 2013; Virtanen et al., 2010)

The physicochemical properties of organic aerosols can be studied directly and indirectly. The Aerodyne Aerosol M~~m~~ass S~~s~~pectrometer (AMS, Canagaratna et al., 2007; DeCarlo et al., 2006; Jayne et al., 2000) enabled direct and online composition measurements of atmospheric particles for the first time. Combining AMS data with statistical dimension reduction techniques such as factor analysis and positive matrix factorization (PMF; Zhang et al., 2011, 2007, 2005; Paatero and Tapper, 1994) allowed researchers to draw conclusions on sources and types of atmospheric organic particulate matter from the relatively complex mass spectra data.

The C~~c~~hemical I~~i~~onization M~~m~~ass S~~s~~pectrometer (CIMS; Lee et al., 2014) coupled with the Filter Inlet for Gases and AEROsols (FIGAERO-CIMS, Lopez-Hilfiker et al., 2014) is a prominent online measurement device~~technique~~ to study both the gas and particle phases of SOA. During particle phase measurements, a key advantage over the AMS is the softer chemical ionization that retains much more of the molecular information of the compound than the electron impact ionization used in the AMS. Typically, the collection of the particulate mass is conducted at room temperature which minimizes the loss of semi-volatile compounds during collection. In addition to the overall chemical composition, the gradual desorption of the particulate mass from the FIGAERO filter yields the thermal desorption behavior of each detected ion, i.e., it is a direct measure of each ion’s volatility. FIGAERO-CIMS measurements have been carried out in both laboratory and field environments to study SOA composition from different VOC precursors and in both rural and polluted environments (Breton et al., 2018; Huang et al., 2018; Lee et al., 2018; D’Ambro et al., 2017; Lopez-Hilfiker et al., 2015). However, the volatility information in these data sets have barely been used.

Besides direct mass spectrometer measurements, SOA properties have been inferred indirectly from growth (e.g. Pathak et al., 2007 and references therein) and isothermal evaporation (Buchholz et al., 2019a; D'Ambro et al., 2018; Yli-Juuti et al., 2017; Wilson et al., 2015; Vaden et al., 2011) measurements. The complexity of organic compounds in these studies can be alleviated with the use of a volatility basis set (Donahue et al., 2006), where organic compounds are grouped based on their (effective) saturation concentration. 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 result in too fast SOA evaporation compared to measured evaporation rates when the volatility basis set is 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 to and the role of vapor wall losses in SOA growth experiments. This raises a need for alternative methods to derive organic aerosol volatility against which the volatilities inferred from the direct particle size measurements can be compared to.

Recently, Buchholz et. al., (2019b) demonstrated that the FIGAERO-CIMS measurements during particle evaporation can be mapped to a volatility distribution of organic compounds by conducting~~on~~ a PMF analysis. On the other hand, Tikkanen et al., (2019) showed that the volatility distribution can be inferred from isothermal particle evaporation measurements by optimizing the evaporation model input to yield~~match~~ the measured evaporation rate at different humidity conditions. In this study, we compare these two approaches for varying oxidation and particle water content conditions. Our main research questions are 1) Are the volatility distributions derived from particle size change during isothermal evaporation and from the FIGAERO-CIMS measurements similar? 2) How ~~to interpret the~~should the PMF results of FIGAERO-CIMS data be interpreted in terms of volatility? 3) Can a recently published glass transition temperature parametrization (DeRieux et al., 2018) combined with the PMF analysis be used to model particle phase mass transfer limitations observed for the~~in~~ evaporation in~~at~~ dry conditions, i.e., in the absence of particle phase water?

2 Methods

2.1 Experimental particle evaporation data

The experimental data we use is the same as reported in Buchholz et al., (2019a,b). We briefly summarize the measurement setup below. We generated the particles with a Potential Aerosol Mass (PAM) reactor (Kang et al., 2007; Lambe et al., 2011) from the reaction of α-pinene with O_3 and OH at three different oxidation levels (average oxygen-to-carbon O:C ratios of 0.53, 0.69, and 0.96). We focus on the lowest O:C (0.53) and medium O:C (0.69) experiments in this work. The closer analysis of the high O:C experiments suggests 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.

We selected~~chose~~ a monodisperse particle population (mobility diameter d_p = 80 nm) with two nano tandem type differential mobility analyzers (nano-DMA; TSI inc., Model 3085) from the initial polydisperse particle population. The size selection diluted the gas phase initiating particle evaporation. The monodisperse aerosol was left to evaporate in a 100 L stainless-steel residence time chamber (RTC). We measured the particle size distribution during the evaporation with a scanning mobility particle sizer (SMPS; TSI inc., Model 3082+3775). The RTC filling took approximately 20 minutes and we performed the first size distribution measurement in the middle of the filling interval. To obtain short residence time data (data before 10 minutes of evaporation) we added a bypass to the RTC which led the sample directly to the SMPS. By changing the length of the bypass tubing, we were able to measure the particle size distribution between 2 s and 160 s of evaporation. We measured the isothermal evaporation up to 4 – 10 hours depending on the measurement. We performed the measurements for each oxidation level both at high relative humidity (RH = 80%) and at dry conditions (RH < 2 %). The change in particle size with respect to time are called evapograms. In an evapogram, the horizontal axis presents evaporation time and the vertical axis shows the evaporation factor (EF), i.e., the measured particle diameter divided by the initially selected particle diameter.

To classify the oxidation level of the particles, we derived the average O:C ratio from composition measurements with a High-Resolution Time-Of-Flight Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.). Further, we conducted detailed particle composition measurements with an Aerodyne Research Inc. FIGAERO, (Lopez-Hilfiker et al., 2014) coupled with a chemical ionization mass spectrometer (CIMS) with iodide as the reagent ion (Aerodyne Research Inc., Lee et al., 2014). 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 α~~a~~-pinene oxidation contains the functional groups required for detection by our FIGAERO-CIMS.

In the FIGAERO inlet, particles are first collected on a PTFE filter. Then the collected particulate mass desorbs slowly due to a gradually heated nitrogen flow. The desorbed gaseous compounds ~~which is~~are then transported into the CIMS for detection. We derived the average chemical composition of the particles by integrating the detected signal of each ion over the whole desorption interval. For each ion, the change of detected signal with desorption temperature is called a thermogram and generally, the temperature at the maximum of the thermogram (T_{max}) is correlated to the volatility of the detected ion. Similar to Bannan et al., (2019) and Stark et al., (2017), we calibrated the T_{max} - volatility relationship using compounds with known vapour pressure. The calibration procedure is described in the supplementary material.

We collected particles for FIGAERO-CIMS analysis at two different stages of the evaporation. We refer to these samples as either “fresh” or “RTC” samples. The fresh samples were collected for 30 minutes directly after the selection of the monodisperse population. The RTC samples of the residual particles were collected for 75 minutes after 3 to 4 hours of evaporation in the RTC~~ for 75 minutes~~. The collected particulate mass was 140–260 ng and 20–70 ng for the fresh and the RTC samples, respectively. More details about sample collection, desorption parameters, and data analysis can be found in Buchholz et al., (2019a).

2.2 The volatility distribution

We represent the myriad of organic compound in the SOA particles with a one-dimensional volatility basis set (1D VBS, below only VBS, Donahue et al., 2006). The VBS groups the organic compounds into ‘bins’ based on their effective (mass) saturation concentration C^*, defined as the product of the compounds activity coefficient and saturation concentration. Generally, a bin in the VBS represents the amount of organic material in the particle and gas phases. In our study, the walls of the RTC have been shown to work as an efficient sink for gaseous organic compounds (Yli-Juuti et al., 2017). Thus, we can assume that the gas phase in our experimental setup does not contain organic compounds, i.e., the amount of organic matter in a bin is the amount in the particle phase. To distinguish from a traditional VBS that groups the organic compounds to bins ~~where~~such that there is a decadal difference in C^* between two adjacent bins, we call the VBS in our work a volatility distribution (VD). We present the amount of material in each VD bin as the dry mole fraction~~s~~, i.e., the mole fraction~~s~~ of the organics, excluding water. In the analysis presented below, we assign properties to each VD bin (e.g. molar mass) treating each bin as if it consisted of only a single organic compound with a single set of properties. ~~We label these pseudo-compounds as “VD compounds” to distinguish them from real organic compounds~~ The physicochemical properties of each VD bin are assumed to be the same. These properties and the ambient conditions of each evaporation experiment are listed in Table 1.~~The physicochemical properties of each VD compound are listed in Table 1 as well as the ambient conditions of each evaporation experiment.~~

2.3 Deriving volatility distribution from an evapogram

We followed the similar approach as in Yli-Juuti et al., (2017) and Tikkanen et al., (2019) to derive a VD at the start of the evaporation from an evapogram. To model the evaporation at high RH, we used a process model (liquid-like evaporation model, hereafter LLEVAP) that assumes a liquid-like particle, i.e., a particle where there are no mass transfer limitations inside the particle and where the mass flux~~rate of change of the mass~~ of a ~~VD compound~~VD bin in the particle phase can be calculated directly from the gas phase concentrations of the~~is~~ ~~VD compound~~VD bin near the particle surface and far away from the particle (Vesala et al., 1997; Lehtinen and Kulmala, 2003; Yli-Juuti et al., 2017). In this case, the main properties defining the evaporation rate are the saturation concentrations of each ~~VD compound~~VD bin and their relative amount in the particle.

We used the LLEVAP model to characterize the volatility range~~s~~ that can be interpreted~~able~~ from the evaporation measurements. We calculated the range~~limits~~ by modelling evaporation of a hypothetical particle that consists of one organic compound evaporating in~~at~~ dry conditions. We calculated the evaporation for ~~iterating~~ the range of $\log_{10}(C^*)$ values from -5 to 5. We determined the minimum C^* value to be the value that still showed~~with~~ "detectable evaporation", i.e., at least 1% change in particle diameter during the evaporation time (up to 6 h) and the maximum C^* value to be the value before "complete evaporation" occurred, i.e., 99% particle diameter change~~evaporation~~ within the first 10 s. The minimum $\log_{10}(C^*)$ calculated with this method was -3 and the maximum $\log_{10}(C^*)$ was 2. We then modelled the particle composition with six ~~VD compound~~VD bins with C^* values between these minimum and maximum values. Each ~~VD compound~~VD bin~~s~~ has a decadal difference in C^* to adjacent ~~VD compound~~VD bin~~s~~ (like in the traditional VBS). We note that based on this analysis all the compounds with $\log_{10}(C^*) < -3$ will not evaporate during the experimental time scale. This means that any compounds with lower C^* than this threshold will be assigned to the $\log_{10}(C^*) = -3$ ~~VD compound~~VD bin. Similarly, any compound with $\log_{10}(C^*) > 2$ will be classified into the $\log_{10}(C^*) = 2$ ~~VD compound~~VD bin or not be detected at all due to evaporating almost entirely before the first measurement point.

We calculated the dry particle mole fraction of each ~~VD compound~~VD bin at the start of the evaporation by fitting the evaporation predicted with the process model to the measured evapograms. Our goal was to minimize the mean squared error in vertical direction between the experimental data and the LLEVAP output. We used the Monte Carlo Genetic Algorithm (MCGA, Berkemeier et al., 2017; Tikkanen et al., 2019) for the input optimization. In the optimization, we set the population size to be 400 candidates, number of elite members to 20 (5% of the population), number of generations to 10, and number of candidates drawn in the Monte Carlo (MC) part to 3420 which corresponds to half of the total process model evaluations done during the optimization. We performed the optimization 50 times for each evapogram and selected the best fit VD estimate for further analysis.

The VD derived from the evapogram~~s~~ is~~are~~ hereafter referred to as the VD_{evap}. The initial composition of the SOA particles in the dry and wet experiments were the same and can be described by the same fitted VD_{evap} as the particles were generated at the same conditions in the PAM and only the evaporation conditions changed.

2.4 Deriving volatility distribution from FIGAERO-CIMS measurement

As shown by Bannan et al., (2019) and Stark et al., (2017), the peak desorption temperature, T_{max}, can be used together with a careful calibration to link desorption temperatures from the FIGAERO filter to C^* values for the detected ions. In principle, this would allow us to assign one C^* value to each ion thermogram. But this assumes that one detected ion characterized by its exact mass is indeed just one compound. In practice, this is not always the case and for some ion thermograms a bimodal structure or distinct shoulders/broadening are visible. This can be caused by isomers of different volatility which cannot be separated even by high resolution mass spectra.

Another complication arises due to the thermal desorption process delivering the collected aerosol mass into the CIMS. Especially, multi-functional, and hence low volatility compounds may thermally decompose before they desorb from the filter, and thus be detected as smaller ions. The apparent desorption temperature is then determined by the thermal stability of the compound and not its volatility. Typically, this decomposition processes start at a minimum temperature and will not create a well-defined peak shape (Buchholz et al., 2019b, Schobesberger et al., 2018) presumably because an observed decomposition product may have multiple sources, especially when including all isomers, and the ion signal for the respective composition may overlap with the signal of isomers derived from true desorption. For example~~E.g.~~, a true constituent of the SOA particle may give rise to an observed main thermogram peak, but it may be broadening and/or tailing if a decomposition product has the same composition. By ignoring this and simply using the T_{max} values, the true volatility of the SOA particle constituents will be overestimated, i.e., the derived VD will be biased towards higher C^* bins.

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.

To separate the multiple sources possibly contributing to each ion thermogram (isomers and thermal decomposition products), we applied the Positive Matrix Factoriz~~s~~ation (PMF, Paatero and Tapper, 1994) to the FIGAERO-CIMS data set. PMF is a well-established mathematical technique in atmospheric science mostly used to identify the contribution of different sources of aerosol particle constituents or trace gases in the atmosphere. PMF represents the measured matrix of time-series of mass spectra, $\boldsymbol{X}$, as a linear combination of a (unknown) number of constant source profiles, $\boldsymbol{F}$, with varying contributions over time, $\boldsymbol{G}$:

$$\boldsymbol{X} = \boldsymbol{G} \cdot \boldsymbol{F} + \boldsymbol{E} \tag{1}$$

$\boldsymbol{E}$ is a matrix containing the residuals between the measured ($\boldsymbol{X}$) and the fitted data ($\boldsymbol{G} \cdot \boldsymbol{F}$). Values for $\boldsymbol{G}$ and $\boldsymbol{F}$ are found by minimiz~~s~~ing this residual, $\boldsymbol{E}_{ij}$, scaled by the corresponding measurement error, $\boldsymbol{S}_{ij}$, for each ion i at each time j

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{E_{i,j}}{S_{i,j}} \right) \tag{2}$$

Each row in $\boldsymbol{F}$ contains a factor mass spectrum and each column in $\boldsymbol{G}$ holds the corresponding time series of contribution by each factor. In the case of FIGAERO-CIMS data, the time series is equivalent to the desorption temperature ramp during the thermogram and will be called “mass loading profile” below. The absolute values (temperature or time) are irrelevant for the performance of PMF as the “x values” are only used to determine the order of the data points but have no influence on the model output (Paatero and Tapper, 1994). This allowed us to combine multiple separate thermogram measurements into one data set and conduct~~ing~~ a PMF analysis. This simplified the comparison of factors between measurements. More details about the PMF method in the specific case of FIGAERO-CIMS data can be found in Buchholz et al., (2019b).

