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Comment on acp-2021-367

Anonymous Referee #1

Referee comment on "Evolution of volatility and composition in sesquiterpene-mixed and α -pinene secondary organic aerosol particles during isothermal evaporation" by Zijun Li et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-367-RC1>, 2021

Overall, I find this an interesting study that adds to our understanding of particle evaporation behavior and the influence of water on particle composition and evaporation behavior. My major comment relates to the definition of "factors" and how the concept of a factor can be consistent with shifting/evolving evaporation profiles between conditions.

L170: It is stated that the evaporation rate in dry SOA particles is slowest owing to "considerable kinetic limitations arising from high particle viscosity." As currently written, this is stated as a categorical result. However, there has not yet been discussion of the extent to which chemical differences in the dry versus wet particles could lead to volatility changes separate from viscosity changes. In fact, later in the same paragraph the authors note that aqueous-phase processing occurs when the particles are exposed to 80% RH. I suggest it would be useful if the authors work to better separate results from conclusions to first demonstrate that one effect must be more important than another in determining the overall behavior.

L208: The authors state that "Each derived factor constitutes a group of organic compounds with the same thermal desorption behavior." While this seems like an a priori true statement, I find it difficult to reconcile with the fact that the authors observe different thermal desorption profiles for the same factors between different conditions. Consider AV2 and AV4 in Fig. 3. Or any of the factors in Fig. 4. The peak desorption temperature and profile shapes change between the different conditions, even at the same RH. This is most evident at high RH. It would seem, therefore, that one factor can have more than one desorption profile and thus different thermal desorption behavior. It would be useful if the authors could provide further discussion regarding such differences for factors. I find it very interesting that the desorption profile for a given factor—presumably,

a collection of molecules—should change so much.

L215: It would be useful to have further discussion of how the “background” factors were identified. The authors retain only 5 factors in their analysis, suggesting that there are 5 background factors. This seems excessive. What does it mean for these to be “predominately in filter blank measurements?”

Fig. S6: I find these “Kroll diagrams” a bit strange. These assume, presumably, that every ion is a unique molecule and not a fragment, correct? It could be more informative (or at least equally informative) to show one diagram that uses the average OsC and average Cnum for each factor.

Definition of factors as V or D: I find it helpful that the authors have worked to classify factors according to their thermal profiles. I think that this helps with understanding. But it would be useful to hear more about how they made decisions in what might be considered in between or marginal cases. For example, for the AV4 α -pinene factor, the desorption profiles are really, really broad and with much intensity remaining out to very high temperatures. And the fresh high RH SV4 SQTmix factor looks pretty similar to the SD5 factor for high RH RTC. As such, there seems to be some ambiguity in the definitions/assignment and it would be helpful if the authors were to address this further.

L263: The authors note that it is difficult to compare between experiments in terms of absolute signals owing to differences and uncertainty in collected mass. However, the authors presumably know the volume of material collected, and using reasonable estimates of density this should allow for comparability to well within a factor of two. Through normalization to the total signal, the authors do work to make the factor-specific observations quantitatively comparable. Use of a second method to estimate the total mass collected would help to validate the normalization method, as there is an implicit (but as best I can tell unstated) assumption that the CIMS response is the same for all factors.

Fig. 5 and 6: I understand the authors' motivation to exclude Tdesorb and NCR values in cases for which the desorption profile is not well-formed owing to limited signal. However, for the NCR I would encourage the authors to put perhaps an open symbol at the lowest NCR value (0.1) as a visual indication to the reader that the signal is very small for that particular factor & condition.

L300: Regarding the authors' discussion of SV4 as an ELVOC and the observation of a major shift in the NCR under humid conditions, I return to my previous comment regarding the identification of this factor as a "V" type to begin with. There is certainly, in my opinion, ambiguity in this identification, which affects the interpretation and determination that this observation is "surprising." Further discussion here would be helpful. For SV2, I'm a little surprised myself to see this identified as being in the "ELVOC range." The peak of this factor profile is fully in the "LVOC" range. Further, the volatility really exists as a continuum with the sharp lines drawn for convenience more than reality (although there is, of course, a tie to physical behavior that underlies these distinctions). Only once things go to high RH does the SV2 factor shift to the ELVOC volatility range. But this is a shift from the dry conditions, indicating that perhaps some chemical change has occurred.

L330: The authors note that chemical transformations could cause changes in Tdesorb and thermogram widths with RH for a given factor. But what is a factor even if the chemical composition has changed? Isn't a factor presumably a collection of molecules (or at least ion signals) that are invariant/grouped together? If chemical changes occur, wouldn't one expect this to end up as a different factor? Or is the argument here that chemical changes occur, but these chemical changes somehow lead to the same mass spectra/factor as before the chemical changes occurred? I suggest that further discussion is warranted. Similarly, on line 337 the authors note that "some of the compounds grouped into AV3 must have evaporated...or continued to react." Can it really be "some" of the compounds if the factor itself is a stable/real thing? (Yes, factors are just mathematical constructs, but they still need to be stable, right?) How does one lose some compounds but not others from a factor and still have it come out as the same factor?

Section 3.3.3: Here, the authors aim to provide general understanding of the nature of the chemical processes or shifts in volatility that occur upon humidification. One thing that I

think could be useful is if the authors were to further compare between the α -pinene and SQTmix. For example, it seems noteworthy that the "D" type factor identified for both exhibit completely distinct behavior. If anything, I would have intuitively thought that the "decomposition" factors would exhibit similar behavior between both chemical systems. Clearly, intuition is not serving me well here, which is why I think that further compare/contrast would help to strengthen the discussion further.