We gratefully thank all reviewers for the careful reading and valuable comments. Below we provide our point-by-point responses to the reviewer's comments. In the following context, **raised comments/suggestions** are marked in **black**, **responses** are presented in **red**, and **changes to the manuscript/supplement information** are indicated in **blue**. The figures and tables in the following response are numbered consecutively in three replies to reviewers. Additionally, we corrected any minor typo that we recognized in the manuscript and supplement.

The legitimate questions about the real meaning of the PMF factors in the context of thermogram data led us to reconsider the strict distinction of type V and D factors. Instead, we now use the term "sample" factor and relabel the factors as AF1 - AF5 (before AV1-AV4 and AD5) and SF1 - SF5 (before SV1-SV4 and SD5) for α-pinene and SQTmix SOA systems. We use the new labels in our responses to be consistent with the revised manuscript. Note that the interpretation of the factors has not changed, only the labels were adjusted to remove some potential for misunderstandings.

Reply to Reviewer 3

This work by Li et al. investigates the changes in volatility and composition of SOA from the oxidation of α-pinene and a sesquiterpene mixture as a result of isothermal evaporation. It details laboratory experiments performed with a FIGAERO-CIMS to obtain volatility information and molecular formulas for species in the SOA. Results from the sesquiterpene mixture were compared to that from α-pinene, and also compared between dry (RH <7%) and wet (RH ~80%) conditions. Positive matrix factorization (PMF) was used to investigate the behavior of individual factors before and after evaporation at the two RH extremes. Unsurprisingly, one result is that the sesquiterpene SOA is more resistant to evaporation than α-pinene, implying lower volatility. They also found that under high RH, more of the signal evaporated. This work is novel, will be of interest to the readers of ACP, and provides valuable information to the community. After addressing the minor general and specific comments below, this manuscript will be suitable for publication in ACP.

General comments

Comment The use of so many acronyms make the manuscript difficult to follow at times. Some examples include:

- the abbreviation of α-pinene to αpin is unnecessary

  We have removed the abbreviation "apin" and replaced that with "α-pinene" through the text.

- changing STG to ΣTG could make it easier for the reader to remember what this stands for

  We do not agree with changing STG to ΣTG for our manuscript. Since we have used subscripts to indicate normalization or scaling for different versions of STG in the section 2.2, using ΣTG would contradict with the original ideas of normalized and scaled STG. Furthermore, we are convinced that mixing capital Greek and Roman letters in this case will instead decrease the readability.

- RTC for residence time chambers is used to refer to both the physical chamber (lines 94-96, 105, 111) and the experiment type (lines 130, 160, 182, etc) which is confusing. When referring to experiment type does it always refer to a specific evaporation time length?

  We disagree with the assumption that the dual use of RTC causes major problems in this context. The label "RTC" for the sample type indicates that the particles were inside the RTC. The "fresh" particles never entered the RTC.

  The labels "fresh" and "RTC" for the two evaporation stages always refer to the same evaporation times as stated in the manuscript (e.g., line 182 original version)

- CNerror is only used once (line 155).

  We have removed the abbreviation CNerror.

Comment This study could benefit from a more robust discussion of, and comparison to, the several previous studies measuring the evaporation of α-pinene SOA

Response We agree that it is important to put new findings in the context of existing studies. Unfortunately, it was difficult to find truly comparable studies for our experiments. We could not find any volatility measurements for SOA from acyclic SQTs that were similar to our SQTmix. For α-pinene, multiple studies of isothermal evaporation at room temperature exist (Vaden et al., 2011; Wilson et al., 2014; Yli-Juuti et al., 2017; D'Ambro et al., 2018; Buchholz et al., 2019; Li et al., 2019; Zaveri et al., 2020; Pospisilova et al., 2021). However, even for a single precursor system, the SOA formation conditions determine the volatility of the formed SOA. Buchholz et al. (2019) show that the VFR(t_R=4h) of α-pinene SOA particles with a wide range of OSc (i.e., from -0.46 to 0.63) is between 0.45 and 0.90. Pospisilova et al. (2021) also show that the degree of photochemical ageing changes the observed isothermal evaporation under dry conditions. In their study, the OSc was between -0.8 and -0.4 (estimated from f_{43} and f_{44} values) and the VFR values at 0.4 to 0.8. Li et al. (2019) showed that the observed isothermal evaporation and the sensitivity to particulate water is different for α-pinene SOA of similar OSc formed from either photooxidation or ozonolysis. D'Ambro et al. (2018) investigated isothermal evaporation of particles collected on a FIGAERO filter. They showed that SOA with different physical age (i.e., produced under similar conditions in different simulation chambers) can exhibit different volatility and apparent composition.

