Response Letter to Referee #2

The authors thank the reviewer for the careful review of our manuscript and helpful comments and suggestions. All the comments (in bold text) are addressed below point by point, with our response following in non-bold text and the corresponding revisions to the manuscript in blue. All updates of the original submission are tracked in the revised version.

General comments:

In this work, "Volatility of aerosol particles from NO3 oxidation of various biogenic organic precursors," the authors examine analytically combining the use of different experiment setups, as a thermodenuder, an isothermal chamber and a FIGARO-CIMS system, formula-based parameterizations and an evaporation model in order to try to estimate volatility from the NO3 oxidation of a-pinene, isoprene and b-caryophyllene, a topic that is very understudied and scarce information exists about these volatility estimations. Volatility estimation is a topic that requires a lot of effort, the combination of different experimental and modeling techniques and sometimes the results about it can be failing or varied. This happens because of the complexity of the mechanisms of aging and reactions that happen in the atmosphere that makes the fate of the precursors highly uncertain. Also using modeling techniques there are many assumptions that have to be made in order to infer volatility that make the problem even more complex. The authors manage to use rigorously a combination of methods and finally provide us with a descriptive analysis of the volatility distributions and composition of SOA formed from nitrate oxidation for the three precursors. In the end the formula-based parameterizations were re-evaluated and showed that improvements in their description have to be incorporated in the future. I find this work very valuable and almost ready to be published while a few comments could be addressed a bit better and some technical corrections could be performed in order to be clearer.

We thank the reviewer for the positive assessment of our manuscript.

Specific comments:

In Table 1 are presented the experiments performed for this work and while most of the results of them are presented experiment 4 is not used in the analysis. It is only referred to figure S2 when trying to show the sensitivity of different initial mass loadings from the nitrate oxidation of a-pinene. Is there any specific reason to not in the main figures as well? Also in the table there are many missing values, this could be explained in the bottom why is it happening as a footnote. Also while the nitrate experiments of a-pinene are 5, is there any reason there are 3 for isoprene and 2 for b-caryophyllene. Probably some description for the decision of the design of these experiments could be helpful in the main article. Finally for the isothermal evaporation experiments while most experiments finish at 240 min some stop after 150 min, this is probably because the experiment had to stop or there was equilibrium and no extra evaporation was noticed after that?

For the evaporation simulation we only used experiments for which we have FIGAREO-CIMS data (so we included exp. 3 and 4 solely to illustrate the mass dependence in the isothermal evaporation chamber for α-pinene + NO₃). Unfortunately, there are two experiments where we have FIGAERO-CIMS data but miss either VTDMA (exp. 5) or isothermal evaporation chamber data (exp. 8). Same for the α-pinene ozonolysis experiments, see exps 1 and 2. In the revised paper, we added this information in the caption.

"…evaporation (experiments marked with hyphens are not simulated due to either missing data about the molecular composition or experimental evaporation data)."

The evaporation model that is used for the analysis from Riipinen, et al. (2010) depends on many parameters and some work has been done to investigate the sensitivity of them as it is done in Figure S3 where there is used a different value for the vaporization enthalpy of 70kJ/mol, different accommodation coefficients of 0.01 and 0.1 compared to unity of the base case as well as a mass-dependent diffusion coefficient. This analysis has been focused only on the ozonolysis of a-pinene though that is not the centre of interest in this work and in any case it showed to have better comparisons with the measurements. The b-caryophyllene nitrate oxidation products seem to have a more bimodal volatility distribution that make it more difficult to capture its "fingerprint" with the VFR in the thermodenuder and isothermal evaporation chamber, it could be probably fruitful to try to see for the three different parameterizations used how changing dHvap (with values of 70 kj/mol but also higher even 150 kj/mol), am (0.01 and 0.1) and mass-dependent diffusion coefficients would change these thermograms. This could be repeated for the isoprene case for a more broad and complete picture for the sensitivity to these parameters.