Once the PMF algorithm was applied to the FIGAERO-CIMS data we calculated the VD from the mass loading matrix ***G***. Due to the very low signal strength of many ions, the CIMS data had been averaged over 20 s leading to enhance the reliability of the high-resolution analysis. This leads to an average desorption temperature difference ΔT_{desorp} ≈ 4°C between two adjacent data points. To overcome this coarse T_{desorp} grid, w~~W~~e interpolated each factor's mass loading profile with a resolution of 100 sample points between two temperature steps to gain sufficient statistics for further analysis. T_{max} was determined as the temperature at~~of~~ the maximum signal in~~of~~ the factor mass loading profile~~series~~. We integrated the factor mass loading profile and defined the temperatures where the value of the integral reaches 25% and 75% of its maximum value. This temperature interval formed the factors desorption temperature range and the corresponding C^* values will be used in Sect. 3.3. We converted the T_{max} values into C^* values and the desorption temperature range into a C^* range with a parametrization derived from calibration measurements (see Supplementary~~Supplementray~~ material for details) with organic compounds with known C^* values.

$$C^* = \frac{\exp\left(\alpha + \beta T_{factor}\right) M_{org}}{R\, T_{ambient}} 10^9 \qquad (3)$$

where C^* is the effective saturation concentration in units μgm^{-3}, M_{org} is the molar mass of the organic compound assumed to be M_{org} = 0.2 kg mol^{-1}, R is the universal gas constant, T_{factor} (in °C in Eq. 3) is the temperature of the mass loading profile and $T_{amibent}$ (in Kelvin in Eq. 3) is the ambient temperature at which~~where~~ the evaporation happens (see Table 1), α and β are the fitted coefficients from the calibration data α=(-1.431±0.31) and β=(-0.207±0.006) °C^{-1}. We applied the lower and higher bounds of the fitting coefficients' uncertainty when we calculated the C^* range in Sect 3.3. Finally, the signal fraction of each factor was calculated by dividing the integral of a factor's signal over the whole temperature range with the sum of integrals of all factors. We compare this signal fraction to the dry mole fraction in the VD_{evap}. We refrained from converting the counts per second signal into moles as no adequate transmission and sensitivity measurements were available for the used FIGAERO-CIMS setup. We refer the volatility distribution calculated from the PMF data using the T_{max} values of each factor as VD_{PMF} later in this work.

With Eq. (3), we can calculate the minimum and maximum C^* values that can be resolved from a FIGAERO thermogram. The desorption temperature was ramped between 27 °C and 200 °C, but defined peaks (and thus T_{max} values) can be detected only between 30 and 180 °C. Thus, the resolvable $\log_{10}$ (C^*) values range from 1.6 to -11.9. It has to be kept in mind that strictly this calibration only applies to the T_{max} values of a single ion thermogram.

2.5 Modelling particle viscosity at dry conditions

To model the mass transfer limitations observed in the evaporation measurements at dry conditions (Buchholz et al., 2019a) we used the k~~K~~inetic multilayer model for gas particle interactions (KM-GAP; Shiraiwa et al., 2012) with modifications described in Yli-Juuti et al., (2017) and Tikkanen et al., (2019). The main modification to the original model was that during evaporation the topmost layer (the quasi static surface layer) merges with the first bulk layer if the thickness of the layer is smaller than 0.3 nm. We calculated the viscosity at each layer of the particle as

$$\log_{10}(\eta_j) = \sum_{i=1}^{N} X_{mole,i,j} \log_{10}(b_i), \tag{4}$$

where $X_{mole,i,j}$ is the mole fraction of the ~~VD compound~~VD bin i in layer j and b_i is a coefficient that describes the contribution of each ~~VD compound~~VD bin to the overall viscosity.

Since we generated the particles in the same environment (PAM chamber) and only the evaporation happened at different conditions, the VD at the start of the evaporation derived from high RH data represents also the composition at the start of the evaporation in~~at~~ dry conditions. Then we can use the best fit VD_{evap} from the high RH data as input for KM-GAP and fit the b_i values in Eq. (4) to the dry data set. We set the minimum and maximum allowed values for b_i to 10^{-15} and 10^{20}, respectively. To estimate the b_i values when modelling the evaporation with VD_{PMF} in~~at~~ dry conditions, we calculated these b_i terms using the mass spectra of each factor (***F*** in Eq. 1) and the Vogel-Tammann-Fulcher (VTF) equation (DeRieux et al., 2018; Angell, 2002, 1995)

$$\eta_i = \eta_\infty \exp\left(\frac{T_{0,i} D}{T - T_{0,i}}\right), \tag{5}$$

where η_i is the viscosity of the ith~~a~~ ~~VD compound~~VD bin / PMF factor.~~ i which~~ η_i can be seen as a proxy for b_i in an ideal solution.~~;~~ η_∞ is the viscosity at infinite temperature, $T_{0,i}$ is the Vogel temperature of the ith VD bin~~ i~~, and D is a fragility parameter. Setting $\eta_\infty = 10^{-5}$ Pa s and $\eta(T_g) = 10^{12}$ Pa s (e.g. DeRieux et al., 2018; Gedeon, 2018), where T_g is the glass transition temperature of a compound yields

$$T_{0,i} \approx \frac{39.14\, T_{g,i}}{39.14 + D}. \tag{6}$$

We calculated T_g for every compound in the PMF mass spectra with a parametrization for SOA matter developed by DeRieux et al., (2018). This parametrization requires the number of carbon, oxygen and hydrogen atoms to calculate the T_g. We then computed T_g for each PMF factor as a mass fraction weighted sum of glass transition temperatures of individual compounds (DeRieux et al., 2018; Dette et al., 2014). Based on the $T_{g,i}$ of~~for~~ each PMF factor, we calculated the viscosity of each PMF factor with Eqs. (5) and (6) and used them as an approximation for b_i. We used fragility parameter value D = 10 in the calculations- according to DeRieux et al., (2018).

3 Results

In this section we first focus on the high RH experiments where evaporation is modelled with the LLEVAP model. We will first compare VD_{evap} to~~and~~ VD_{PMF} for which~~nwhe~~ the C^* of a PMF factor is determined from the factor's T_{max} value. Then, we compare the volatility distributions where the C^* of a PMF factor is determined as a range from the 25th and 75th percentile desorption temperatures. Lastly, we study the volatility distributions in~~at~~ dry conditions. 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 relevant for the evaporation process. On a quantitative level we study what is the evaporation behavior of the particles based on the determined VD and how do they compare to the measured evaporation.

3.1 PMF solution interpretation

Figure S2 shows mass loading profiles derived from the FIGAERO-CIMS measurements of medium and low O:C particles at high RH. The corresponding factor mass spectra can be found in Fig. S3 and Fig. S4. A key step in any PMF analysis is determining the "right" number of factors as this can affect the interpretation of the results. We carefully investigated the Q/Q_{exp}, time series of scaled and unscaled residuals, and the ability of a PMF solution to capture the characteristic behavior of as many single ion thermograms as possible (see Buchholz 2019b for details). Based on this analysis, a 7-factor solution was chosen for the medium O:C cases and a 9-factor solution for the low O:C ones.~~A 7-factor solution was chosen for the medium O:C cases and a 9-factor solution for the low O:C ones (see Buchholz 2019b for details)~~. The two additional factors in the low O:C case were needed to capture a contamination on the FIGAERO filter during the dry, fresh sample (factors LC1 and LC2 in Fig. S2 and Fig. S4). As these two factors were clearly an artifact introduced by the FIGAERO filter sampling, we omitted their contribution for the following analysis. From careful comparison of the factor profiles and mass spectra with filter blank measurements, we determined that factor MB1 in the medium O:C case and factor LB1 in the low O:C case describe the filter/instrument background and are thus also excluded from the VD comparison presented below.

Factors 1-5 in both O:C cases exhibit a monomodal peak shape and can thus be characterized by their T_{max} values.~~,~~ F~~f~~actor MD1 in the medium O:C case and factor LD1 in the low O:C case needs to be investigated more closely, as their~~its~~ factor mass spectrum and the sometimes bimodal mass loading profile suggest that these~~is~~ factors contain~~s~~ compounds stemming from both direct desorption (desorption T<100 °C) and thermal decomposition (desorption T>100 °C, see Buchholz et al., 2019b for details). To account for this, the factor is split into two with the first half containing the signal from desorption temperatures below 100 °C (factor M/LD1a) and the second half containing that above 100 °C (factor M/LD1b). We treat these factors separately. We note that now the latter half of the split factor is dominated by thermal decomposition products so that the apparent desorption temperature is actually the temperature at which thermal decomposition leads to products which desorb at this temperature. This apparent desorption temperature is thus a lower limit for the decomposing parent compound, i.e., the true volatility of these parent compounds is even lower. However, the desorption temperatures are so high that they lead to $\log_{10}(C^*) < -3$ and are thus below the comparable range for $\mathrm{VD}_{\mathrm{evap}}$. Figure 1 (high RH data) and Fig. S10 (dry condition data) show the mass loading profiles derived from FIGAERO-CIMS measurements of medium and low O:C particles after we excluded the contamination and background factors and split the decomposition factors.

3.2 Volatility distribution comparison at high RH based on factor T_{max}

To compare $\mathrm{VD}_{\mathrm{evap}}$ and $\mathrm{VD}_{\mathrm{PMF}}$, we need to determine the time interval in the evapogram that the $\mathrm{VD}_{\mathrm{PMF}}$ represents. We collected the fresh samples directly after the size selection. As the particles were collected ~~on a filter~~ for 30 minutes, the collected sample represents particles that have evaporated from 0 up to 30 minutes in the organic vapour free air. We note that this is different from the standard FIGAERO-CIMS sample collection where the particles are collected in a quasi-equilibrium with the surrounding gas phase and no significant evaporation occurs (Lopez-Hilfiker et al., 2014). For RTC samples, we also need to consider ~~also~~ that not all particles have evaporated for the same time due to the filling of the RTC for ca. 20 minutes. We determined the minimum time the particles have evaporated in the RTC as the time when we started the sample collection minus the RTC filling time. We determined the maximum evaporation time in the RTC to be the time when we stopped the sample collection plus the filling time. These minimum and maximum comparison times are shown in Table S1 and they are referred to as minimum and maximum (sample) evaporation time. The mean (sample) evaporation time is defined to be at the middle of the sample collection interval. For simplicity, we will show in the main text the results from the analysis where the FIGAERO-CIMS samples were assumed to represents the particles at the mean sample evaporation time. We show the analysis where the samples were assumed to represent the particles at minimum and maximum evaporation time in the supplementary material. The choice of sample evaporation time does not affect the conclusions we draw about the analysis presented in this section.

Figure 2 shows $\mathrm{VD}_{\mathrm{evap}}$ and $\mathrm{VD}_{\mathrm{PMF}}$ for medium (Fig. 2a-b) and low O:C (Fig. 2c-d) particles in~~at~~ high RH experiments. In the $\mathrm{VD}_{\mathrm{PMF}}$ calculated from T_{max} value of each factor (black crosses), the factors fall into three different volatility classes within our chosen particle size and experimental time scale: practically non-volatile ($\log_{10}(C^*) \leq -2$), slightly volatile ($-2 < \log_{10}(C^*) \leq 0$,) and volatile ($\log_{10}(C^*) > 0$). We use these three volatility classes to compare the volatility distributions in Fig. 3 where each ~~VD compound~~VD bin are grouped to these three volatility classes. Figure 3 ~~presents the $\mathrm{VD}_{\mathrm{PMF}}$ where C^* of each factor is calculated from the T_{max} value and~~ compares ~~this~~ $\mathrm{VD}_{\mathrm{PMF}}$ to what $\mathrm{VD}_{\mathrm{evap}}$ is at the mean time the FIGAERO samples had evaporated prior to collection. We show the same comparison for the minimum and maximum evaporation time in Fig. S5 and Fig. S6.

After the volatility class grouping is applied, we see that there are differences between VD$_{evap}$ and VD$_{PMF}$. With VD$_{PMF}$ of the fresh samples there are excess amount of matter in the lowest volatility class (volatility class 1) and less material in the volatility class 2 compared to VD$_{evap}$, for~~In~~ both oxidation condition. In addition, the VD$_{PMF}$ of low O:C fresh sample shows more material in the highest volatility class (volatility class 3)~~, in VD$_{PMF}$~~ compared to VD$_{evap}$.~~.~~

To investigate the observed discrepancies further, we used the VD$_{PMF}$ shown in Fig. 2 as an input to the LLEVAP model and calculated the corresponding isothermal evaporation behavior (i.e. the evapogram). We show these simulated evapograms in Fig. 4a for the medium O:C case and in Fig. 4b for the low O:C condition together with the simulated evapogram calculated using VD$_{evap}$ as an input for the LLEVAP model. The simulated evapograms calculated with the VD$_{PMF}$ of the fresh samples do not match the measured evapograms~~ predicting less evaporation~~, while the evapogram calculated with VD$_{evap}$ agrees well with the experimental evapogram (black lines in Fig. 4), as expected since this is the goal of the VD$_{evap}$ determination. The simulation calculated with the VD$_{PMF}$ of the fresh sample (light blue lines in Fig. 4 for the mean evaporation time and Fig. S7 for other evaporation times) shows slower evaporation than the observations or the simulation calculated with VD$_{evap}$.~~.~~ This is consistent with the results show in Fig. 3 where the VD$_{PMF}$ contained more low volatility material than the VD$_{evap}$.

Figure 4 also shows~~ also~~ the simulated evapograms calculated with VD$_{PMF}$ of the RTC samples (light brown lines in Fig. 4 and Fig. S7). in these cases, the particles size decreases little within the simulation time scale. With medium O:C particles, the simulated evaporation matches~~ well to~~ the measured evaporation well. With low O:C particles, the evaporation calculated with VD$_{PMF}$ is too fast. The shape of the evapogram does not match the measured one.

3.3 Applying desorption range to characterize the volatility of PMF factors

The T$_{max}$ value is a practical choice for the characteristic temperature of the desorption process. However, as we saw i~~o~~n Sect. 3.2, the VD$_{PMF}$ calculated from the peak desorption temperatures did not produce the measured evapogram when used as an input for~~to~~ the LLEVAP model. Working under the assumption that all material collected on the FIGAERO filter, including the higher volatility material, is detected in the CIMS and then captured in the PMF analysis, we will relax the assumption that the volatility of the factor is characterized strictly by the T$_{max}$ value of the factor and investigate the VD$_{PMF}$ further. We will explore how the VD$_{PMF}$ changes when the desorption temperature and the resulting C* are interpreted to contain uncertainty and if the VD$_{PMF}$ considering these uncertainty ranges is consistent with the observed isothermal evaporation. The uncertainty in the desorption temperature raises from the facts that compounds volatilize from the FIGAERO filter throughout the heating and, therefore, one value might not be adequate to characterize the C* of a factor and that each PMF factor contains multiple compounds with distinct C*.