Although there are multiple studies of isothermal evaporation of α-pinene SOA particles, very few studies provide molecular information that is comparable to our approach. D'Ambro et al. (2018) conducted FIGAERO-CIMS measurements of particles that were allowed to evaporate on the filter after collection. Although the α-pinene SOA particles in the study may not be directly comparable to the particles in our study, some of their findings share similarities with the interpretation of our PMF factors. For each ion, they explain the observed isothermal evaporation behavior with a model containing 3 components with different apparent volatility: (i) free monomers that evaporate from particles according to their C* values, (ii) ELVOC compounds that do not evaporate from the particles at room temperature but decompose upon heating to be detected as the single ion, and (iii) reversible oligomers that decompose into the corresponding free monomers with time or heat. In our data set, many individual ions show contributions from multiple factors. AF1 and SF1 are predominantly containing compounds that behave like "free monomers". AF5 and SF5 are mostly ELVOC compounds that are detected as thermal decomposition products. The behavior described for "reversible oligomers" is in line with the complex behavior of the PMF factors which we associate with aqueous-phase processes. As D'Ambro et al. (2018) only applied their model investigation to particle evaporation at 50% RH and above, it is impossible to determine whether the particle phase processes affecting the reversible oligomers are linked to the presence of particulate water. Note that the approach of D'Ambro et al. (2018) deploys a ion-by-ion model fitting, while our PMF analysis inspects the behavior of all ions in the data set at once.

We added the summary of this to the appropriate place in section 3.3.3 and 4 of the manuscript to give a stronger context for our findings.

Change Section 3.3.3

Although there are multiple studies of isothermal evaporation of α-pinene SOA particles, very few studies provide molecular information that is comparable to our approach. D'Ambro et al. (2018) conducted FIGAERO-CIMS measurements of particles that evaporated on the filter after collection. Although the α-pinene SOA particles in the study may not be directly comparable to the particles in our study, some of their findings share similarities with the interpretation of our PMF factors. For each ion, they explain the observed isothermal evaporation behavior with a model containing 3 components with different apparent volatility: (i) free monomers that evaporate from particles according to their C* values, (ii) ELVOC compounds that do not evaporate from the particles at room temperature but decompose upon heating to be detected as the single ion, and (iii) reversible oligomers that decompose into the corresponding free monomers with time or heat. In our data set, many individual ions show contributions from multiple factors. AF1 and SF1 are predominantly containing compounds that behave like "free monomers". AF5 and SF5 are mostly ELVOC compounds that are detected as thermal decomposition products. The behavior described for "reversible oligomers" is in line with the complex behavior of the PMF factors which we associate with aqueous-phase processes. As D'Ambro et al. (2018) only applied their model investigation to particle evaporation at 50% RH and above, it is impossible to determine whether the particle phase processes affecting the reversible oligomers are linked to the presence of particulate water. Note that the approach of D'Ambro et al. (2018) deploys a ion-by-ion model fitting, while our PMF analysis inspects the behavior of all ions in the data set at once.