Thank you for this suggestion. We have now conducted similar sensitivity tests as done for α-pinene + O₃ in the original manuscript for the other investigated systems (see Figs. below, which have been added as supplementary figures in the revised manuscript). These figures demonstrate that the sensitivities are rather similar and independent of the exact chemical system.
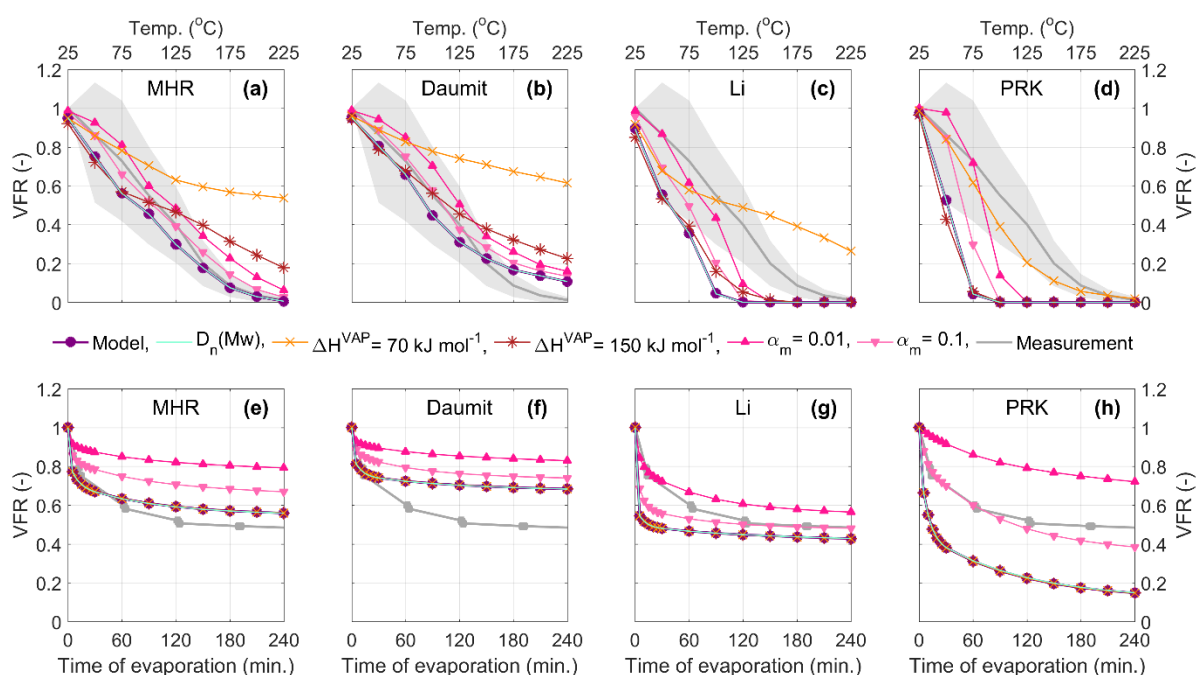
Figure S3 Sensitivity study for the thermodenuder- (upper row, panels a, b, c and d) and isothermal evaporation model (lower row, panels e, f, g and h) based on α-pinene ozonolysis with a fixed vaporization enthalpy, $\Delta H^{VAP} = 70$ kJ/mol (yellow), reduced accommodation (αm, set to be either 0.1 or 0.01 (pink)), and a mass-dependent diffusion coefficient (cyan). The original model output is presented in purple together with the measurements displayed in grey.
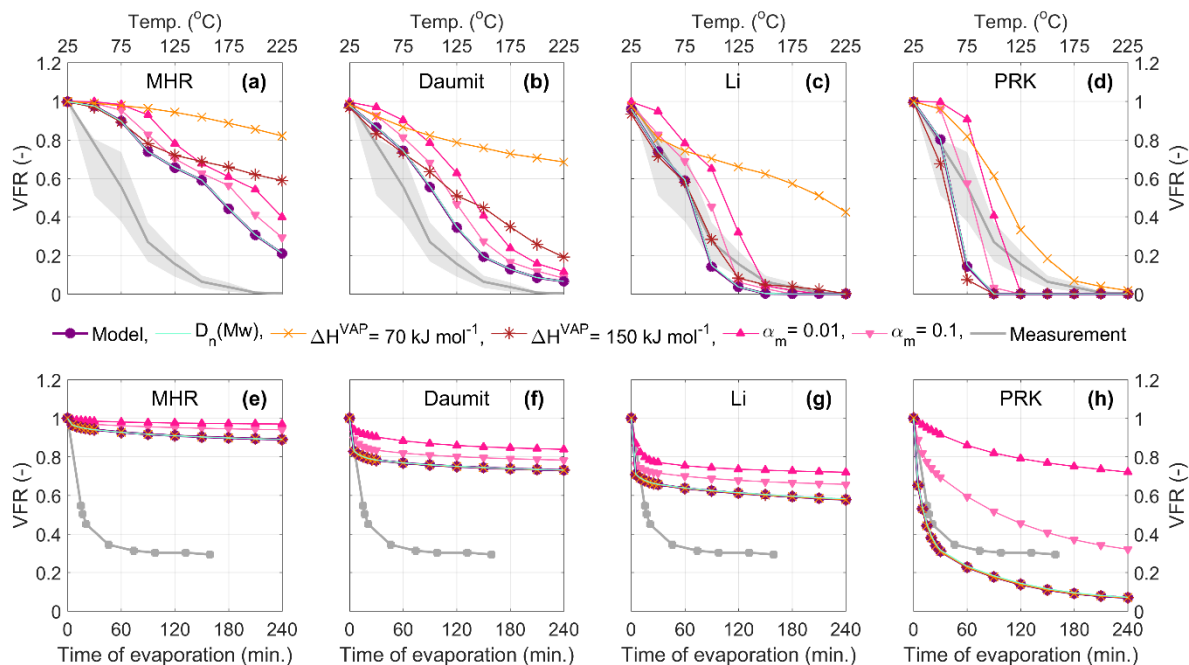