We calculated the 25th and 75th percentiles of the desorption temperatures of each factor and converted them to effective saturation concentrations as described in S~~s~~ect.~~ion~~ 2.4 (see diamond markers in Fig. 1). We show the resulting C* ranges in

Fig. 2 as horizontal solid lines where the line colo~~u~~r matches the colo~~u~~r of the factors in Fig. 1. We then ran the MCGA optimization by setting the~~a~~ number of compounds equal to the number of PMF factors, the molar fraction for each compound at the FIGAERO-CIMS sampling time fixed to the molar fraction of the corresponding factor and ~~set~~ the C^* as the optimized variables restricted to the range corresponding to the 25th and 75th percentile desorption temperature. In the optimization the goodness-of-fit statistics was calculated as a mean squared error similar to the determination of VD_{evap}.

As the fresh samples were collected between 0 and 30 minutes from the start of the evaporation, we sought for a fitting set of C^* values for evaporation starting at 0, 15 and 30 minutes. Again, w~~W~~e show the results for the mean sample evaporation time (15 min) in the main text and the results for the other evaporation times in the supplementary material. Due to scarcity of particle size measurements at the collection time of the RTC sample, we will apply this analysis only to the VD_{PMF} of the RTC sample at its minimum evaporation time. In each optimization, we set the initial particle diameter to be the same as what is simulated with VD_{evap}. We derived 50 C^* estimates for both samples~~ and each evaporation time~~. From these 50 estimates we chose the best fit evapogram. We refer to these optimized volatility distributions as $VD_{PMF,opt}$ to separate them from the VD_{PMF} where we used T_{max} to characterize C^* of a PMF factor.

We show the optimized C^* values forming $VD_{PMF,opt}$ in Table 2 (see Table S2 for results with minimum and maximum sample evaporation times). Figure 5 shows the best fit evaporation simulations calculated with $VD_{PMF,opt}$. The other sample evaporation times are displayed in the supplementary material Fig. S8. For both oxidation condition, the simulations~~ were the fresh sample is set to represent the evaporating particles at mean or maximum sample evaporation time~~ resemble the experimental evapogram and evapogram calculated with VD_{evap}, although the simulation of the~~in~~ medium O:C condition shows a 5 times larger goodness-of-fit value compared to the simulation calculated with VD_{evap}. ~~The simulations starting from maximum evaporation time of the fresh samples show similar results while the simulations starting from the minimum sample evaporation time results in too slow evaporation (Fig. S8).~~ The evapograms determined with the $VD_{PMF,opt}$ of the RTC samples agree with the measured evaporation as well.

Overall, the~~se~~ results demonstrate that the information derived from the fresh and RTC FIGAERO-CIMS samples can describe the volatility of the evaporating particles, when uncertaint~~y~~ies in the desorption temperature are considered.

3.4 Comparison of the volatility distribution of the fresh and RTC sample in~~at~~ high RH conditions

In this section, we compare $VD_{PMF,opt}$ of the fresh samples to VD_{PMF} of the RTC sample to study if the two VD are similar. We compare the two VD at the mean evaporation time of the RTC sample. We calculated the evapograms with the $VD_{PMF,opt}$ of the fresh sample as the initial particle composition and recorded the mole fraction of each factor at the mean evaporation time of the RTC sample (216 minutes for medium O:C particles and 211 minutes for low O:C particles). Figure 6a and Fig.

6c show this comparison for both medium O:C and low O:C particles. The factors are grouped into the three volatility classes described in Sect. 3.2. In Fig. 6 we show the results from the analysis where VD$_{PMF,opt}$ was optimized by assigning the fresh sample composition at the mean sample evaporation time. Similar comparisons using minimum and maximum evaporation time of the fresh sample are~~is~~ ~~given~~shown in Fig. S9. To ensure that the factors are grouped to the same volatility classes for each studied VD, we used the C* values of the VD$_{PMF,opt}$ at the mean sample evaporation time as basis ~~according to which~~for the grouping~~ is done~~.

T~~Assuming that the fresh sample represents particles from the middle of the sampling interval (mean evaporation time), t~~he compositions simulated based on the VD$_{PMF,opt}$ of the fresh samples are comparable to the corresponding VD$_{PMF}$ of the RTC sample in both oxidation conditions (Fig. 6). The agreement is good, especially for the low O:C case for which the VD$_{PMF,opt}$ showed a slightly smaller contribution in volatility class 1 and a corresponding higher contribution in volatility class 2 compared to the VD$_{PMF}$ of the RTC sample (Fig. 6c). For the medium O:C case, the VD$_{PMF,opt}$ predicted a higher contribution of volatility class 1 and a lower contribution of volatility class 2 compared to VD$_{PMF}$ (Fig 6a). ~~For medium O:C conditions, the agreement between VD$_{PMF,opt}$ and VD$_{PMF}$ improved when using the VD$_{PMF,opt}$ of maximum fresh sample evaporation time, while VD$_{PMF,opt}$ of minimum fresh sample evaporation time show higher contribution of volatility class 2 and lower contribution of volatility class 1 compared to the VD$_{PMF}$ of the RTC sample.~~

These results show that the particle composition measured after few hours of evaporation is consistent with the composition predicted based on the composition observed at the start of evaporation while~~and~~ considering uncertainties of the interpreted C* values. ~~The level of the agreement changes depending on which evaporation time the fresh FIGAERO-CIMS sample is assumed to represent. For medium O:C particles the VD$_{PMF}$ and VD$_{PMF,opt}$ are more consistent when the fresh sample is assumed to represent particles at the maximum sample evaporation time. For low O:C particles the VD$_{PMF,opt}$ resembles the VD$_{PMF}$ of the RTC sample best at mean evaporation time.~~

3.5 Volatility distribution comparison in~~at~~ dry conditions

Next, we analyzed the evaporation experiments in~~under~~ dry conditions where the evaporation rate was reduced compared to the high RH conditions. We interpreted this difference as an indication of particle phase diffusion limitations in~~at~~ dry conditions (Yli-Juuti et al., 2017). Using the initial particle composition information obtained from the high RH experiments and the FIGAERO-CIMS data, we explored the effect of particle viscosity on the evaporation process. 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.

First, we investigated the range of particle viscosities that are required to explain the observed slower evaporation in~~at~~ dry conditions. For this, we simulated the particle evaporation in dry conditions based only on the evapogram data. We used the VD_{evap} (i.e., the initial particle composition obtained by optimizing mole fractions of ~~VD compound~~VD bins with respect to the observed evapogram in~~at~~ high RH conditions) as the initial particle composition estimate~~condition~~ for the simulations and optimized the b_i values (Eq. 3) for each ~~VD compound~~VD bin. The best fit simulation from this optimization agrees well with the observed size decrease in the dry experiments for both low and medium O:C particles (Fig. 8, black line). Based on these simulations, the viscosity of the particles needs to increase from below 10^5 Pa s to approximately 10^8 Pa s during the evaporation in order to explain the evaporation rate observed for the dry particles.

Second, we tested the performance of the composition dependent viscosity parameterization by DeRiuex et al. (2018) used together with the PMF results. For this, we calculated the volatility distribution, $VD_{PMF,dry}$, based on the T_{max} values of the factors from the fresh sample of the evaporation experiment at dry conditions (in the same way as for VD_{PMF} for the high RH case). The mole fraction of each factor was calculated from the mass loading profile to give~~giving~~ the initial mole fraction of each ~~VD compound~~VD bin for the simulations. We assigned this $VD_{PMF,dry}$ as the particle composition at the mean evaporation time of the fresh sample, i.e. 15 minutes, and simulated the particle evaporation from there onwards. The particle size at the beginning of the simulation (i.e. at 15 minutes of evaporation) was taken from the above simulations optimized based only on the evapogram data, which fitted well to the measurements. We calculated the viscosity parameter b_i value for each ~~VD compound~~VD bin as described in Section 2.5 based on the mass spectra of the factor and the parameterization by DeRieux et al. (2018). This resulted in too high viscosity for particles to evaporate in practice at all during the length of the experiment for both low and medium O:C particles (grey dashed line in Fig. 8). Therefore, we also conducted a simulation where the viscosity parameter b_i value for each factor was calculated based on the viscosity parameterization by setting the T_g values of all compounds 30 K lower than the parametrization predicted, which is in line with the uncertainties reported by DeRiuex et al. (2018). In this case, the simulated evaporation was faster than observed for the medium O:C conditions (grey solid line in Fig. 8a) and similar to the evapogram calculated with the VD_{evap} for low O:C conditions (grey solid line in Fig. 8b). This suggest that the observed evaporation rate at dry conditions and the viscosity parametrization by DeRieux et al. (2018) may be consistent with each other within the uncertainty range of the viscosity parametrization and the uncertainty range of the C^* of PMF factors.

Similar to Fig. 3, we show in Fig. 7 the comparison of $VD_{PMF,dry}$ (C^* from T_{max}) to the VD_{evap} in~~at~~ dry conditions and at the mean sample evaporation time with the ~~VD compound~~VD bins grouped into the three volatility classes. We show the mass loading profiles and the volatility distributions of experiments in~~at~~ dry conditions~~s~~ in Fig. S10 and Fig. S11. Figure S12 shows the same comparison as Fig. 7 for other sample evaporation times. For medium O:C particles, $VD_{PMF,dry}$ calculated from the fresh sample has more contribution of volatility classes 1 and 3 and less of volatility class 2 compared to the corresponding VD_{evap}. For the low O:C particles, the $VD_{PMF,dry}$ of the fresh sample has more contribution of volatility class 3 and less of volatility classes 1 and 2 compared to the VD$_{evap}$. For medium O:C particles, the differences between the VD$_{PMF,dry}$ and VD$_{evap}$ leave open the possibility that the underestimated evaporation rate calculated using VD$_{PMF,dry}$ is partly a result of inaccuracy in volatility description and not solely due to the high estimated viscosity. For the low O:C particles, the underestimated evaporation most likely stems from the high estimated viscosity since ~~the~~ VD$_{PMF,dry}$ is shifted towards higher volatility compounds than ~~the~~ VD$_{evap}$.

As a third investigation of~~n~~ the viscosity, we used again the PMF results of the fresh sample in~~at~~ dry conditions to initialize the particle composition in the model at the mean fresh sample evaporation time~~, i.e., at 15 minutes~~. The mole fraction of each factor was calculated from the mass loading profile giving the initial mole fraction of each ~~VD compound~~VD bin for the simulations similar to the high RH analysis. Then, using the MCGA algorithm together with the KM-GAP model, we estimated the b_i coefficient and C^* of each ~~VD compound~~VD bin by optimizing the KM-GAP simulated evapogram to the measured evapogram in~~at~~ dry conditions. This way we obtained both the initial volatility distribution (VD$_{PMF,dry,opt}$) and viscosity parameters b_i simultaneously. For this optimization, we restricted the C^* values of the factors based on the 25th and 75th percentile of the desorption temperature of the factors~~,~~ (similarly ~~as~~to what was done above for VD$_{PMF,opt}$)~~,~~ and the viscosity parameter b_i values based on the DeRieux et al. (2018) parameterization. The b_i values calculated with the original parametrization by DeRieux et al., (2018) were set as the upper limit for the b_i values. The lower limit for the b_i values were calculated by setting the glass transition temperature of each compound 30 K lower than the parametrization predicted. As above,~~ also~~ in these simulations the initial particle size was also taken from the simulations where the optimization was based on only the evapogram data. For both medium and low O:C particles, it was possible to find a set of C^* and b_i values that produced an equally good match to experimental data as the VD$_{evap}$ (purple and yellow lines in Fig. 8).

Figure~~s~~ 6b and Fig. 6d show the comparison of the measured and simulated particle composition, grouped into the three volatility classes, at the RTC sample collection time for the dry experiments for low and medium O:C particles. The measured composition is the VD calculated from the PMF results of the RTC samples in~~at~~ dry conditions. The optimized C^* values of the factors from the corresponding dry experiment were used for these VD. The simulated particle composition is taken from the optimized model run (optimized VD$_{PMF,opt,dry}$ and b_i) at the mean RTC sample collection time similar to the high RH cases presented in Fig. 6a and Fig. 6c. For low O:C particles there is a clear discrepancy: the VD$_{PMF,dry,opt}$ implies~~y~~ a much larger relative contribution from the volatility classes 2 and 3 and a smaller contribution from the volatility class 1 compared to the measurements. This inconsistency may be related to the rather high viscosities in the simulations. The viscosity of the low O:C particles in this optimized simulation was rather high, $\eta > 10^8$ Pa s, throughout the evaporation, slowing the evaporation of the higher volatility compounds. Similar evaporation curve could be obtained with lower viscosity and lower volatilities of the VD bins~~compounds~~.

4 Discussion

Qualitatively, VD$_{PMF}$ and VD$_{PMF,dry}$ capture ~~qualitatively~~ the evaporation dynamics well in all studied cases, although quantitatively there were discrepancies. For the VD$_{PMF}$ of the fresh samples, the first and second factor desorb at low heating temperatures (below 100 °C) indicating that these factors represent high volatility organic compounds that evaporate almost completely from the particles in the experimental time scale of our isothermal evaporation experiments. In the RTC samples, these factors show significantly lower or non-existing signal strength relative to the other factors. The factors that desorb at high temperatures show an increase in the relative signal strength in the RTC samples compared to the fresh samples which is consistent with the expected increase in relative contribution of lower volatility compounds along evaporation. These findings indicate that the FIGAERO-CIMS measurements of α-pinene SOA and the applied PMF method give a good overall picture of the evolution of the volatility distribution during evaporation.

In addition to the PMF method used here, also other ways of characterizing SOA compound volatilities or VBS from FIGAERO-CIMS thermograms have been suggested (e.g. Stark et al., 2017). These include, for example, the more straightforward method of calculating the C^* of each detected ion based on their T_{max}, using Eq. (3) and lumping them into a traditional VBS. While such other methods may capture the volatility distributions sufficiently, the benefit of PMF method is that it offers a new way to understand what happens inside the particles, e.g. during the heating in FIGAERO. Here we have evaluated this method with respect to its ability to capture the volatilities of SOA.

At high RH, the VD$_{PMF}$ that was derived from T_{max} of each factor’s mass loading profile did not produce evapogram similar to the measured ones, when the VD$_{PMF}$ was used as an input for~~to~~ the LLEVAP model. This reflects the sensitivity of the particle evaporation to the C^* values and suggest that the VD$_{PMF}$ is not directly applicable as a particle composition estimate for detailed particle dynamics study. When we allowed uncertainty in the C^* values of each factor we were able to explain most of the discrepancy between the simulated and measured evapograms. ~~The simulated evapograms, after optimizing the C^* of each factor from their appropriate ranges, are close to the experimental values for all other cases except when the FIGAERO sample is interpreted to represent particles at the start of fresh sample’s collection interval (minimum evaporation time).~~ Our results also demonstrate the need for careful investigation of the representative time of the sample when filter-collected samples are applied for dynamic processes such as evaporation.

In this study we assumed a quite large uncertainty range for the desorption temperature of each PMF factor and it is not certain that the determination of VD$_{PMF,opt}$ would be successful if the allowed ranges for C^* of PMF factors would be lower. Thus, there remains work to be done in studying what is the total uncertainty that rises from combining the FIGAERO-CIMS measurements with the PMF method and to what extent the PMF factors can be thought to represent surrogate organic compounds for the purpose of detailed SOA dynamics studies.