Section 4

To our knowledge, this is the first study investigating the volatility of SOA particles from a mixture of farnesene and bisabolene which are acyclic and monocyclic sesquiterpenes of atmospheric relevance. For α-pinene, multiple studies of isothermal evaporation at room temperature exist (Vaden et al., 2011; Wilson et al., 2014; Yli-Juuti et al., 2017; D'Ambro et al., 2018; Buchholz et al., 2019; Li et al., 2019; Zaveri et al., 2020; Pospisilova et al., 2021). However, even for this single precursor system, the formation conditions determine the isothermal evaporation behavior of the formed SOA and thus must be carefully considered when comparing different studies. The detailed composition of particles determines their volatility, viscosity, and behavior towards particulate water. Generally, particles containing increasing amounts of higher oxidized compounds will exhibit lower volatility (Buchholz et al., 2019; Zaveri et al., 2020; Pospisilova et al., 2021), but may be more likely to be susceptible to aqueous-phase reactions (Buchholz et al., 2019). Unfortunately, not all previous studies provide an O/C, OSc value or similar proxy to estimate the degree of oxidation, which makes further comparisons difficult.

Specific comments

Comment Line 78: I think it could be helpful to the reader to 1) specify the mixture of sesquiterpenes, at least with respect to the most dominant species present, and 2) show their structures somewhere.

Response We agree with the reviewer and added a sentence to clarify the composition of the sesquiterpene mixture.

Change Section 2.1

[…] Farnesene isomers (40%, acyclic) and bisabolene isomers (40%, monocyclic) are the two dominant species in the mixture of sesquiterpene, followed by other unidentified sesquiterpenes (Ylisirniö et al., 2020). […]

Comment Paragraph starting line 78: please add your SOA loadings to this paragraph. If there was much more than typical ambient (>~50 ug/m3), can you please comment in the results and discussion section how your results may or may not be affected from partitioning more SVOC to the SOA than would be observed in ambient?

Response The polydisperse SOA mass loading is indeed higher than typical ambient aerosol concentration (399 ± 16 and 128 ± 16 μg m^{-3}, for α-pinene and SQTmix respectively). However, our previous study investigated the same type of SOA and found that the majority of compounds were within the range of LVOC and ELVOC. Such volatility range would not be affected by the mass difference between this study and typical ambient concentration. We added this information and our reasoning of why this does not impact the relevance of our findings in section 2.1.

Change Section 2.1

[…] For all evaporation experiments of one SOA system, the aerosol mass concertation in the OFR was very similar. Assuming a particle density of 1.4 g cm^{-3}, the mass concertation of polydisperse α-pinene and SQTmix SOA from the OFR was estimated to be 399 ± 16 and 128 ± 16 μg m^{-3}, respectively. It has been found that compounds with C* of 0.1 μg m^{-3} and below dominates the SOA composition in a previous study using the same type of SOA (Ylisirniö et al., 2020). Even though the aerosol mass concentration in the OFR in our study is higher than the typical ambient level by one order of magnitude, such difference would not affect the gas-particle partitioning behavior of compounds with C* $\leq$ 0.1 μg m^{-3}. […]

Comment Line 81: Do you think forming the SOA at one RH and evaporating it at a different RH will affect your results? Do you think there is a long or short equilibration time between formation and evaporation RH?

Response One of the main objectives of this study is to investigate the evaporation of SOA particles under different RH conditions. Generating the SOA at one RH guarantees the same initial composition for the follow-up isothermal evaporation under different RH conditions. Observed differences in evaporation are then linked to the impact of RH and not a potentially different starting composition.

The equilibration time between formation and evaporation RH is supposed to be very short. According to the Figure S8 in Bones et al. (2012), the half-time to dry 80-nm sucrose (note that sucrose has amorphous solid phase state at dry conditions at 293K) particles from initially 40% RH at 293 K is less than 1 s.

Comment Line 93-96:

Was there anything in these evaporation chambers to absorb desorbing vapors (for example activated charcoal)? If not, do you think there's a role for re-partitioning?

Response We did not use activated charcoal as a vapor absorbent. Instead, the polished stainless wall acted as a perfect sink for the vapors. The model simulation of a previous study using the same setup suggested that the vapor wall losses in the RTC were fast with a vapor wall loss coefficient greater than 10^{-2} s^{-1} (Yli-Juuti et al., 2017).