Figure S4 Sensitivity study for the thermodenuder- (upper row, panels a, b, c and d) and isothermal evaporation model (lower row, panels e, f, g and h) based on α-pinene + NO₃ with a fixed vaporization enthalpy, $\Delta H^{VAP} = 70$ kJ/mol (yellow), reduced accommodation (αm, set to be either 0.1 or 0.01 (pink)), and a mass-dependent diffusion coefficient (cyan). The original model output is presented in purple together with the measurements displayed in grey.
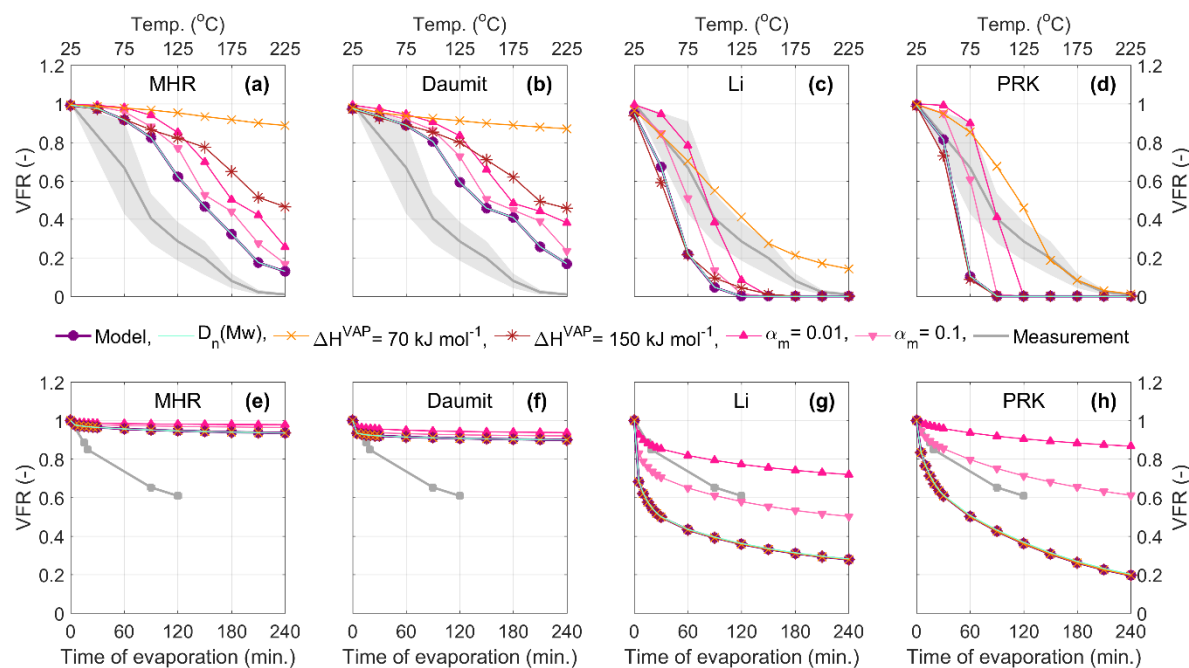
Figure S5 Sensitivity study for the thermodenuder- (upper row, panels a, b, c and d) and isothermal evaporation model (lower row, panels e, f, g and h) based on Isoprene + NO_3 with a fixed vaporization enthalpy, $\Delta H^{VAP} = 70$ kJ/mol (yellow), reduced accommodation (αm, set to be either 0.1 or 0.01 (pink)), and a mass-dependent diffusion coefficient (cyan). The original model output is presented in purple together with the measurements displayed in grey.
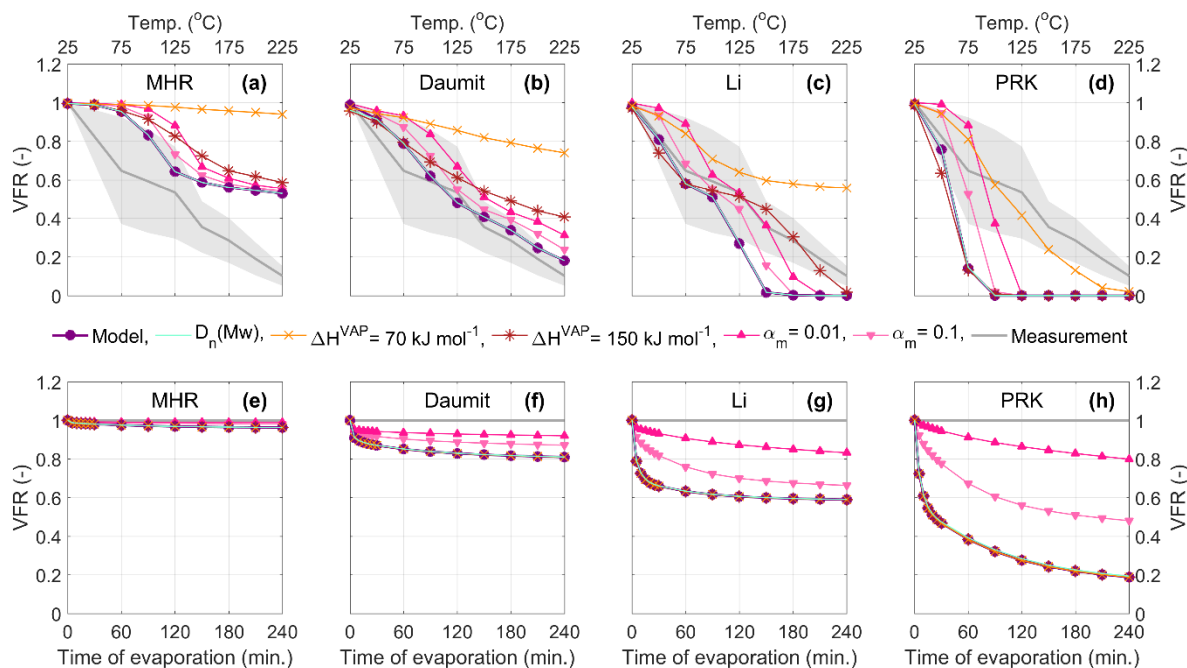