We note that care has to be taken when PMF results are transferred to volatility distributions, especially with regard to separating the contribution of instrument background and contamination from the true sample. When the sample mass was low (in the low O:C RTC sample) we noticed that the first half of the bimodal (factor LD1a) resulted in a high mole fraction even though the absolute signal strength of the factor did not change between the fresh and the RTC sample, which is usually an indication that this signal is caused by instrument background. However, the signal strength of this factor was low enough in all cases to not affect the overall VD estimation. More details on the interpretation of B- and D-type factors and potential factor blending can be found in Buchholz et al, (2019b).

In dry conditions~~At low RH~~, $VD_{PMF,dry}$ of the fresh sample in low O:C case showed noticeably higher amount of high volatility matter than VD_{evap}. ~~-~~This discrepancy between the volatility distributions is not expected and raises a need for further studies on the role of viscosity and possible particle phase chemistry to SOA particle dynamics. Future studies should investigate the possibility of chemical reactions that modify the volatility of organic compounds and how viscosity is described in process models.

5 Conclusions

We compared volatility distributions derived from FIGAERO-CIMS measurements with PMF analysis to volatility distributions derived from fitting a process model to match measured size change of particles during isothermal evaporation. 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.

In all studied experimental data sets, we were able to capture the measured evaporation with the fitting method. ~~With~~In high RH experiments, VD_{PMF} deviated from VD_{evap} especially when the FIGAERO samples were collected at the early stages of the evaporation. However, qualitatively, both types of VD evolved similarly, i.e., the fraction of lower volatility compounds increased, and the fraction of higher volatility compounds decreased during the evaporation of the particles. These results suggest that the changes in FIGAERO-CIMS derived volatility distributions over the isothermal evaporation are consistent with the observed isothermal evaporation and the detailed SOA dynamics are sensitive for the uncertainties in the C^* values.

The volatility distribution derived ~~from~~ with the PMF method at high RH agreed with the observed isothermal evaporation better when we interpreted the volatility of each factor as a range of possible C^* values and optimized the C^* values within~~from~~ these ranges with respect to the measurements. These results suggest that the FIGAERO-CIMS measurements combined with PMF method does not only provide qualitative information of the volatilities of the SOA constituents but it also has potential for quantitative investigation of the volatility distributions. However, more work is needed to constrain the uncertainties rising from the conversion of the FIGAEO-CIMS desorption temperatures to C^* values~~.~~ and it should be noted that deriving the volatilities based on only the T_{max} of PMF factors may not be sufficient for representing detailed SOA dynamics.

In~~At~~ dry conditions, we were able to simulate the evapograms based on the PMF results using the VTF equation and the glass transition temperature parametrization of DeRieux et al., (2018)~~ when~~if both C^* and viscosity parameters where optimized and allowed to contain reasonable uncertainties. For both oxidation conditions the measured composition at the later stages of evaporation suggested considerably lower volatility than the simulations. These results suggest that the tested viscosity parameterization is not in disagreement with the observed SOA evaporation, however the uncertainties related to the method are significant from the point of view of simulating SOA dynamics.

Based on our analysis we conclude that using the PMF method with FIGAERO-CIMS thermogram data is good for estimating the volatility distribution of organic aerosols when the organic compounds present in the particle phase have low volatilities with respect to the sample collection and analysis time scale. Specifically, VD_{PMF} is useful for extracting information about organic compounds that do not evaporate during the evaporation measurements at room temperature. VD_{PMF} is applicable to detailed particle dynamics studies when desorption temperature of the factor is characterized with a range around the T_{max} value. Furthermore, combining $VD_{PMF,opt}$ with detailed process modelling and input optimization could allow quantification of other physical or chemical properties of organic aerosols since the FIGAERO-CIMS data constrains the particle composition and effectively decreases the search space that needs to be explored with global optimization methods.

Code availability: The process models used in this study can be acquired upon request from the corresponding author. The MCGA code is~~ can be obtained from~~ available in https://doi.org/10.5281/zenodo.3759733

Author contributions: OPT, AB, SS, AV and TYJ designed the study. OPT did the calculations with support from AB and TYJ, except for the PMF calculations which were done by AB. AY developed the calibration method to calculate C^* from desorption temperature with support from SS. All authors participated in the interpretation of the data. OPT wrote the paper with contributions from all co-authors.

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Table 1: The ambient conditions and properties of the organic compounds used in estimating the VD_{evap}. The variables are, from top to bottom, temperature (T) during the evaporation, relative humidity (RH), gas phase diffusion coefficient ($D_{g,org}$), molar mass (M), particle phase density (ρ), particle surface tension (σ) and mass accommodation coefficient (α). Rows that only have one value are the same in every column.

Variable	Medium O:C High RH	Low O:C High RH	Medium O:C dry	Low O:C dry
T (K)	293.85	293.75	293.75	293.35
RH (%)	82.4	83.5	0	0
$D^{a,b}_{gas}$ ($cm^2\ s^{-1}$)	0.05			
M^b ($g\ mol^{-1}$)	200			
ρ^b ($kg\ m^{-3}$)	1200			
σ^b ($mN\ m^{-1}$)	40			
α^b	1			

[a)] The gas phase diffusion coefficients are scaled to correct temperatures by multiplying with a factor of $(T/273.15)^{1.75}$ (Reid et al., 1987)

[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).

Table 2: The best fit C^* values for medium O:C and low O:C high RH experiments when C^* values of PMF factors were optimized with respect to the measured isothermal evaporation. C^* values were optimized by assuming the FIGAERO-CIMS sample represents particle composition at the mean sample evaporation time for the fresh sample and the minimum sample evaporation time for the RTC sample. The C^* values are rounded to two significant digits and are in units $\mu g m^{-3}$. C^* values below 10^{-3} $\mu g m^{-3}$ are not reported explicitly since the evapogram fitting method is not sensitive to these values.

	Medium O:C fresh sample	Medium O:C RTC sample	Low O:C fresh sample	Low O:C RTC sample
Factor M1/L1	$4.96 \cdot 10^{-1}$	36.10	$3.06 \cdot 10^{-1}$	$<10^{-3}$
Factor M2/L2	$2.89 \cdot 10^{-1}$	$4.12 \cdot 10^{-1}$	$3.55 \cdot 10^{-1}$	$2.40 \cdot 10^{-2}$
Factor M3/L3	$9.93 \cdot 10^{-3}$	$4.42 \cdot 10^{-3}$	$2.87 \cdot 10^{-2}$	$7.13 \cdot 10^{-3}$
Factor M4/L4	$< 10^{-3}$	$< 10^{-3}$	$1.54 \cdot 10^{-3}$	$< 10^{-3}$
Factor M5/L5	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Factor D1a	$7.68 \cdot 10^{-1}$	69.35	130.03	$1.04 \cdot 10^{-1}$
Factor D1b	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$

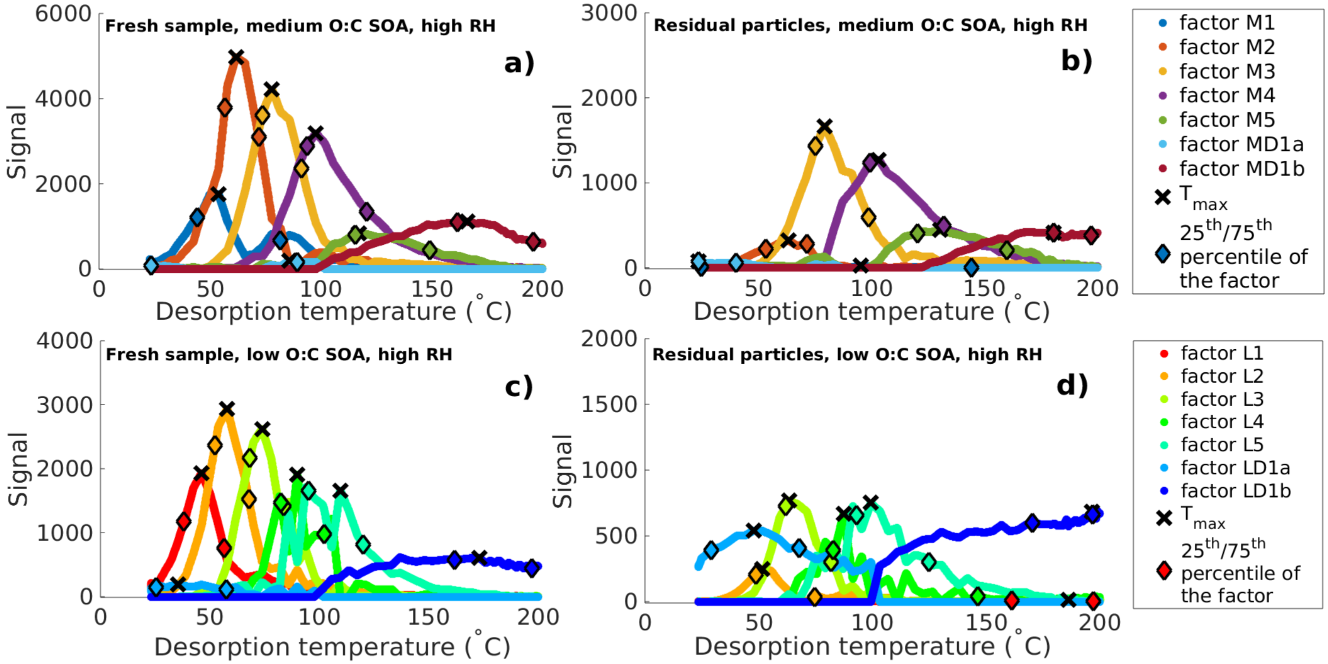

Figure 1: Main positive matrix factorization (PMF) mass loading profiles for thermal desorption of secondary organic aerosol (SOA) from α-pinene at high RH conditions

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA after 173-259 minutes of evaporation in a residence time chamber (RTC), i.e., the RTC sample

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 168-254 minutes of evaporation in the RTC, i.e. the RTC sample.

Black crosses indicate the peak desorption temperature T_{max} and the diamonds mark the 25th and 75th percentiles of ~~each factor's~~ the area of each factor.

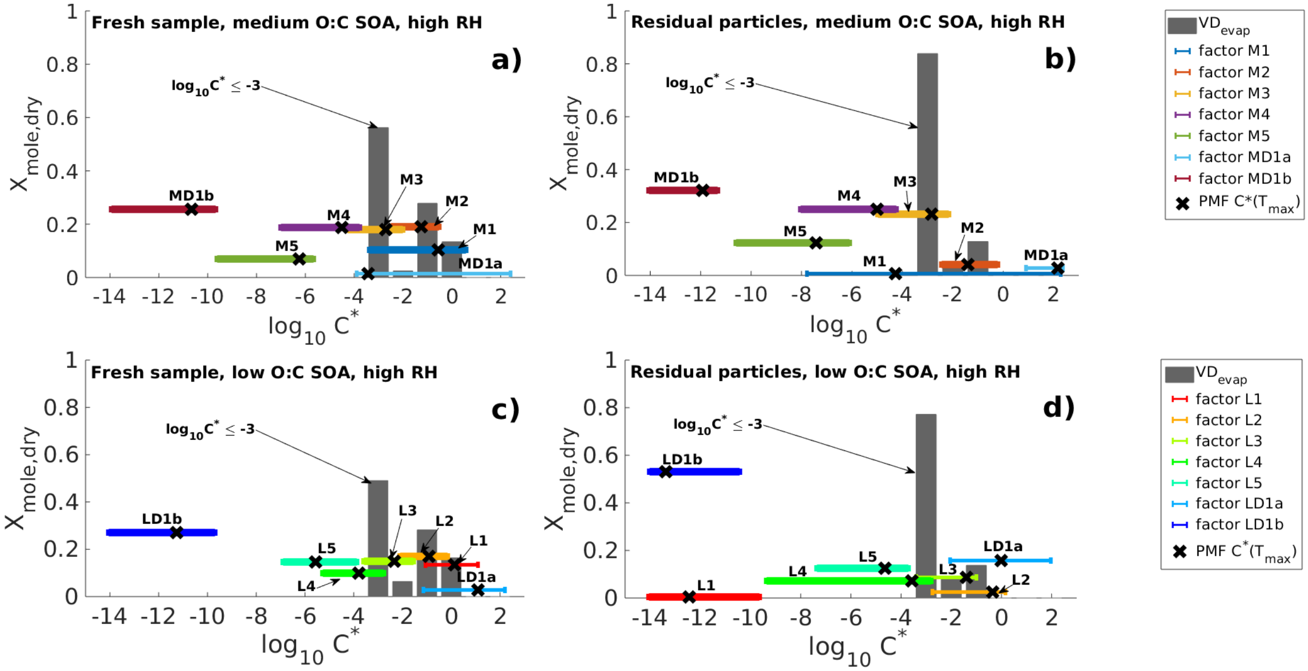

Figure 2: Volatility distributions in high RH experiments determined from model fitting (VD_{evap}) and PMF analysis of FIGAERO-CIMS data (VD_{PMF}) for the same four cases shown in Fig. 1.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

VD_{evap} is shown for the best fit simulation (grey bars) at the mean evaporation time of the FIGAERO-CIMS sample. Black crosses show the $\log_{10}(C^*)$ calculated for each PMF factor from the peak desorption temperature T_{max}. The horizontal coloured lines show the range of $\log_{10}(C^*)$ calculated from the 25th and 75th percentiles of each PMF factor's mass loading profile.

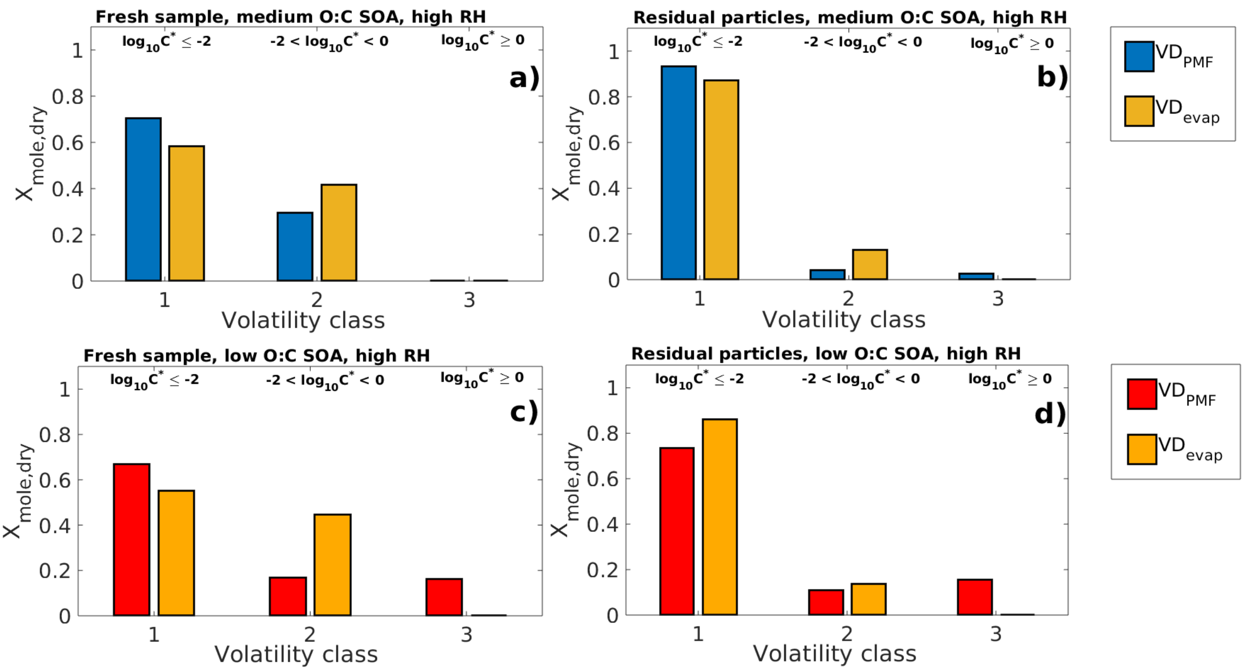

Figure 3: Comparison of VD_{PMF} and VD_{evap} at the mean sample evaporation time in high RH experiments for the same four cases shown in Fig. 1.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

The ~~VD compound~~VD bins shown in Fig. 2 are grouped into three different volatility classes based on their evaporation tendency with respect to the measurement time scale and particle size. The limits for each volatility class are shown at the top and are the same for each subfigure. The VD_{PMF} shows lower overall volatility than the VD_{evap} except for subfigure d (RTC sample of low O:C SOA) where the VD_{PMF} shows higher overall volatility than the VD_{evap}.