It is unlikely that re-partitioning takes place in our setup. We additionally characterized our RTC with 80-nm octo-ethylene glycol (PEG8) particles under dry conditions at the same experimental temperature (294 K). The corresponding evapogram is presented in the Figure R11. Applying the eq 1 in Salo et al. (2010) with the parameters used by Krieger et al. (2018), we yielded a saturation vapor pressure of 1.35×10^{-7} Pa for PEG8, which is consistent with the reported value of 9.2 ×10^{-8} Pa at 298 K in Krieger et al. (2018). Thus, we conclude that the vapor wall loss would not impact particle volatility and composition in the experiments.

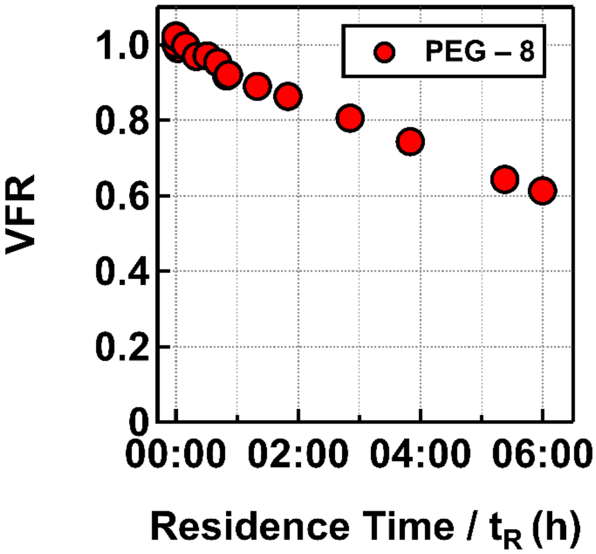


Figure R11. Evapogram of 80-nm octaethylene glycol (PEG8) particles under dry condition at 294 K.

Comment	The workflow isn't obvious—were all particles sent sequentially through each stage laid out in i-iii, or did particles only go into one evaporation chamber? If particles only went into one type of reaction chamber, was the reasoning behind having 3 types to achieve different lengths of evaporation time?
Response	Yes, we had 3 different paths for the SOA samples to achieve different lengths of evaporation time. All particles were sent to only one of the three stages listed as i – iii. We corrected the corresponding sentence by changing "and" to "or".
Comment	Do you expect the same evaporation behavior and results in each chamber (i.e. no impacts from air volume to wall surface area, etc)?
Response	We compared the VFR values measured at the longest residence times (i.e., 40 min) in the mini-RTC with the corresponding points in the large size RTC. They agreed within the experimental uncertainties. For the large RTC, we tested if the mass loading inside the chamber affects the observed evaporation. No changes were observed for particle mass concentrations between 0.5 and 2.5 ug m^{-3} (50 – 250 ng organic material inside the RTC). This agrees with the model calculations which found fast uptake of vapors on the walls and no saturation effects for this mass loading range (Yli-Juuti et al., 2017).

	The typical mass loading were 50 ng and 12.5 ng in the large and mini-RTC in the present study.
Comment	Line 94: “***a*** 25 L… chamber***s***”— was one chamber used or multiple? If multiple, were they all identical?
Response	It should be singular. We corrected the typo.
Comment	Line 115: saturation vapor *pressure* or *concentration*?
Response	We decided to use saturation vapor concentration in the revised manuscript for consistency.
Comment	Line 120: instead of “the appearance”, “the shape” might be more easily understood, but ok as-is.
Response	We still go with the appearance.
Comment	Line 145: half the sum thermogram signal or mass?
Response	It should be signal, and we clarify it by adding ‘signal’.
Change	Section 2.2 […] (T_{50}, at which half of the cumulative STG(T) signal is reached) […].
Comment	Line ~190: Can you please discuss why the overall volatility is lower under wet versus dry conditions, yet under these low-volatility wet conditions more signal is lost after evaporation?
Response	The particles collected on the FIGAERO filter are the residual particles after evaporation. If more of the more volatile compounds are removed before collection (i.e., VFR is lower), the remaining material is of lower volatility. Also, the amount of evaporated material does not necessarily predict the volatility of the remaining particles. One can imagine a sample with 20% SVOC and 80% ELVOC material vs a second sample with 50% of each. If the volatility distribution of the ELVOC fraction is the same, the STG after removal of the SVOC fraction will be the same for both samples. But the VFR will be very different (0.8 vs 0.5).
Comment	Line 200: Couldn’t this be tested by comparing the signal to mass concentration under dry versus wet conditions? If the mass concentration is equivalent, you could determine what percent of signal was lost presumably due to evaporation of high volatility material during the SOA collection time. Or if the mass concentration was