Figure S6 Sensitivity study for the thermodenuder- (upper row, panels a, b, c and d) and isothermal evaporation model (lower row, panels e, f, g and h) based on β-caryophyllene + NO_3 with a fixed vaporization enthalpy, $\Delta H^{VAP} = 70$ kJ/mol (yellow), reduced accommodation (αm, set to be either 0.1 or 0.01 (pink)), and a mass-dependent diffusion coefficient (cyan). The original model output is presented in purple together with the measurements displayed in grey.

In Figure 3 the authors show the volatility distributions in the form of VBS as derived from the three different parameterizations that are examined, while someone can see the composition in ELVOCs, LVOCs and SVOCs it would be useful here to also add in the figure somewhere what is the average C* from each parameterization for each case of precursor. This would make it clearer understanding which parameterization shows higher or lower volatilities for each case.

Thank you for this suggestion, we have added this information to the legend of the new Fig. 3 in the revised manuscript.

Technical corrections:

Table 1: In footnote change S5 to S4 (there is no figure S5)

Accepted.

Line 227: Change 240 s to 240 min.

Accepted.

Line 228: model inputs instead of input

Accepted.

Line 229: Change concentrations estimated to concentration estimates to be clearer

Accepted.

Line 267: change to "agree with the VTDMA data"

Accepted.

Line 327: A bit complicated sentence, rewrite clearer

Change to "Finally, with the PRK parametrization, the VBS distributions of all systems are similar and in a narrow range between -3 to 1, which suggests that this parameterization is the least sensitive."

In Figure 4 I think the shading should change because right now it is not very easy and clear to see the differences, especially in the green shades.

