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 2

Li et al. conducted laboratory experiments to investigate the change in volatility and composition during the evaporation of SOA formed from alpha-pinene and a mixture of sesquiterpenes. They conducted two types of experiments, isothermal evaporation and thermo-desorption using the FIGAERO CIMS. They ran the experiments under different RH conditions to probe possible diffusive limitations and water-induced changes in composition. This study is well within the scope of the journal. However, there are some important missing pieces of information that affect the final conclusions. My comments are the following:

Comment What were the mass concentrations of these experiments? How variable were the concentrations in dry and high RH experiments? It is unclear if the change in volatility (and composition) was due to the difference in mass loading which to the first order, determines the volatility distribution in the particles.

Response We would like to thank the reviewer for bringing up the important issue. We didn't address the well enough in the text. 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 loadings of polydisperse α-pinene and SQTmix SOA from the OFR were estimated to be 399 ± 16 and 128 ± 16 μg m^{-3}, respectively (Table R3).

Table R3. Summary of OFR Mass Concertation for α-pinene and SQTmix particle evaporation experiments

Evaporation RH	OFR Mass Confrontation (μg m^{-3})[a]	
	α-pinene	SQTmix
Dry (< 7% RH)	389 ± 9	112 ± 6
Intermediate (40% RH)	379 ± 10	123 ± 4
High RH (80% RH)	430 ± 16	149 ± 3

Note: [a]The OFR was always maintained at 40% RH for all evaporation experiments of one SOA system

For the α-pinene case, the mass concentration of organic material after size selection was 4.47 and 5.31 μg cm^{-3} under dry and high RH conditions, respectively. For the SQTmix case, the corresponding values were 0.97 and 1.39 μg cm^{-3} under dry and high RH conditions. For each SOA system of interest, the differences in mass concentration between dry and high RH conditions would not be large enough to significantly shift the volatility distribution of compounds in the condense phase.

The differences between dry and high RH conditions were caused by the necessary adjustment in experimental details and not by changes in the SOA production in the OFR. We have added the information on mass concentration of SOA particles after size selection to the text.

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}.

Section 3.1.2

For each SOA system of interest, similar mass concentration of organic material after size selection was ensured for both dry and high RH conditions so that the volatility distribution of compounds in the condensed phase were not significantly affected. For the α-pinene case, the mass concentration of organic material after size selection was 4.47 and 5.31 $\mu g\ cm^{-3}$ under dry and high RH conditions, respectively. For the SQTmix case, the corresponding values were 0.97 and 1.39 $\mu g\ cm^{-3}$ under dry and high RH conditions.

Comment Here particles were generated using an OFR, and the average O/C value (from Table S1) is on the high end compared to the O/C from most of the alpha-pinene SOA generated in chamber experiments. In fact, many studies on SOA viscosity were done using chamber SOA. The authors should discuss the effects of the highly oxidized (and polar) nature of the particles on the evaporation behavior and how would this affect the comparison to other studies.

Response The O/C level is indeed high for the investigated SOA systems in this study. Current studies on SOA viscosity not only explore different types of chamber-generated SOA particles (Renbaum-Wolff et al., 2013; Maclean et al., 2021) but also investigate wide ranges of atmospheric relevant compounds with O/C as high as this study, such as 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA, O/C = 0.75), levoglucosan (O/C = 0.83), sucrose (O/C = 0.92) and citric acid (O/C = 1.17) (Lienhard et al., 2015). Regarding the impact of O/C level on the particle evaporation, Buchholz et al. (2019) have suggested that increasing O/C levels overall makes SOA particles more resilient to evaporation. Under dry conditions, this is partly due to an increase in viscosity. But the decrease in isothermal evaporation is mostly caused by the decrease in volatility with increasing O/C level. Detailed process modelling showed that already at 40% RH SOA particles behave liquid-like, and kinetic limitations linked to high viscosity do not play a major role (Buchholz et al., 2019, Tikkanen et al., 2020, Li et al., 2019).

The biggest discrepancy between OFR-generated SOA and ambient/chamber SOA may be the fraction of organic hydro-peroxides. They may be formed in much larger fractions than usual due to the high HO_2 concentrations in the OFR, which will favor the respective path for RO_2 radicals (Peng et al., 2019). A higher (hydro-)peroxide fraction may be linked to some of the observed aqueous phase processes as was suggested in Buchholz et al. (2019). However, hydro-peroxide have been detected in ambient samples (Tong et al., 2021) and thus their behavior is relevant to better understand the processes linked to particle volatility and aqueous phase processes.

We have added a new paragraph to section 4 in which we put our work in context of other volatility studies and discuss the atmospheric relevance of our findings

Change 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.