different but the signal was the same, you'd have a hint that the SOA under the two conditions may have been made via two different pathways (e.g. reactive uptake at high RH vs. vapor-pressure driven condensation at low RH).

Response Neither reactive uptake nor vapor pressure driven condensation should play a major role during sampling the monodisperse aerosol onto the filter. Note that gas-phase compounds were diluted by orders of magnitudes during the size selection step. Instead of vapor uptake, the evaporation during the sample collection will take place, as discussed in section 2.1. The small amounts of compounds evaporating from the particles are quickly removed by the stainless-steel tubing walls or will be removed with the sample flow.

Comment Line 239: I think it makes sense to reference some of the papers on thermal decomposition upon heating with a FIGAERO here (or above).

Response We add a reference (D'Ambro et al., 2018; Schobesberger et al., 2018; Yang et al., 2021) as requested.

Comment Line 255: Would help to directly reference the figure in place of saying "above"

Response Now we refer to the corresponding figures instead of using "above".

Comment Line 265: excl = excluding? Please write out complete word for clarity

Response We exchanged excl with excluding throughout the manuscript.

Comment Line 270: rational should be rationale

Response We changed it as requested.

Comment Line 285: "decreases with *evolving* isothermal…" or "with *increasing* isothermal…"?

Response We changed it as requested.

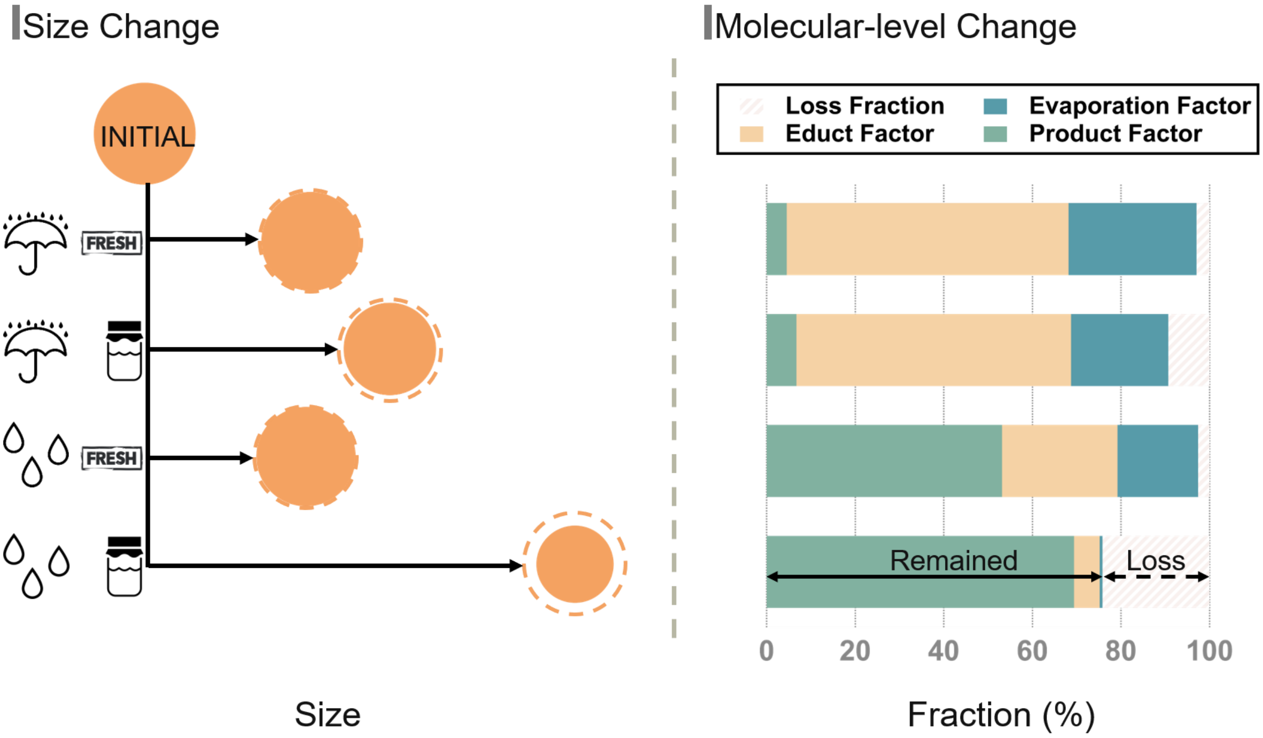
Comment Line 287: if the NCR doesn't decrease with decreasing VFR couldn't this also mean that nothing is happening to the compounds, that they are neither being lost or produced?