We have tried to address this problem by changing the shades of the different colours slightly. Additionally, we have separated the different precursors and oxidants to one figure each in the supplementary (new Fig. S8-11), presenting one VBS per subplot.
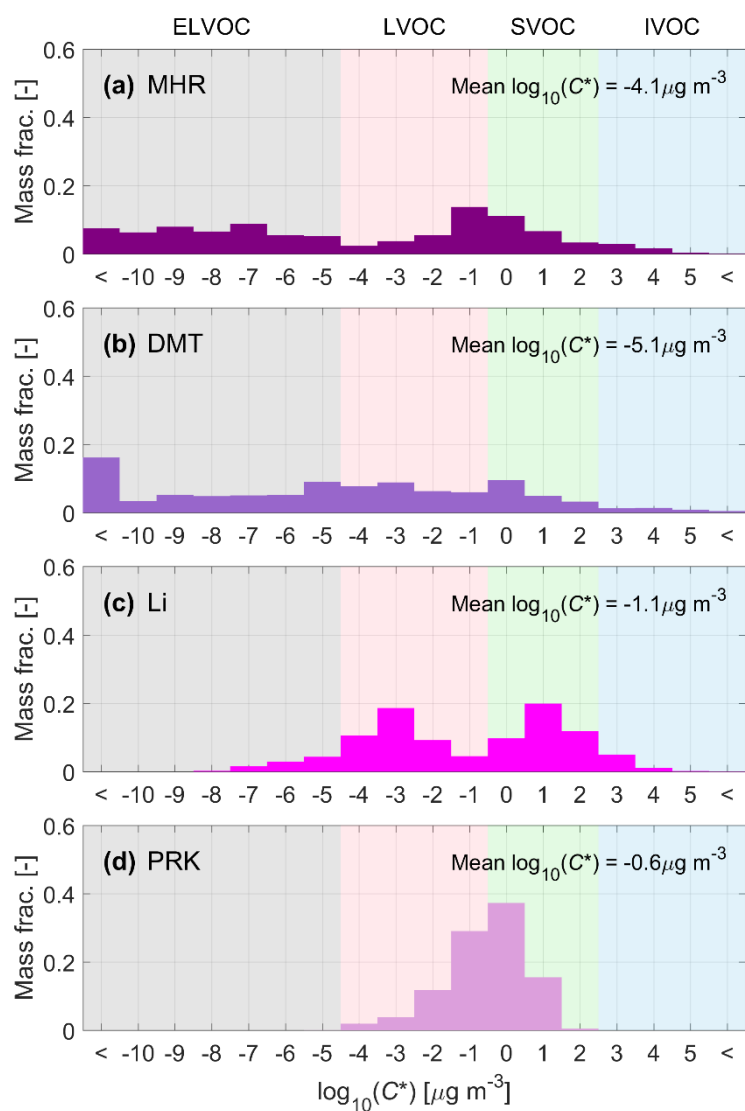
Figure S8. Volatility distributions in the form of VBS as derived from the molecular composition for α-pinene ozonolysis, presented for each parameterization separately; (a) MHR: Mohr et al., 2019 (b) DMT: Daumit et al., 2013 (c) Li: modified Li et al., 2016 and (d) PRK: Peräkylä et al., 2020).
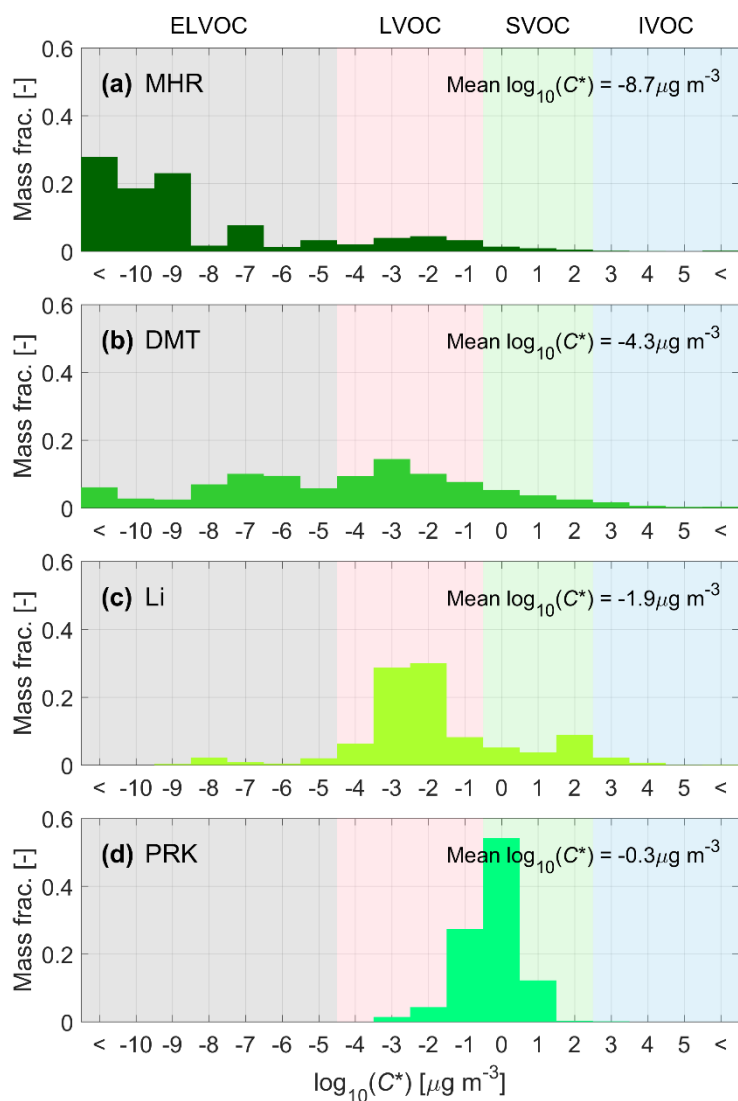