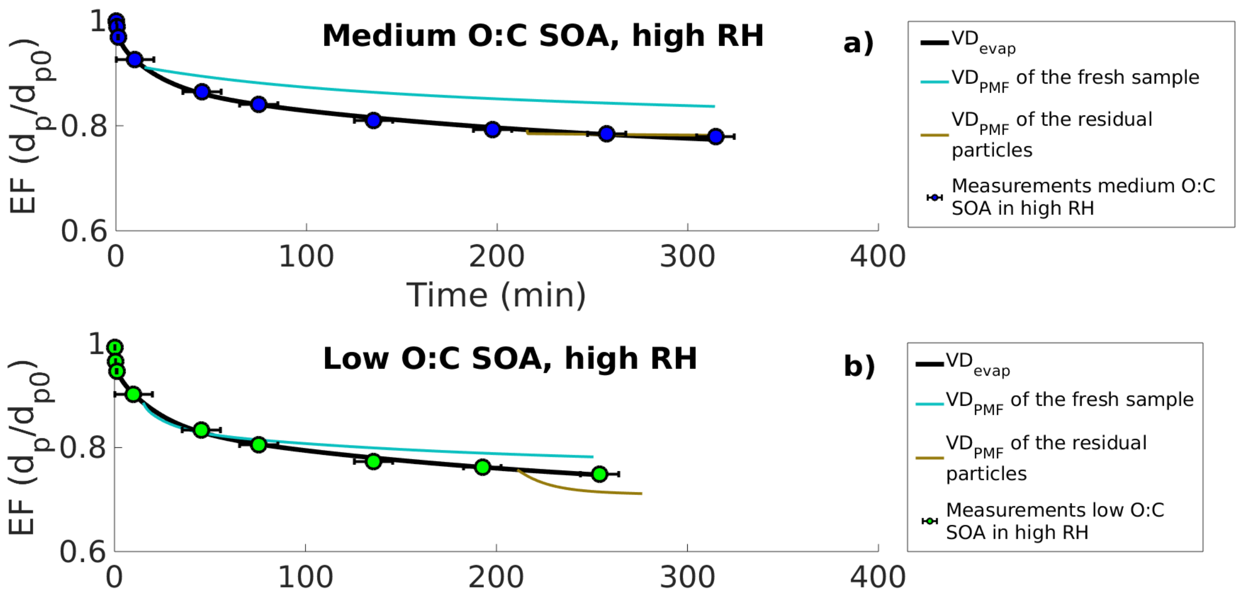

Figure 4: Evapograms of high RH experiments showing the evaporation factors (remaining fraction of the initial particle diameter; circles) and their uncertainty in time for a) medium O:C SOA and b) low O:C SOA, LLEVAP simulated evapograms calculated using the best fit VD_{evap} (black solid lines) and LLEVAP simulated evapograms calculated with VD_{PMF} (turquoise lines for VD_{PMF} of fresh SOA and light brown lines for simulation with VD_{PMF} of the residual particles evaporated 173-259 minutes and 168-254 minutes for medium O:C and low O:C SOA, respectively). The evapograms calculated with the VD_{PMF} of fresh samples ~~SOA~~ show lower rate of evaporation than the evapogram calculated with the VD_{evap} consistent with volatility distribution shown in Fig. 3. The evapograms calculated with the VD_{PMF} of the residual particles (the RTC sample) show a similar rate of evaporation for medium O:C SOA and a faster rate of evaporation for low O:C SOA compared to evapograms calculated with VD_{evap} similarly consistent with Fig. 3.

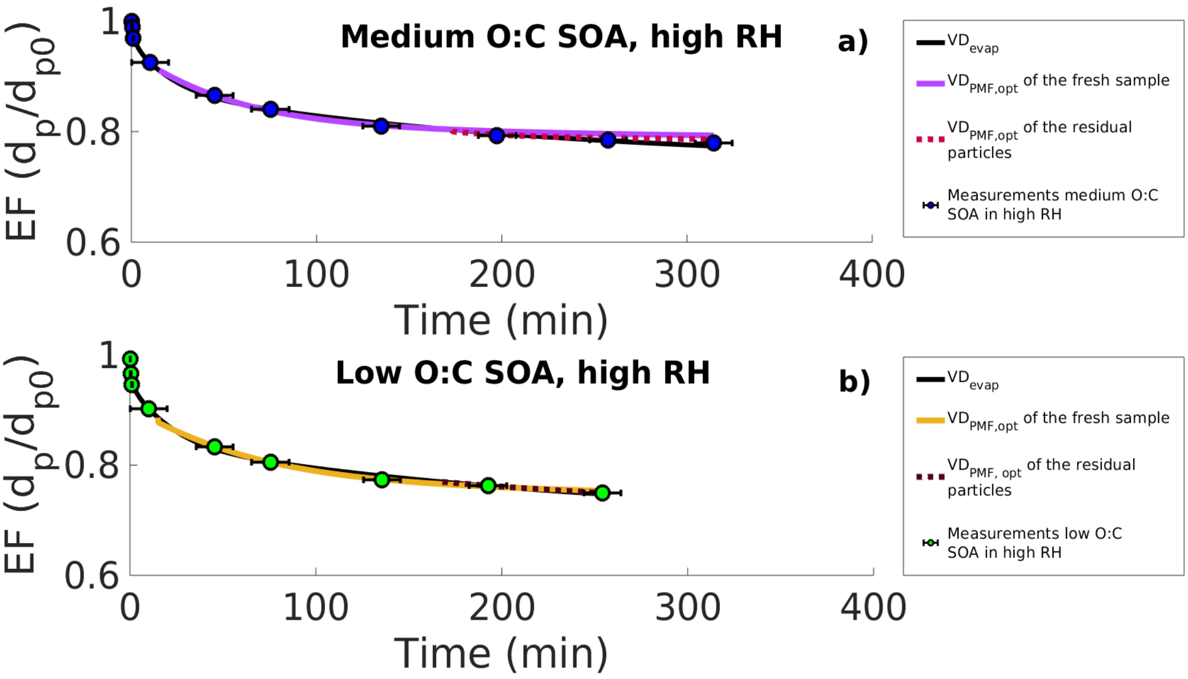

Figure 5: Evapograms of high RH experiments showing the evaporation factors (circles), their uncertainty in time (black whiskers), the best fit simulated evapogram calculated with VD_{evap} (black solid line) and the best fit simulated evapograms calculated with the volatility distribution where the effective saturation concentration (C^*) of each PMF factors are fitted to the measurements ($VD_{PMF,opt}$).

a) Medium O:C SOA

b) Low O:C SOA.

The colored solid lines are for the fresh SOA and the dashed lines for the residual particles collected from the RTC after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. For fitting, the C^* of each PMF factor were allowed values from their respective 25th and 75th percentile desorption temperature shown in Fig. 1.

All the evapograms calculated with the $VD_{PMF,opt}$ match the measured evaporation highlighting that the volatility distribution determined from the FIGAERO-CIMS data with the PMF method can describe the dynamics of evaporating SOA particles when uncertainties in the C^* of the factors are considered.

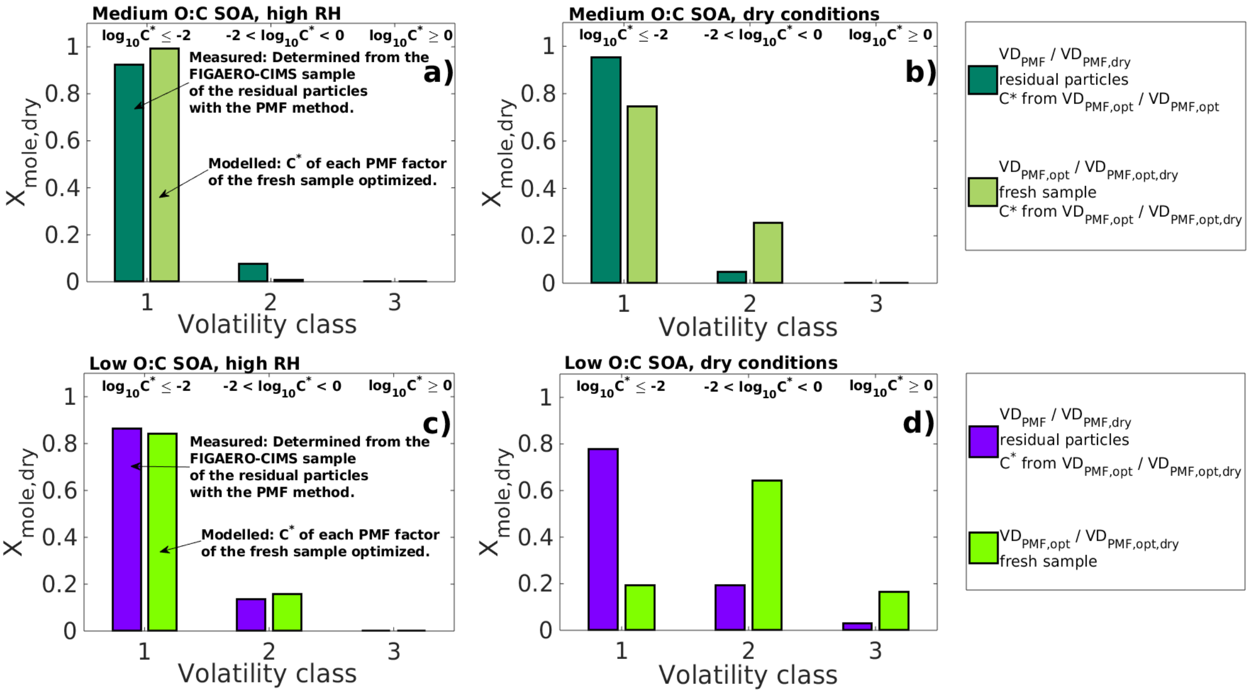

Figure 6: Comparison of the simulated particle composition (VD$_{PMF,opt}$, VD$_{PMF,opt,dry}$) to the particle composition determined from the residual particles collected from the RTC (VD$_{PMF}$/VD$_{PMF,dry}$) after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. The comparison is done at the mean evaporation time of the residual particles. The simulated compositions (VD$_{PMF,opt}$ in a and c, VD$_{PMF,opt,dry}$ in b and d) are taken from the best fit simulated evapogram obtained from the optimization of the C* values of fresh sample’s PMF factors to the measured evapogram. The volatility of individual ~~VD compound~~VD bins are grouped into three volatility classes similar to Fig. 3. The limits for each volatility class are shown at the top and are the same for each subfigure. The C* values from VD$_{PMF,opt}$/VD$_{PMF,opt,dry}$ were used for corresponding VD$_{PMF}$/VD$_{PMF,dry}$ when the volatility grouping was calculated in order to ensure the comparability.

a) Medium O:C SOA in high RH experiment

b) Medium O:C SOA in dry condition~~low RH~~ experiment

c) Low O:C SOA in high RH experiment

d) Low O:C SOA in dry condition~~low RH~~ experiment.

In the high RH cases (sub~~g~~figures a and c) the volatility distributions simulated based on VD$_{PMF,opt}$ of the fresh SOA are similar to the measured VD$_{PMF,}$ while for the dry condition ~~the low RHfor~~ cases (subfigures b and d) the volatility distributions simulated based on VD$_{PMF,opt,dry}$ show higher volatility than the measured VD$_{PMF}$.

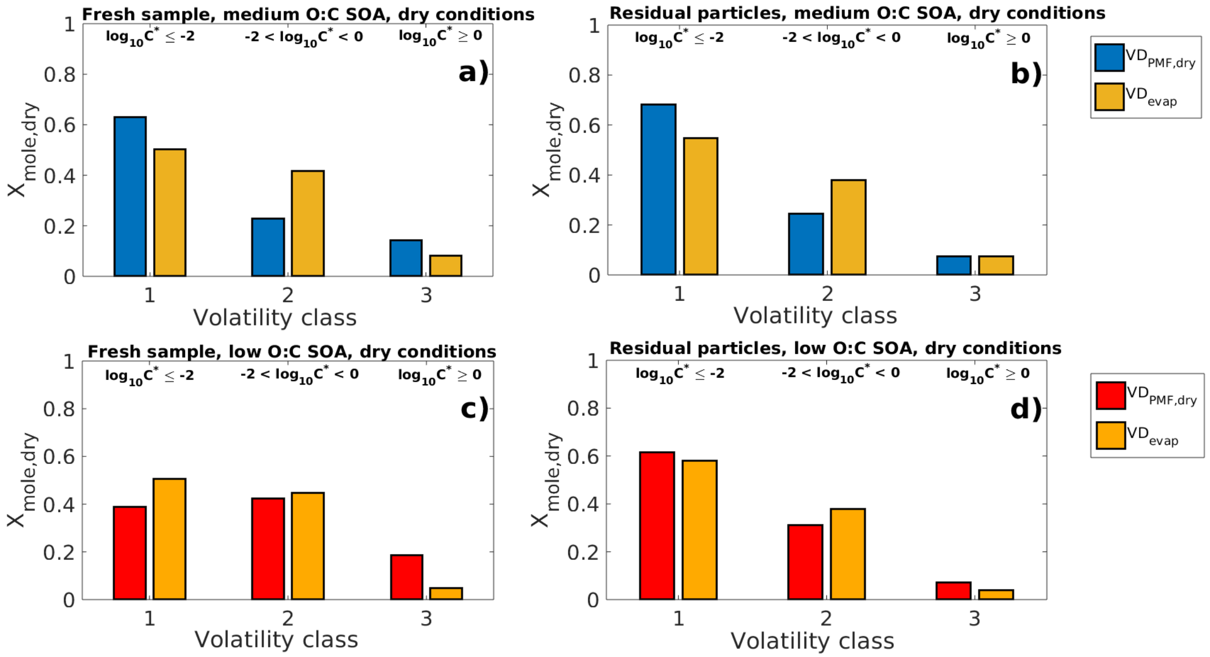

Figure 7: Comparison of $\mathrm{VD}_{\mathrm{PMF,dry}}$ (volatility distribution with~~herew~~ C^* ~~is~~ calculated from the peak desorption temperature, T_{max}, of each PMF factor) and $\mathrm{VD}_{\mathrm{evap}}$ (volatility distribution determined by fitting LLEVAP model to measured evapogram) at the mean evaporation time of the SOA samples in dry condition experiments. The ~~VD compound~~VD bins are grouped into three ~~different~~ volatility classes similar to Fig. 3. The limits for each volatility class are shown at the top and are the same for each subfigure.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA after 170-256 minutes of evaporation (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 152-238 minutes of evaporation (the RTC sample).