Comment Did the presence of moist on the FIGAERO filter in high RH experiments affect the thermograms? Did the authors conduct any tests to make sure that for a single compound, or a mixture of known compounds, high RH did not change the shape of the thermograms?

Response This is indeed a relevant point. Unfortunately, we did not conduct any test with individual compounds to validate the humidity independence of thermograms, and at the moment we are not able to perform the measurement due to the deployment situation of our CIMS. We will explore this as soon as our FIGAERO-CIMS is available.

However, to address this comment using the existing data, we carefully compared the single ion thermograms of multiple ions under dry and high RH conditions for this study, as shown in Figure R8. We do not observe systematic shifts in T_{desorp} for all compounds between two RH conditions. From this we conclude that there could not be a general change in the shape of the thermograms simply due to the higher RH.

Note that the inlet and filter material (PTFE) is extremely hydrophobic. A drop of water, placed on the filter with a syringe, does not soak into the filter but rather remains on the surface until it has evaporated. This proved to be a challenge for calibration purposes but means that it is unlikely that the filter itself becomes “moist”.

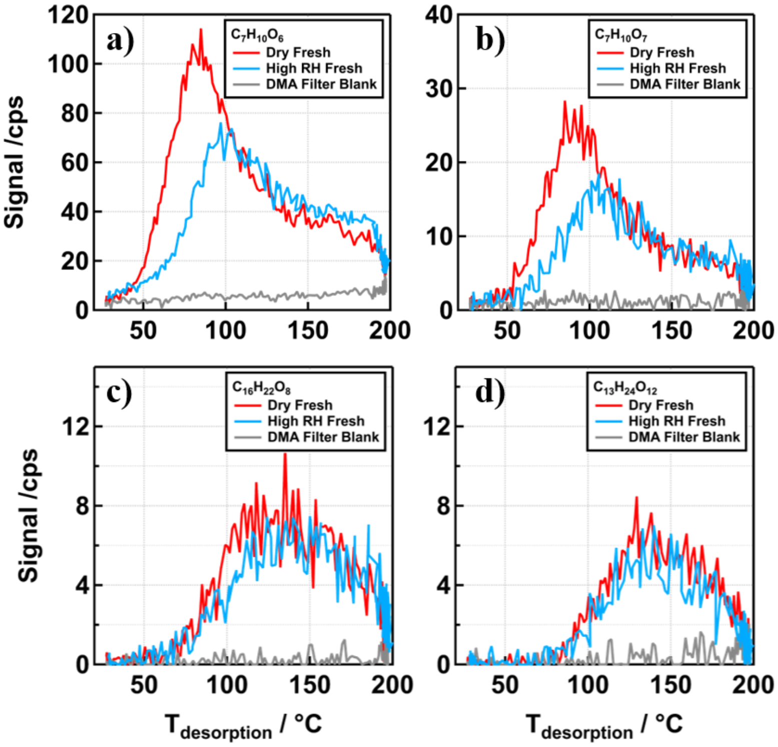

Figure R8. Ion thermograms of compositions consistent with $C_7H_{10}O_6$ (a), $C_7H_{10}O_7$ (b), $C_{16}H_{22}O_8$ (c) and $C_{13}H_{24}O_{12}$ (d) in dry fresh (red), high RH fresh (blue) and DMA filter blank (grey) samples

Comment How was the relationship between Tdesorp and volatility determined (Figure 2a)? Did the authors do any calibration using known compounds?

Response The relationship between T_{desorp} and volatility was derived by calibrating the FIGAERO-CIMS against a series of polyethylene glycols (PEG, chain length 5-8 units) particles with 80 nm electrical mobility diameter. The detail of the calibration procedure and results can be found in Ylisirniö et al. (2021). We refer to this method in the line 114 in the original manuscript and now added the calibration parameters to the Supplement.

Comment What was the vapor wall loss in the residence time chamber? How did vapor wall loss affect particle volatility and composition in the experiments?

Response The model simulation of a previous study using the same setup has 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).

We additionally characterized our RTC with 80-nm octaethylene glycol (PEG8) particles under dry conditions at the same experimental temperature (294 K). The corresponding evapogram is presented in the Figure R9. 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 is fast enough to keep the gas phase concentrations of organics negligible low in the RTC and therefore the vapor wall loss rate would not impact particle volatility and composition in the experiments.