Figure S9. Volatility distributions in the form of VBS as derived from the molecular composition for the nitrate oxidation of α-pinene, presented for each parameterization separately; (a) MHR: Mohr et al., 2019 (b) DMT: Daumit et al., 2013 (c) Li: modified Li et al., 2016 and (d) PRK: Peräkylä et al., 2020).
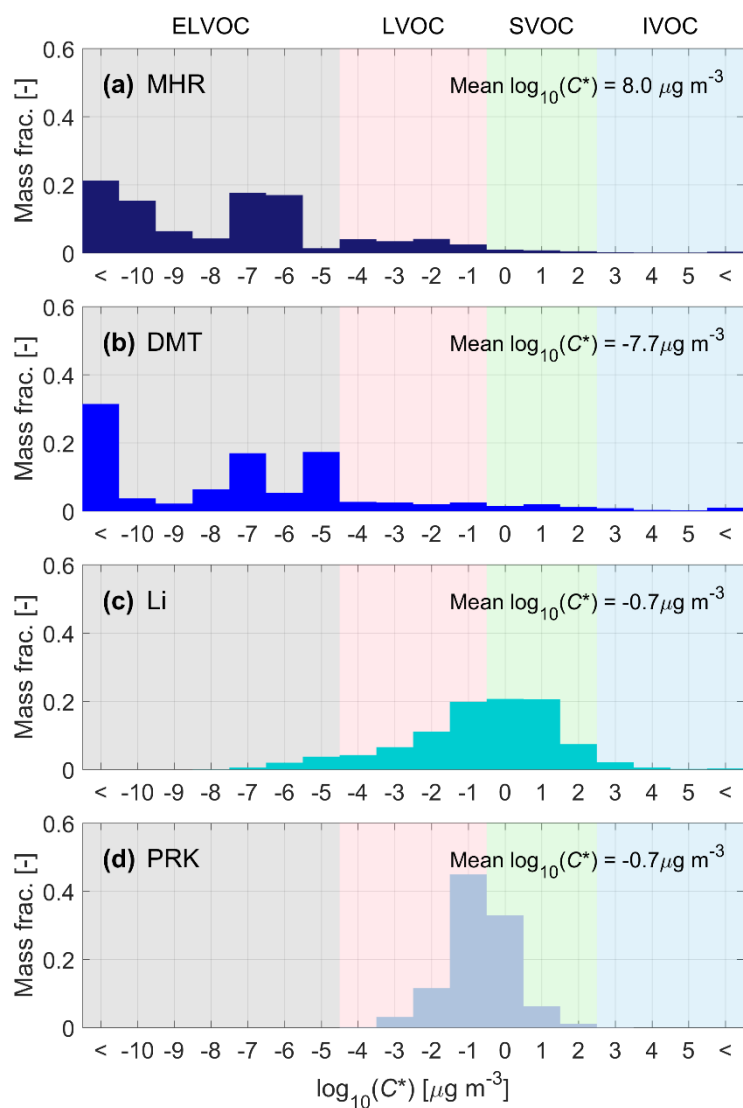
Figure S10. Volatility distributions in the form of VBS as derived from the molecular composition for the nitrate oxidation of isoprene, presented for each parameterization separately; (a) MHR: Mohr et al., 2019 (b) DMT: Daumit et al., 2013 (c) Li: modified Li et al., 2016 and (d) PRK: Peräkylä et al., 2020).