The $\mathrm{VD}_{\mathrm{PMF,dry}}$ shows lower overall volatility than the $\mathrm{VD}_{\mathrm{evap}}$ for medium O:C SOA. For low O:C SOA the $\mathrm{VD}_{\mathrm{PMF,dry}}$ shows higher volatility for fresh sample and similar volatility compared to the $\mathrm{VD}_{\mathrm{evap}}$ after 152-238 minutes of evaporation.

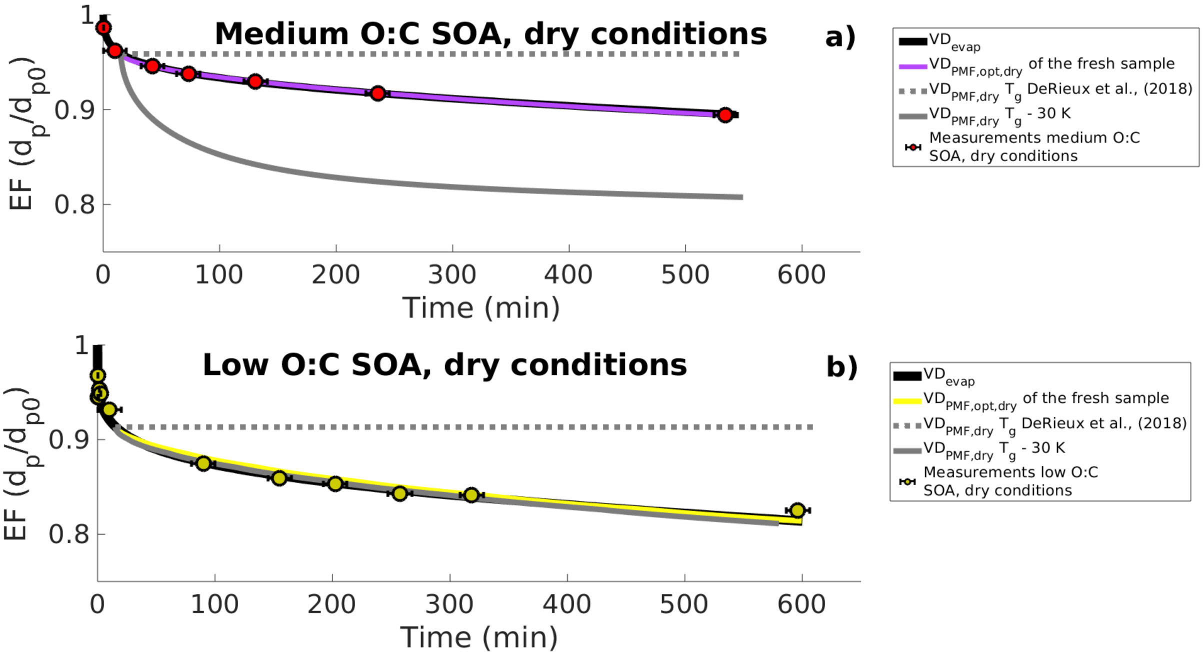

Figure 8: Evapograms showing the measured isothermal evaporation of a) medium O:C SOA b) low O:C SOA in dry condition experiments and their uncertainty in time (red and yellow markers and black whiskers) together with the simulated evapograms. The best fit simulated evapogram calculated with VD_{evap} (obtained from high RH experiments) and optimizing b_i is shown with black solid line. Grey lines show the minimum and maximum possible evaporation calculated with $VD_{PMF,dry}$ (C^* of PMF factors calculated from T_{max}) at~~nd~~ the highest (the original parametrization of DeRieux et al., (2018), grey dashed lines) or the lowest (30 K subtracted from the T_g of every ion, grey solid line) studied viscosity. Purple and yellow solid lines show the best fit simulated evapograms calculated with the optimized $VD_{PMF,opt,dry}$ (based on the assumption that the FIGAERO sample represents particles at the mean of the sample collection interval) and b_i restricted based on the DeRieux et al. (2018) parameterization. The figure shows, similar to Fig. 5, that the volatility distribution determined from the FIGAERO-CIMS data with the PMF method is consistent with the measured evaporation of the SOA particles once the uncertainty in the effective saturation concentration and the glass transition temperature parametrization of DeRieux et al., (2018) are considered.

Supplementary material

FIGAERO-CIMS calibration

Figure S1 shows the results of the T_{max} to P_{sat} calibration measurements done using polyethylene glycols (PEG) solutions in acetonitrile with 5 to 8 glycol units (blue dots). A b~~B~~ivariate linear fit (Pitkänen et al., 2016; York et al., 2004) ~~,~~that takes the uncertainties of the points into account was then applied to normal logarithm of the P_{sat} values as a function of~~vs.~~ measured T_{max} values. Literature values of P_{sat} with uncertainties were taken from Krieger et al., (2018) and standard deviation of three T_{max} measurements was used as uncertainty for T_{max} values.

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York, D., Evensen, N. M., Martínez, M. L. and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, American Journal of Physics, 72(3), 367–375, doi:10.1119/1.1632486, 2004.

Table S1: Minimum, mean and maximum time that the particles have evaporated during the FIGAERO sample collection. All times are relative to the start of RTC filling.

Sample	Minimum evaporation time (min)	Mean evaporation time (min)	Maximum evaporation time (min)
Medium O:C high RH fresh	0	15	30
Medium O:C high RH RTC	173	216	259
Medium O:C dry fresh	0	15	30
Medium O:C dry RTC	170	213	256
Low O:C high RH fresh	0	15	30
Low O:C high RH RTC	168	211	254
Low O:C dry fresh	0	15	30
Low O:C dry RTC	152	195	238

Table S2: The best fit C^* values for medium O:C and low O:C high RH experiments when C^* values of PMF factors were optimized with respect to the measured isothermal evaporation. For each experiment three different results are given which correspond to simulations initialized with the PMF mole fraction at the minimum, mean and maximum time that the particles have evaporated during the sample collection (See Table S1). The C^* values are rounded to two significant digits and are in units μgm^{-3}. C^* values below 10^{-3} μgm^{-3} are not reported explicitly since the evapogram fitting method is not sensitive to these values.

	Medium O:C fresh sample min evap. time	Medium O:C fresh sample mean evap. time	Medium O:C fresh sample max evap. time	Medium O:C RTC sample min evap. time	Low O:C fresh sample min evap. time	Low O:C fresh sample mean evap. time	Low O:C fresh sample max evap. time	Low O:C RTC sample min evap. time
Factor M1/L1	3.47	$4.96 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$	36.10	11.40	$3.06 \cdot 10^{-1}$	$8.91 \cdot 10^{-2}$	$<10^{-3}$
Factor M2/L2	$2.89 \cdot 10^{-1}$	$2.89 \cdot 10^{-1}$	$2.17 \cdot 10^{-1}$	$4.12 \cdot 10^{-1}$	$6.79 \cdot 10^{-1}$	$3.55 \cdot 10^{-1}$	$3.63 \cdot 10^{-1}$	$2.40 \cdot 10^{-2}$
Factor M3/L3	$1.00 \cdot 10^{-2}$	$9.93 \cdot 10^{-3}$	$2.11 \cdot 10^{-3}$	$4.42 \cdot 10^{-3}$	$2.88 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$	$9.55 \cdot 10^{-3}$	$7.13 \cdot 10^{-3}$
Factor M4/L4	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$1.55 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Factor M5/L5	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Factor D1a	96.63	$7.68 \cdot 10^{-1}$	$9.86 \cdot 10^{-2}$	69.35	133.83	130.03	$3.49 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$
Factor D1b	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$

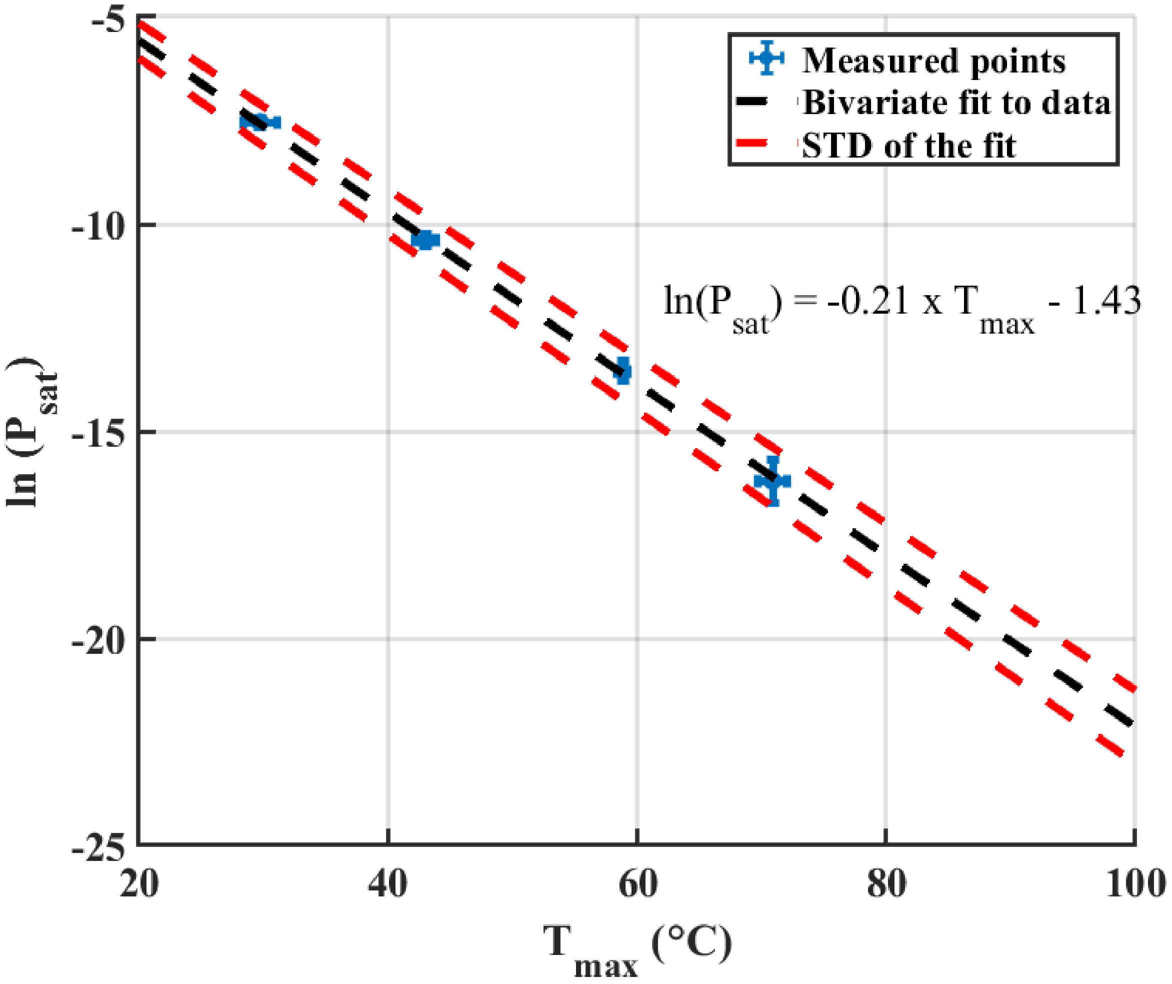

Figure S1: Calibration measurements and fitted parametrization which connects the maximum desorption temperature T_{max} to saturation vapor pressure P_{sat}.

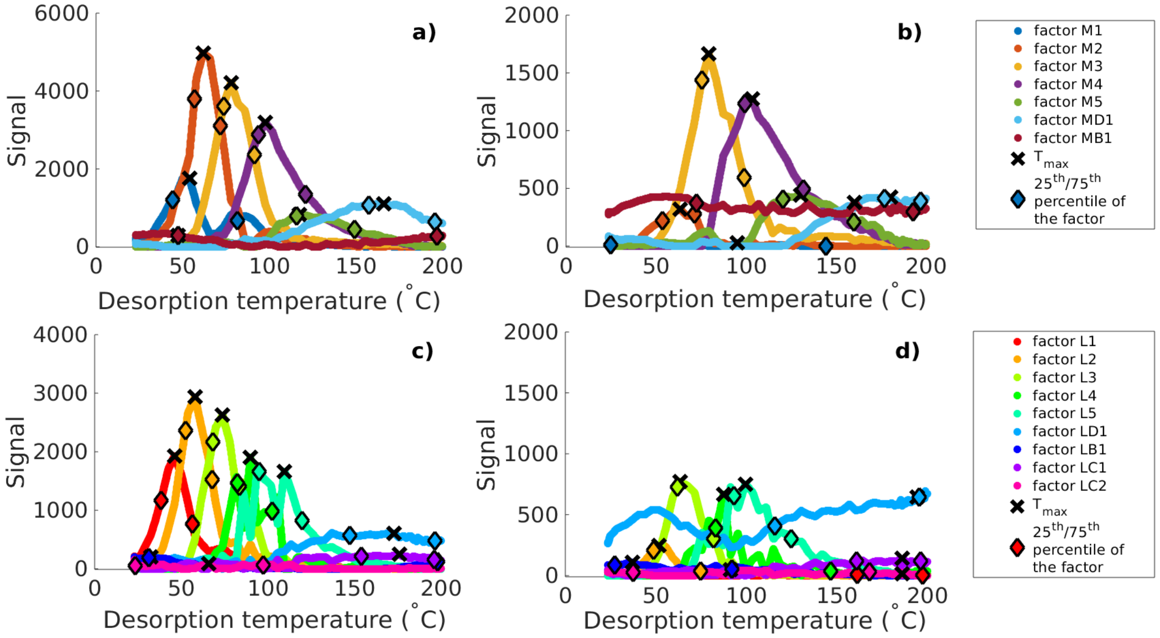

Figure S2: Full positive matrix factorization (PMF) mass loading profiles for thermal desorption of secondary organic aerosol (SOA) from α-pinene at high RH conditions.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA after 173-259 minutes of evaporation in a residence time chamber (RTC), i.e. the RTC sample

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 168-254 minutes of evaporation in the RTC, i.e. the RTC sample.

The black crosses show the peak desorption temperature T_{max} and the diamonds show the 25th and 75th percentiles of the factors area. In medium O:C samples' analysis, factor MB1 is omitted and factor MD1 is divided into a new factors MD1a and MD1b. In low O:C samples' analysis, factors LC1 and LC2 are omitted and factor LD1 is divided into new factors LD1a and LD1b. See Sect. 3.1 in the main text for details.