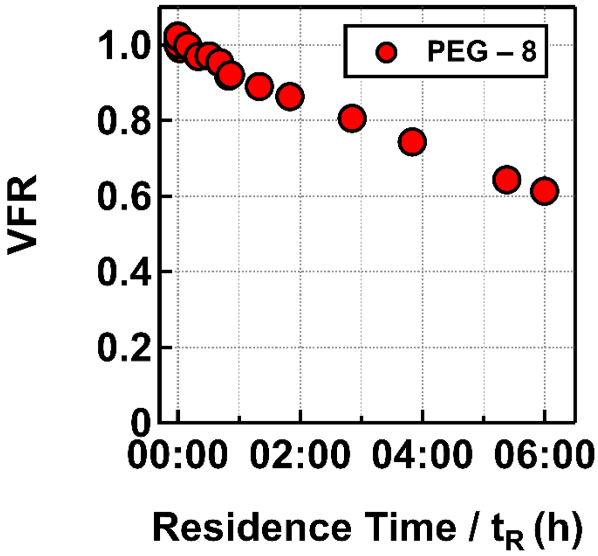

Figure R9. Evapogram of 80-nm octaethylene glycol (PEG8) particles under dry condition at 294 K.

Comment Based on Figure 3b, it seems that the authors did not observe O3 and O4 species that are known to be major a-pinene oxidation products (e.g., pinic acid, pinoic acid). What is the reason for that?

Response We see how this misunderstanding happened. The O content of the individual molecules is not visible in Figure 3b. The chemical formulas in Figure 3b stand for the average composition of the sample factors instead of individual molecules. We did indeed observe O3 and O4 species. As shown in the Figure R10, signals of compositions corresponding to the three mentioned α-pinene oxidation products (i.e., pinic acid, pionic acid and norpinic acid) are clearly higher than the background noise. Note that these only representing the contribution to the particle phase. Especially, pinonic acid is expected to reside predominantly in the gas phase at the chosen conditions (Lopez-Hilfiker et al., 2015).

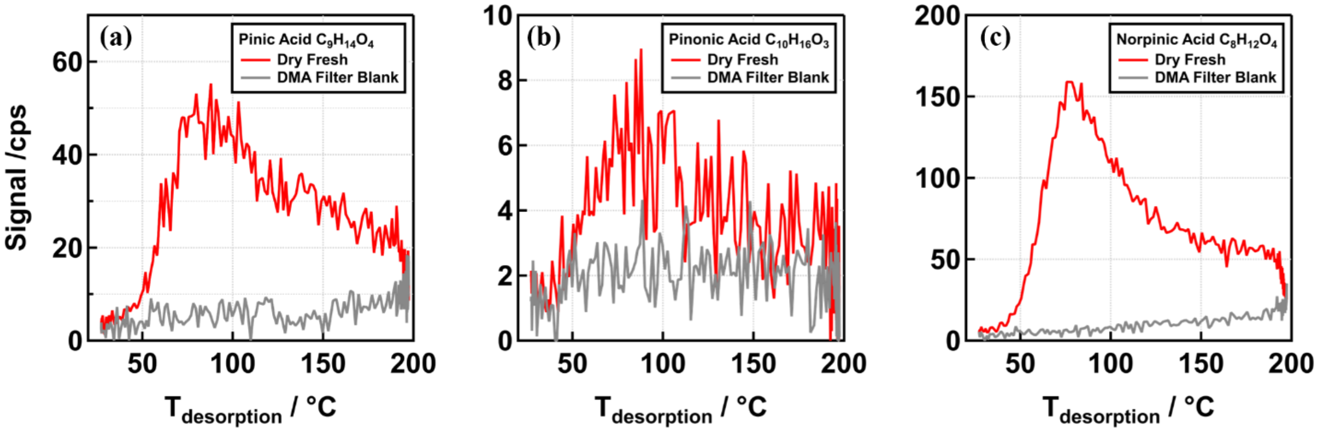

Figure R10. Ion thermograms of compositions consistent with pinic acid (a), pinonic acid (b) and norpinic acid (c) in dry fresh (red) and DMA filter blank (grey) samples

References

Buchholz, A., Lambe, A. T., Ylisirniö, A., Li, Z., Tikkanen, O.-P., Faiola, C., Kari, E., Hao, L., Luoma, O., Huang, W., Mohr, C., Worsnop, D. R., Nizkorodov, S. A., Yli-Juuti, T., Schobesberger, S., and Virtanen, A.: Insights into the o: C-dependent mechanisms controlling the evaporation of α-pinene secondary organic aerosol particles, Atmos. Chem. Phys., 19, 4061-4073, 2019.

D'Ambro, E. L., Schobesberger, S., Zaveri, R. A., Shilling, J. E., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., and Thornton, J. A.: Isothermal evaporation of α-pinene ozonolysis SOA: Volatility, phase state, and oligomeric composition, ACS Earth and Space Chemistry, 2, 1058-1067, 2018.

Krieger, U. K., Siegrist, F., Marcolli, C., Emanuelsson, E. U., Gøbel, F. M., Bilde, M., Marsh, A., Reid, J. P., Huisman, A. J., and Riipinen, I.: A reference data set for validating vapor pressure measurement techniques: Homologous series of polyethylene glycols, Atmos. Meas. Tech., 11, 49-63, 2018.