Figure S11. Volatility distributions in the form of VBS as derived from the molecular composition for the nitrate oxidation of β-caryophyllene, presented for each parameterization separately; (a) MHR: Mohr et al., 2019 (b) DMT: Daumit et al., 2013 (c) Li: modified Li et al., 2016 and (d) PRK: Peräkylä et al., 2020).
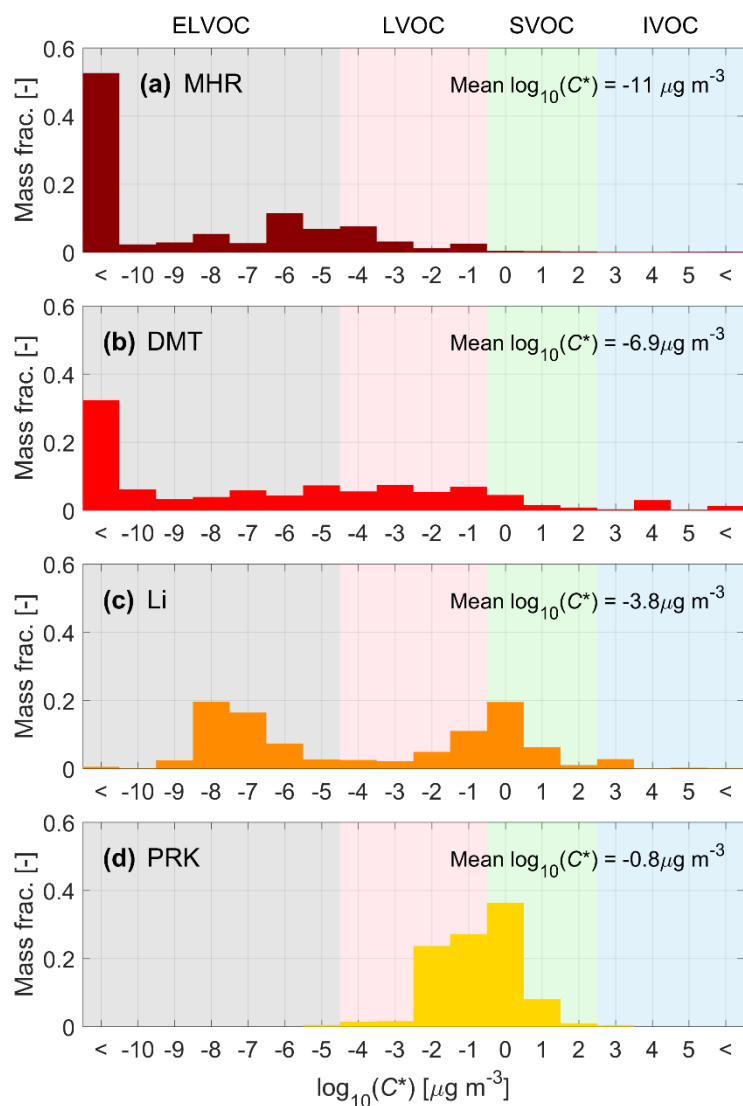
Line 378 Change Though to Although