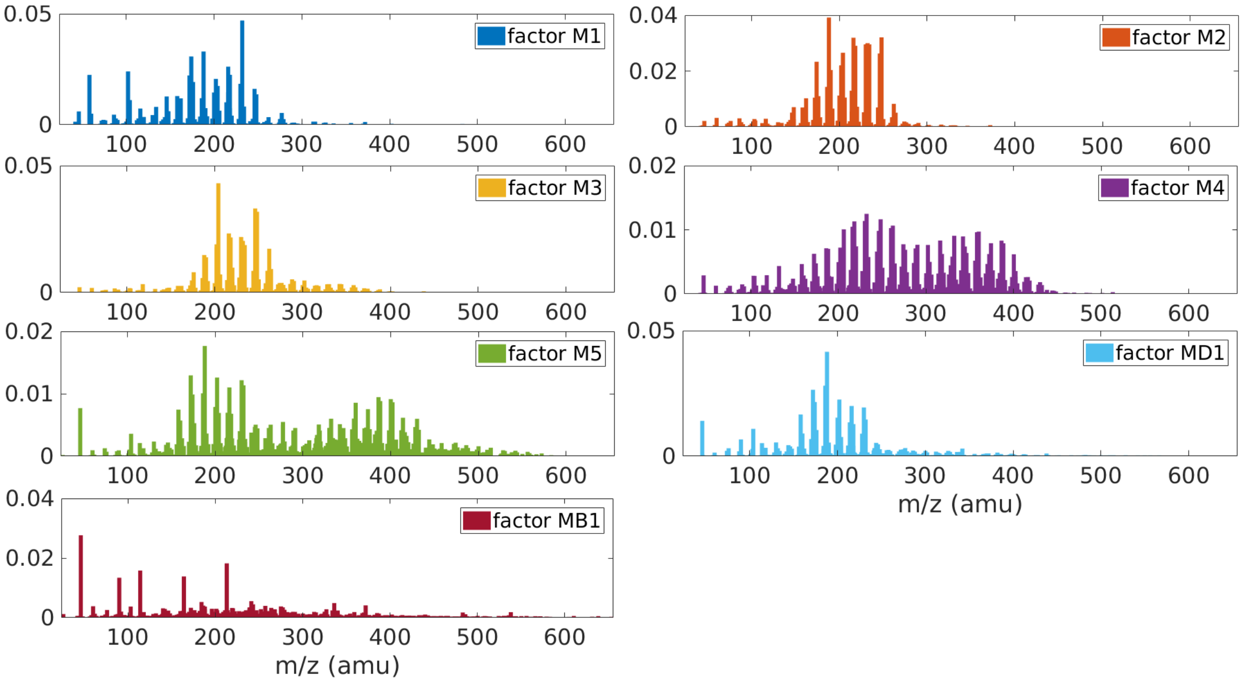

Figure S3: PMF mass spectra for medium O:C samples. These factors correspond to factors shown in Fig. S2.

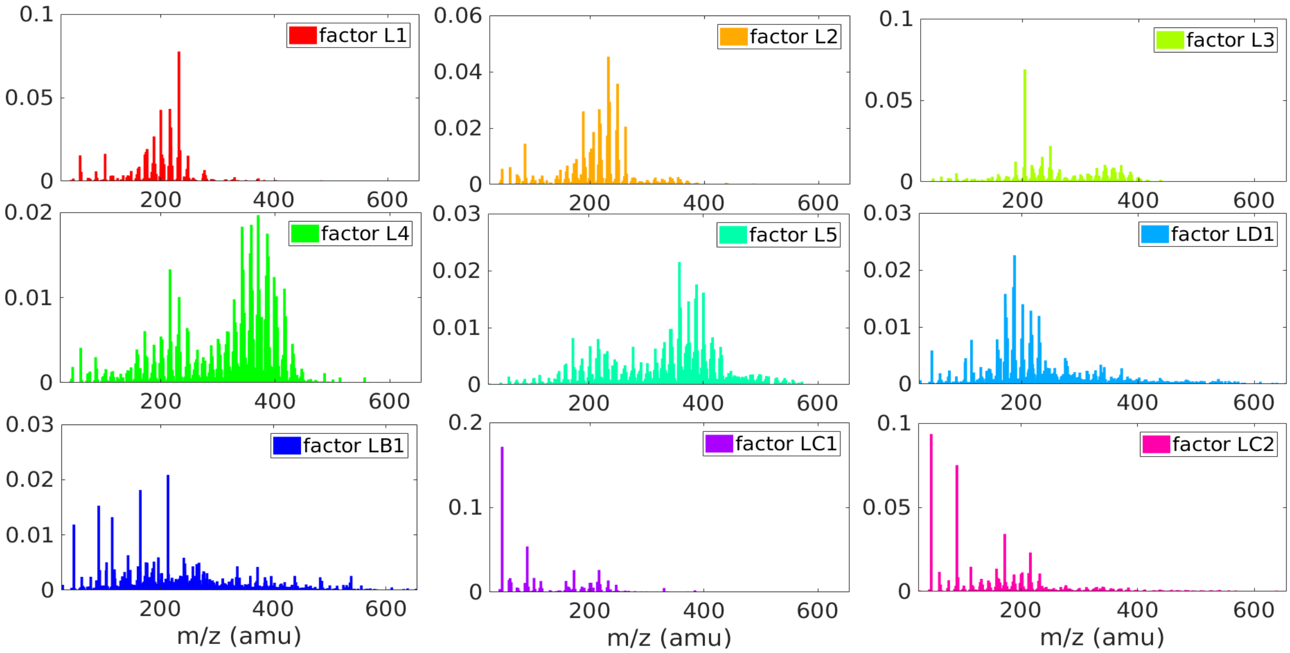

Figure S4: PMF mass spectra for low O:C samples. These factors correspond to factors shown in Fig. S2.

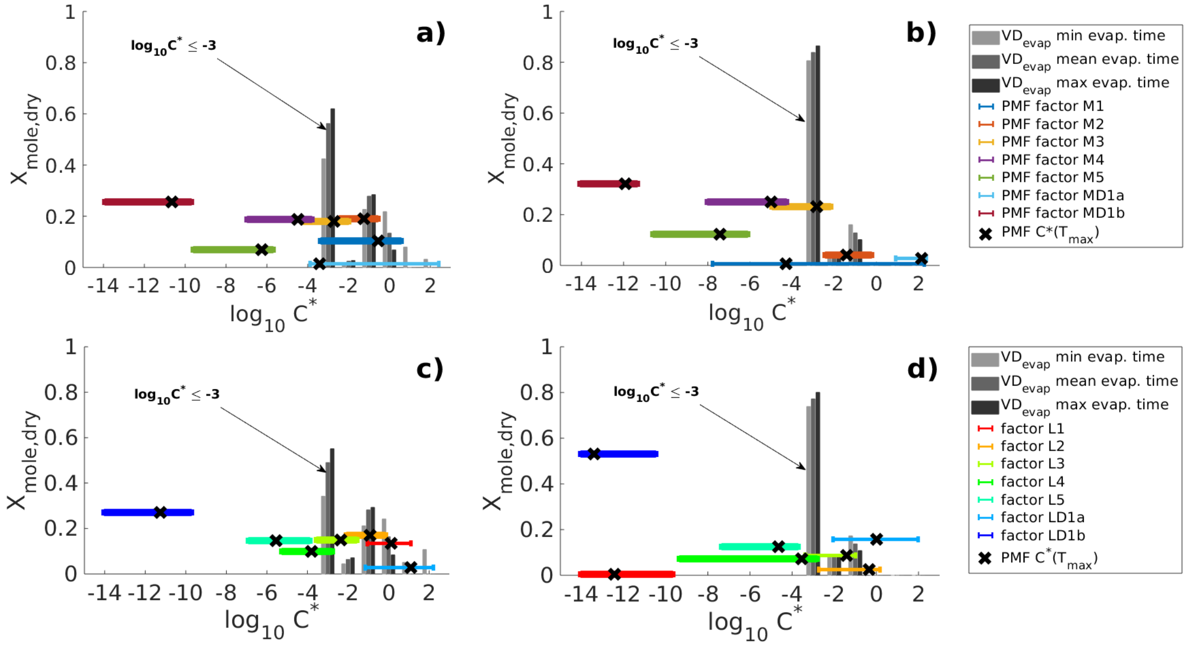

Figure S5: Volatility distributions in high RH experiments determined from model fitting of evapogram data (VD_{evap}) and PMF analysis of FIGAERO-CIMS data (VD_{PMF}) for the same four cases shown in Fig. S2

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

VD_{evap} is shown for the best fit simulation (grey bars). The different grey shades show the VD_{evap} in the simulation at minimum, mean and maximum time that the particles have evaporated when the FIGAERO sample was collected (see Table S1). Black crosses show the $\log_{10}(C^*)$ calculated for each PMF factor from the peak desorption temperature T_{max}. The horizontal colored lines show the range of $\log_{10}(C^*)$ calculated from the 25^{th} and 75^{th} percentiles of each PMF factors mass loading profile.

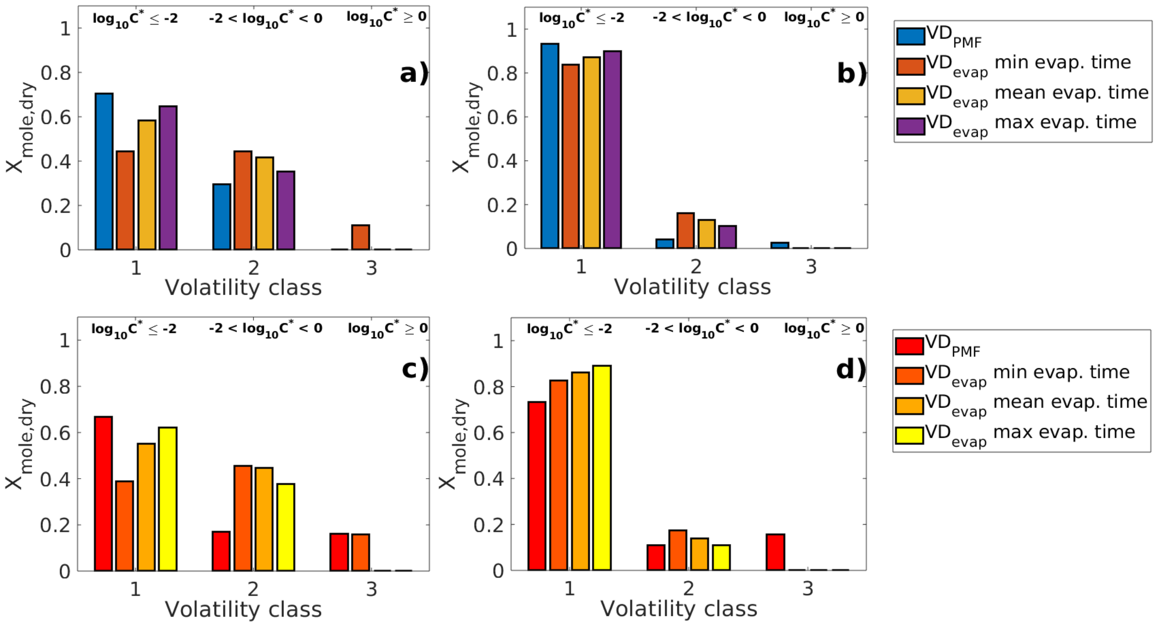

Figure S6: Comparison of VD$_{PMF}$ and VD$_{evap}$ in high RH experiments for the same four cases shown in Fig. S2.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

The VD compounds are grouped into three different volatility classes. Min, mean and max evaporation time refer to the FIGAERO sample collection times presented in Table S1. The VD compounds shown in Fig. S5 are grouped into three different volatility classes based on their evaporation tendency with respect to the measurement time scale and particle size. The limits for each volatility class are shown at the top and are the same for each subfigure.

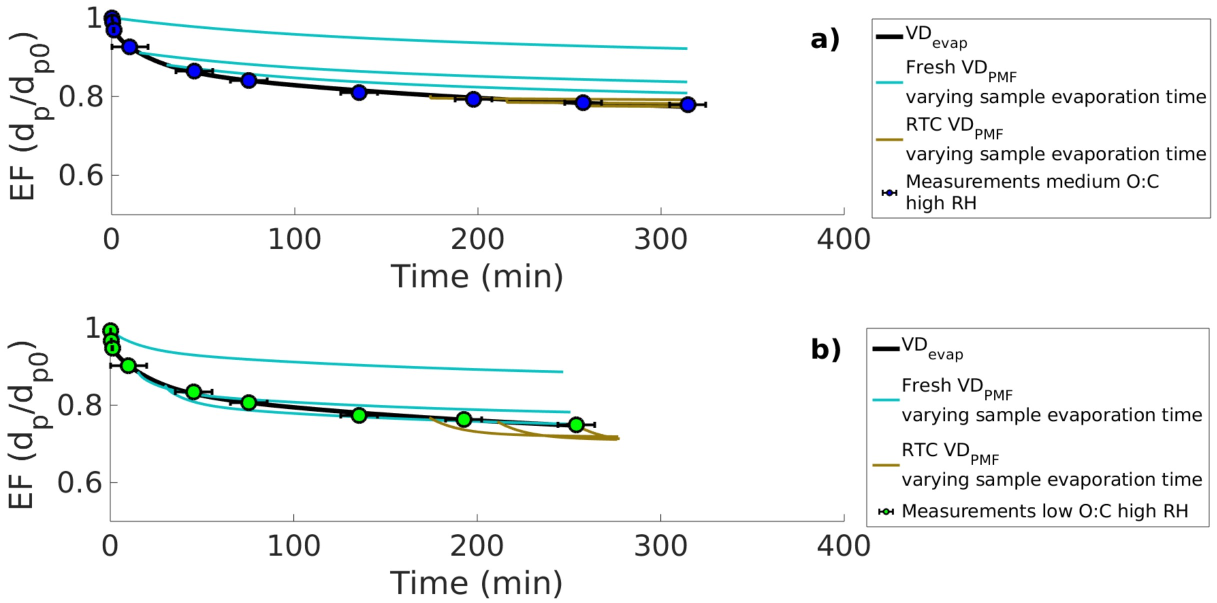

Figure S7: Evapograms of high RH experiments showing the measured evaporation factors (remaining fraction of initial particle diameter; circles) and their uncertainty in time for a) medium O:C SOA and b) low O:C SOA, LLEVAP simulated evapograms calculated using the best fit VD_{evap} (black solid lines) and LLEVAP simulated evapograms calculated with VD_{PMF} (turquoise solid lines for VD_{PMF} of fresh samples and light brown solid lines for VD_{PMF} of the RTC samples). The three turquoise and brown lines present model simulations where the fresh and RTC sample, respectively, were assumed to represent the particle composition at the minimum, mean or maximum evaporation time of the sample (see Table S1).