Response Yes, if NCR does not change, the compounds in this factor either do not change or the loss and production are balance. However, in this specific sentence, we were trying to describe the implication of "complex" behavior of NCR. With complex we mean that instead of a simple decrease, the NCR values show a "zigzag" patter for samples with

	increasing isothermal evaporation. We have adjusted this sentence to avoid this misunderstanding.
Change	Section 3.3 On the other hand, complex behavior of the NCR with increasing isothermal evaporation (e.g., a decrease followed by an increase) indicates that the main loss mechanism of the compounds is likely chemical transformation.
Comment	line 303: can you speculate on other possible loss mechanisms?
Response	The other possible loss mechanism is aqueous-phase reaction. We discussed this in section 3.3.3. We clarified the existing section by adding “(i.e., aqueous-phase process)”.
Change	Section 3.3.1 […] (i.e., aqueous-phase process) […]
Comment	Line 307: Is it possible that there is different gas-phase chemistry or SOA formation pathways (i.e. reactive uptake vs. condensation) at high RH, so these species don’t necessarily have to be produced in the particle phase?
Response	The RH in the OFR was always 40% to ensure that the initial composition of each SOA system was the same in the dry and high RH experiments. The change in RH occurred in the size selection step in the NanoDMA where also the gas phase is diluted. After this dilution, the concentrations in the gas phase are so low that no significant contribution back to the particle phase occurs. Instead, the particles evaporate. The evaporated compounds are quickly lost to the stainless-steel walls of the tubing and the RTC.
Comment	Line 319: figure 2, panels a & b only, correct?
Response	Yes. Now we add “a” and “b” for clarification
Comment	Line 331: figure 3, panel a only, correct? And figure 6 panel a?
Response	Yes. Now we add “a” for each figure.
Comment	Line 333: is it possible that there are more compounds grouped into the factor under wet conditions, instead of more signal of the same number of compounds?
Response	No. For each factor, the PMF-resolved factor mass spectrum does not change between conditions. This is the working principle of PMF. However, the residual (i.e.,

	overestimation vs underestimation) may be different for compounds in the factor. For details, please see the answer to the second comment of reviewer #1 and the new Supplement section S1.2.3.
Comment	Line 393: Should have a reference for α-pinene having largest emissions globally
Response	We add a reference (Guenther et al., 2012) as requested.
Comment	Line 397: sentence "These findings are generally…" is redundant
Response	We delete the sentence as requested.
Comment	Line 740/ Figure 2: Putting the y-axis in panels a & b on the same scale would make these easier to compare.
Response	Since we do not compare the same stage between different RH conditions, we decided to use the smaller scale for the panel (b) to enhance the smaller signal of the RTC stage. We do not compare the absolute signal intensity between the different RH conditions. Therefore, the same y-axis scale will not add information to this figure.
Comment	Key figure: is time on the x-axis for both the left and right figure/schematic?
Response	We apologize for the misunderstanding. The axis of the left panel is particle size while the right one is fraction. We add axis labels for both figures. The top-to-bottom orders are identical for figures on the two sides.
Change	

Evaporation of Sesquiterpene-mixed SOA Particles



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