Accepted.

Line 387 something is missing, rewrite "and experimental approach developed by the authors"

Change to "than that estimated by other parameterisations, e.g. SIMPOL (Pankow and Asher, 2008) and PRK, as well as that obtained by experimental approaches".

Line 399: Change to "an hydroxyl"

"a hydroxyl group" should be correct.

Line 408: Change to "of the observations"

Change to "all three systems to get predictions closer to the observations."

Line 450: Taken together, change the expression, suggest that the SOA … contain, rewrite a bit the sentence.

The original sentence is revised to "By comparing the volatility information from different parameterizations with that derived from temperature-dependent evaporation in VTDMA and isothermal evaporation chambers, our study suggests…"

In Supplementary:

Figure S1: Change Narve, 2019 to NArVE campaign 2019 as it is mentioned in the article or This work

Accepted.

Figure S3: Change blue to cyan (you use cyan color)

Accepted.

Figure S3: Describe a,b,c,d,e,f in legend.

The figure caption is revised to "Sensitivity study for the thermodenuder- (upper row, panels a, b, c and d) and isothermal evaporation model (lower row, panels e, f, g and h) based on α-pinene ozonolysis with a fixed vaporization enthalpy, ΔH^{VAP} = 70 kJ/mol (yellow), reduced accommodation (αm, set to be either 0.1 or 0.01 (pink)), and a mass-dependent diffusion coefficient (cyan). The original model output is presented in purple together with the measurements displayed in grey."

References

Riipinen, Ilona, et al.

> 2010 Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics. Atmospheric Environment 44(5):597-607.