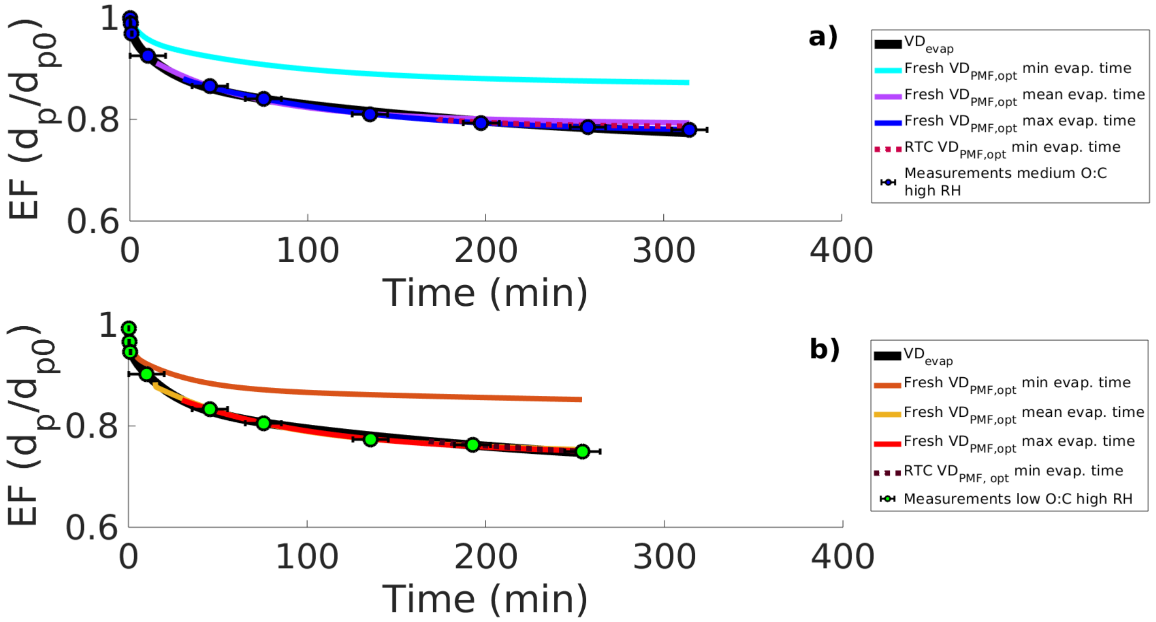

Figure S8: Evapograms of high RH experiments showing the measured evaporation factors (circles) and their uncertainty in time (black whiskers), the best fit simulated evapogram calculated with VD_{evap} (black solid line) and the best fit simulated evapograms calculated with the volatility distribution where the effective saturation concentration (C^*) of each PMF factors are fitted to the measurements ($VD_{PMF,opt}$).

a) Medium O:C SOA

b) Low O:C SOA.

The colored solid lines are for the fresh SOA with varying starting time of the simulation. These simulations assumed that the fresh sample represented the particle composition at the minimum, mean or maximum evaporation time of the fresh FIGAERO-CIMS sample. ~~and t~~The dashed lines are showing the simulations based on ~~for~~ the SOA collected from the RTC after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. For these residual particle samples, the FIGAERO-CIMS sample was assumed to represent the minimum evaporation time of the sample (see Sect. 3.2 in the main text).~~.~~ For fitting, the C^* of each PMF factor were allowed values from their respective 25th and 75th percentile desorption temperature shown in Fig. S5.

The simulations of the fresh samples that start at the mean or maximum evaporation time resemble the measured evaporation and the evaporation simulations calculated with the VD_{evap}. The simulation of the fresh sample that starts from the minimun evaporation time does not produce evaporation curve similar to the measurements. The results highlight the fact that it is not likely that the fresh sample consists of particles that have just entered the residence time chamber.

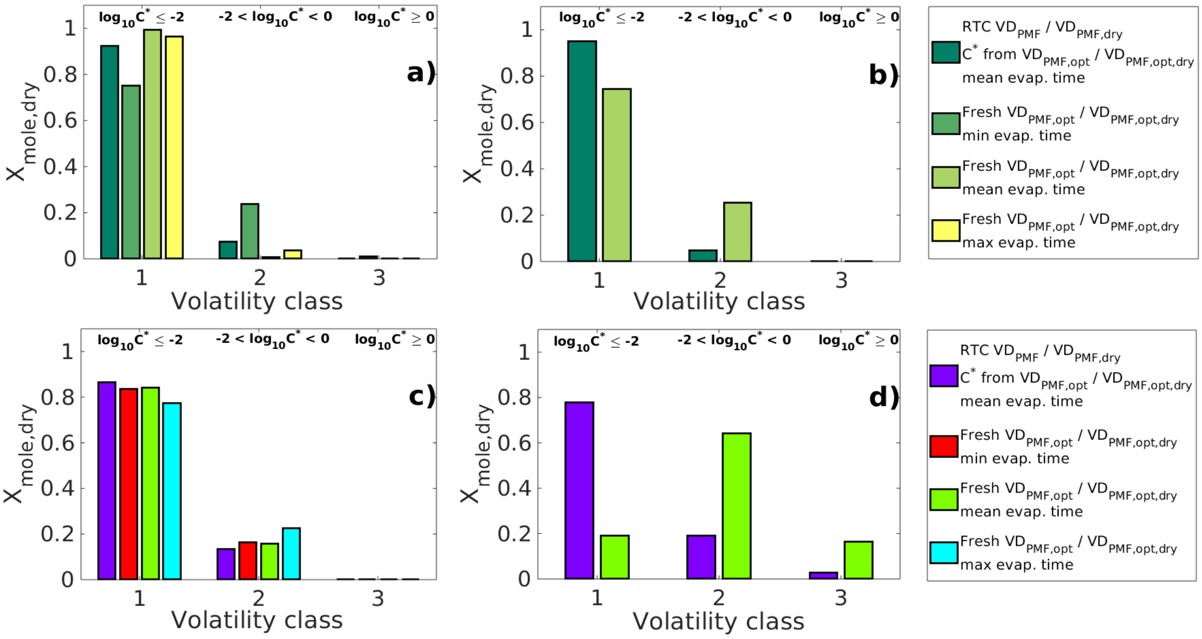

Figure S9: Comparison of the simulated particle composition (VD$_{PMF,opt}$, VD$_{PMF,opt,dry}$) at varying assumed sample evaporation times to the particle composition determined for SOA collected from the RTC (VD$_{PMF}$/VD$_{PMF,dry}$) after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. The simulated compositions (VD$_{PMF,opt}$ in a and c, VD$_{PMF,opt,dry}$ in b and d) are taken from the best fit simulated evapogram obtained from the optimization of the C* values of fresh sample PMF factors to measured evapogram. The volatility of individual VD compounds are grouped into three volatility classes similar to Fig. S6. The limits for each class are shown at the top and are the same for each subfigure. The C* values from VD$_{PMF,opt}$/VD$_{PMF,opt,dry}$ at the mean evaporation time were used for corresponding VD$_{PMF}$/VD$_{PMF,dry}$ when the volatility grouping was calculated in order to ensure the comparability.

a) Medium O:C SOA in high RH experiment
b) Medium O:C SOA in low RH experiment
c) Low O:C SOA in high RH experiment
d) Low O:C SOA in low RH experiment.

The results of medium O:C SOA in high RH experiments show that the VD$_{PMF}$ best resembles the VD$_{PMF,opt}$ of the maximum evaporation time, although the difference to the mean evaporation time is not significant. For low O:C SOA in high RH experiments, the results show that the VD$_{PMF}$ best resembles the VD$_{PMF,opt}$ of the mean evaporation time.
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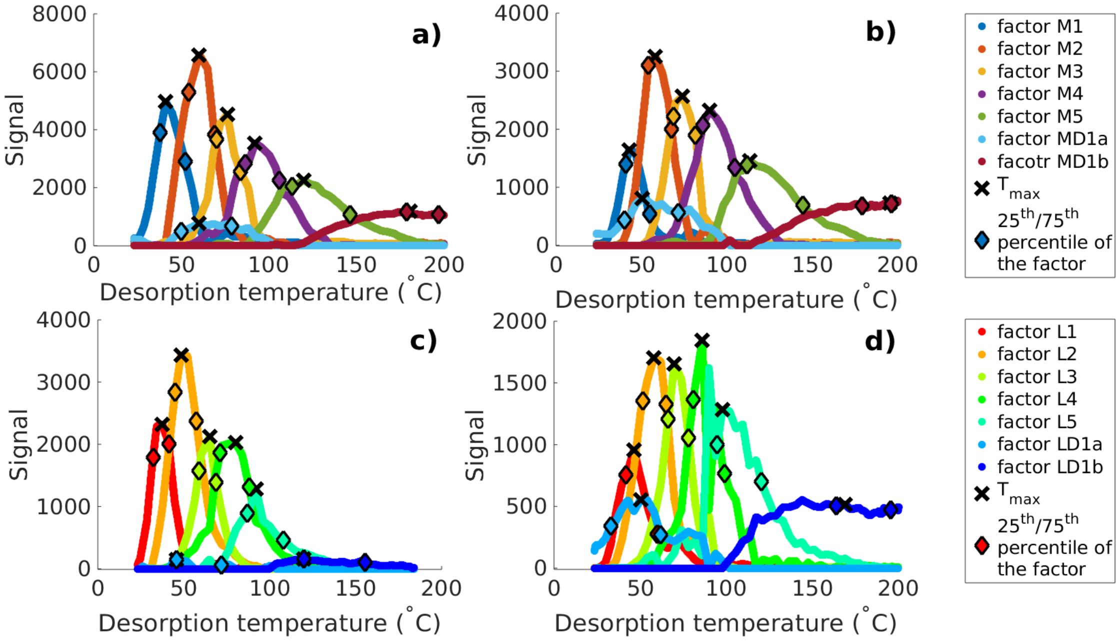

Figure S10: Main PMF mass loading profiles from experiments done in dry conditions.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA after 170-256 minutes of evaporation in a residence time chamber (RTC), i.e. the RTC sample

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 152-238 minutes of evaporation in the RTC. The black crosses show the peak desorption temperature T_{max} and the diamonds show the 25th and 75th percentiles of the factors area.

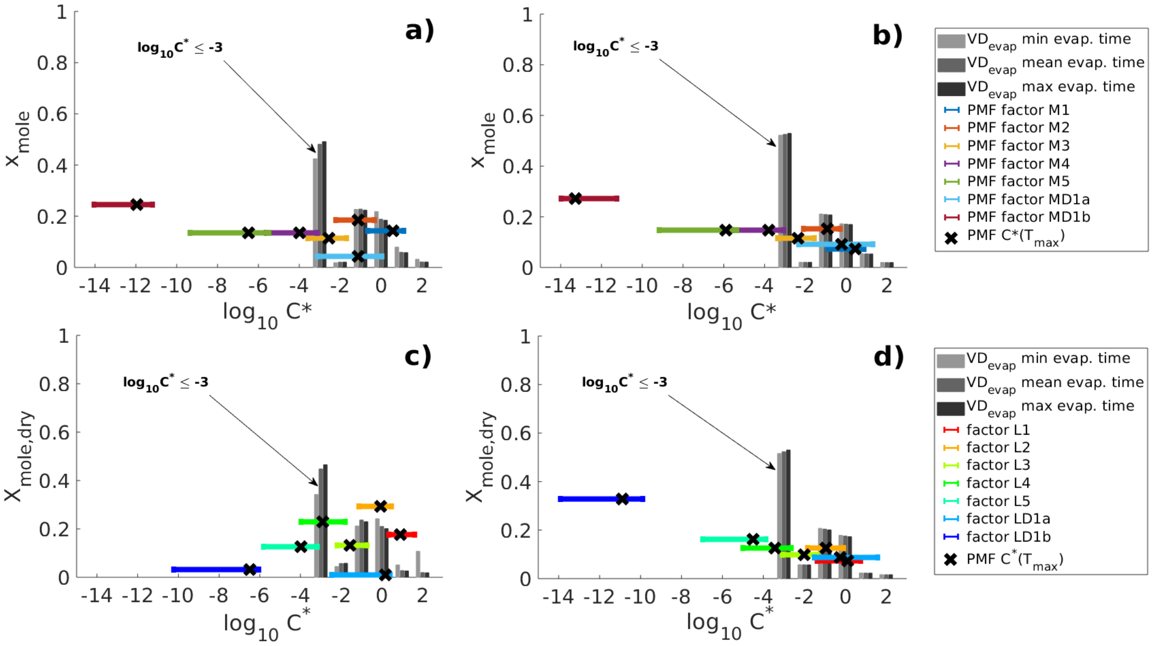

Figure S11: Volatility distributions in dry condition~~s~~ experiments determined from model fitting to the evapogram data (VD_{evap}) and PMF analysis of FIGAERO-CIMS data (VD_{PMF}) for the same four cases shown in Fig. S10.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

VD_{evap} is shown for the best fit simulation (grey bars). The different grey shades show the VD_{evap} in the simulation at minimum, mean and maximum time that the particles have evaporated when the FIGAERO sample was collected (see Table S1). Black crosses show the $log_{10}(C^*)$ calculated for each PMF factor from the peak desorption temperature T_{max}. The horizontal colored lines show the range of $log_{10}(C^*)$ calculated from the 25th and 75th percentiles of each PMF factors mass loading profile.

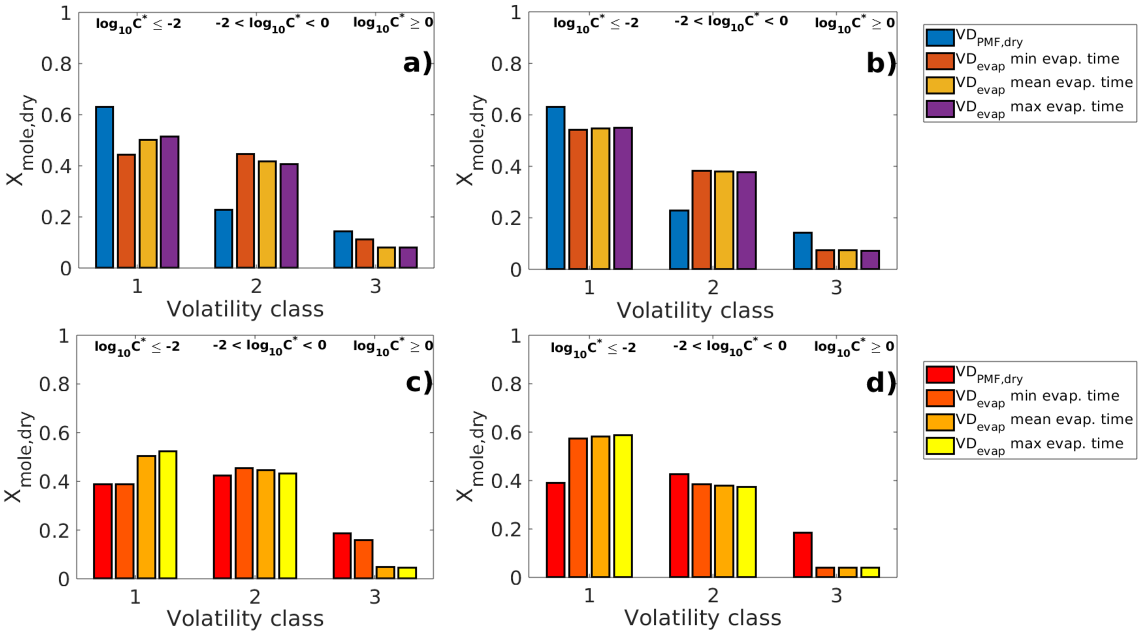

Figure S12: Comparison of $VD_{PMF,dry}$ (volatility distribution where C^* is calculated from T_{max} of each PMF factor) and VD_{evap} (volatility distribution determined by fitting LLEVAP model to measured evapogram) at varying sample evaporation times in dry condition experiments. The VD compounds are grouped into three different volatility classes similar to Fig. S6. The limits for each volatility class are shown at the top and are the same for each subfigure.

a) Fresh sample of medium O:C SOA

b) Residual particle of medium O:C SOA after 170-256 minutes of evaporation (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 152-238 minutes of evaporation (the RTC sample).