Li, Z., Tikkanen, O.-P., Buchholz, A., Hao, L., Kari, E., Yli-Juuti, T., and Virtanen, A.: Effect of decreased temperature on the evaporation of α-pinene secondary organic aerosol particles, ACS Earth and Space Chemistry, 3, 2775-2785, 2019.

Lienhard, D. M., Huisman, A. J., Krieger, U. K., Rudich, Y., Marcolli, C., Luo, B., Bones, D. L., Reid, J. P., Lambe, A. T., and Canagaratna, M. R.: Viscous organic aerosol particles in the upper troposphere: Diffusivity-controlled water uptake and ice nucleation?, Atmos. Chem. Phys., 15, 13599-13613, 2015.

Lopez-Hilfiker, F., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Carrasquillo, A., Daumit, K., and Hunter, J.: Phase partitioning and volatility of secondary organic aerosol components formed from α-pinene ozonolysis and OH oxidation: The importance of accretion products and other low volatility compounds, Atmos. Chem. Phys., 15, 7765-7776, 2015.

Maclean, A. M., Smith, N. R., Li, Y., Huang, Y., Hettiyadura, A. P., Crescenzo, G. V., Shiraiwa, M., Laskin, A., Nizkorodov, S. A., and Bertram, A. K.: Humidity-dependent viscosity of secondary organic aerosol from ozonolysis of β-caryophyllene: Measurements, predictions, and implications, ACS Earth and Space Chemistry, 5, 305-318, 2021.

Peng, Z., Lee-Taylor, J., Orlando, J. J., Tyndall, G. S., and Jimenez, J. L.: Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance, Atmos. Chem. Phys., 19, 813-834, 2019.

Pospisilova, V., Bell, D. M., Lamkaddam, H., Bertrand, A., Wang, L., Bhattu, D., Zhou, X., Dommen, J., Prevot, A. S., and Baltensperger, U.: Photodegradation of α-pinene secondary organic aerosol dominated by moderately oxidized molecules, Environ. Sci. Technol., 55, 6936-6943, 2021.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of alpha-pinene secondary organic material and implications for particle growth and reactivity, Proc. Natl. Acad. Sci. U. S. A., 110, 8014-8019, 2013.

Salo, K., Jonsson, Å. M., Andersson, P. U., and Hallquist, M.: Aerosol volatility and enthalpy of sublimation of carboxylic acids, The Journal of Physical Chemistry A, 114, 4586-4594, 2010.

Tong, H., Liu, F., Filippi, A., Wilson, J., Arangio, A. M., Zhang, Y., Yue, S., Lelieveld, S., Shen, F., and Keskinen, H.-M. K.: Aqueous-phase reactive species formed by fine particulate matter from remote forests and polluted urban air, Atmos. Chem. Phys., 21, 10439-10455, 2021.

Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proc. Natl. Acad. Sci. U. S. A., 108, 2190-2195, 2011.

Wilson, J., Imre, D., Beránek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics of laboratory-generated secondary organic aerosols at elevated relative humidity, Environ. Sci. Technol., 49, 243-249, 2014.

Yli-Juuti, T., Pajunoja, A., Tikkanen, O. P., Buchholz, A., Faiola, C., Vaisanen, O., Hao, L., Kari, E., Perakyla, O., Garmash, O., Shiraiwa, M., Ehn, M., Lehtinen, K., and Virtanen, A.: Factors controlling the evaporation of secondary organic aerosol from alpha-pinene ozonolysis, Geophys. Res. Lett., 44, 2562-2570, 2017.

Ylisirniö, A., Barreira, L. M. F., Pullinen, I., Buchholz, A., Jayne, J., Krechmer, J. E., Worsnop, D. R., Virtanen, A., and Schobesberger, S.: On the calibration of FIGAERO-tof-CIMS: Importance and impact of calibrant delivery for the particle-phase calibration, Atmos. Meas. Tech., 14, 355-367, 2021.

Ylisirniö, A., Buchholz, A., Mohr, C., Li, Z., Barreira, L., Lambe, A., Faiola, C., Kari, E., Yli-Juuti, T., Nizkorodov, S. A., Worsnop, D. R., Virtanen, A., and Schobesberger, S.: Composition and volatility of secondary organic aerosol (SOA) formed from oxidation of real tree emissions compared to simplified volatile organic compound (VOC) systems, Atmos. Chem. Phys., 20, 5629-5644, 2020.

Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Zawadowicz, M. A., Suski, K., China, S., Bell, D. M., Veghte, D., and Laskin, A.: Particle-phase diffusion modulates partitioning of semivolatile organic compounds to aged secondary organic aerosol, Environ. Sci. Technol., 54, 2595-2605, 2020.