

Answers to Referee #2

The authors appreciate the time the reviewer has spent on our manuscript, helping us produce a higher quality, understandable publication. All the requested corrections and suggestions are addressed and introduced to the revised version of the manuscript.

Detailed Comments

1) It should be made clear in the abstract, body, and conclusion that this study estimates the effective volatility distribution of SOA after it has formed and undergone aging (particle-phase reactions) and not the volatility distribution of the condensing organic gases that produced the SOA. While the authors do not imply the latter, some readers may inadvertently misinterpret the results and incorrectly apply them for modeling purposes if the caveat is not explicitly stated.

Reply: This is correct, and this issue will be clarified through the whole manuscript.

This then brings up the question of the usefulness of the results. If the estimated volatility distribution of SOA does not represent the volatility distribution of the condensing organics then where and how would one use this information? What is it that we have learned from this exercise that is of value? To drive this point further, it is possible that the semi-volatile fraction of the condensing organics may be more than 40%, such that some then undergoes particle-phase reactions to form low- and extremely low-volatile compounds. Upon heating the SOA in the VTDMA, these newly formed compounds (e.g., dimers, oligomers) may partially decompose back to the original species or may even fragment (especially at higher temperatures) to something completely different before evaporating. However, these processes are not examined in the present study. The evaporation model simply assumes that the three lumped species (with different volatilities) do not chemically interact. Thus, it is difficult to draw any useful or meaningful conclusions out of the present analysis.

Reply: Indeed, the volatility distribution of SOA studied here did not represent the volatility distribution of the condensing organic compounds in the gaseous phase. However, it provides “one side of the story” in the form of insights into the volatility (and hence e.g. the evaporation potential) of the compounds that are present in the particle phase (of course with the caveat of the effects of the elevated temperature). This will be useful input for closure studies combining this information with

condensation studies aiming to derive how the aerosol size distributions are affected by given gas-phase species. In fact, we are working on such a closure study for future. Furthermore, the results are useful to compare the volatility of the boreal forest aerosol to similar results from other sites (e.g. Cappa and Jimenez 2010; Cappa and Wilson, 2011; May et al., 2013a). Finally, it also provides insight into the usefulness and applicability (and limitations) of TD setups for inferring information about aerosol volatility. We will add discussion on these issues to the revised manuscript.

2) Furthermore, since the VTDMA experiments were carried out under dry conditions, the boreal forest SOA is expected to be viscous (Virtanen et al. 2010 Nature), especially at 25 C, such that there would be significant particle-phase diffusion limitation for the evaporating species. Perhaps the evidence for this limitation is present in Figure 3, which shows that the model tends to be way more evaporative than observed at the lower temperatures—in fact, the first data point indicates no evaporation (MFR = 1). This can potentially skew the effective volatility distribution estimated by the model quite a bit.

Reply: The referee is right that the kinetics of evaporation of non-liquid particles may be somewhat affected by the diffusion coefficient of a viscous solution (Tong et al., 2011). However, it should be noted that the ambient data were mixtures of organics, water and inorganics, for which it is difficult to quantify the potential diffusivity impacts. We will add brief discussion on this issue to the revised manuscript.

3) It is stated that the residence time inside the thermodenuder was around 2.5 s. Does this mean that the evaporation model was run for just 2.5 s to simulate each data point? Also, does the model assume that the aerosol instantly reaches the targeted temperature the moment it enters the thermodenuder? Can the authors estimate the time it takes the aerosol to reach the target temperature? The model should account for it if it's comparable to the residence time.

Reply: Yes, the evaporation model was run for 2.5s to simulate each data point, since measured evaporation time is 2.5 s in this case. The temperature profile was measured with a temperature sensor (Rotronic HC2-CO4) inside the heating tube at flow rate of 2 L/min with setting temperature at 100 °C (see Fig.1). As shown in Fig. 1, the temperature did not reached the targeted temperature at the moment the aerosols entered the thermodenuder but increased slowly at the entrance of the heating tube and reached the targeted temperature ± 5 °C at around 20 cm

from the entrance. The temperature stayed at this value before falling near the exit, 45 cm from the entrance of the heating tube. This distance with temperature within ± 5 °C of the targeted one was used for calculation the residence time of the heating section. The obtained residence time was then applied in the model analysis. It was assumed that the particles were instantaneously thermally equilibrated with the surrounding gas phase. We think this is a reasonable assumption with respect to the time scales relevant for the evaporation, as the system was in atmospheric pressure

4) Please show error bars on the VTDMA measurements displayed in Figures 2 and 3.

Reply: We will add error bars on the VTDMA measurements data to the revised manuscript.

5) The authors state that the agreement between the VTDMA results and the PMF- derived results as reasonable when it is quite the opposite. The linear correlation coefficient (r) of 0.4 indicates there is not a good correlation between the VTDMA- and PMF-based results (Figure 5c,d). The coefficient of determination (r^2) is only 0.16, which means only 16% of the variation can be explained by the linear relationship between the two methods. It is clear that the comparison of VTDMA and PMF results was not quite successful. I suggest that the authors revise the text at all the appropriate places and describe the results of correlation as they are.

Reply: Thank you for pointing this out, we agree. Consequently, we will make revisions in line 44-47 of the revised manuscript:

‘In general, the best agreement between the VTDMA results and the PMF-derived mass fractions of organics was obtained when $\Delta H_{VAP} = 80$ kJ/mol was set for all organic groups in the model, with a linear correlation coefficient of around 0.4. However, this still indicates that only about 16% (R^2) of the variation can be explained by the linear regression between the results from these two methods.’

Discussion in line 388-400 will be revised as: ‘Using the enthalpy value of 60 kJ/mol for all organic groups, the modeled mass fraction of SVOA was higher than the SVOA from the PMF analysis. The opposite is true for LVOA, while using ΔH_{VAP} values of 100 kJ/mol for all organic groups, the comparison results differed significantly from the 1:1 line. With enthalpy value of 80 kJ/mol for organics, the VTDMA-based OA

composition was approximately equal to the ones from the PMF results, however, with a linear correlation coefficient of only 0.4. This relatively low correlation coefficient suggests that additional information on each of the method is needed to analyze the potential links between the AMS and volatility data. Moreover, Paciga et al. (2016) studied the volatility distribution of the PMF-derived organics and estimated that almost half of the SVOC, which was determined from PMF, is semi-volatile, while 42% is low-volatile and 6% is extremely low-volatile. This suggests that the two PMF-derived organic groups, commonly labeled for their oxidation levels, might not be directly linked to their actual volatilities.

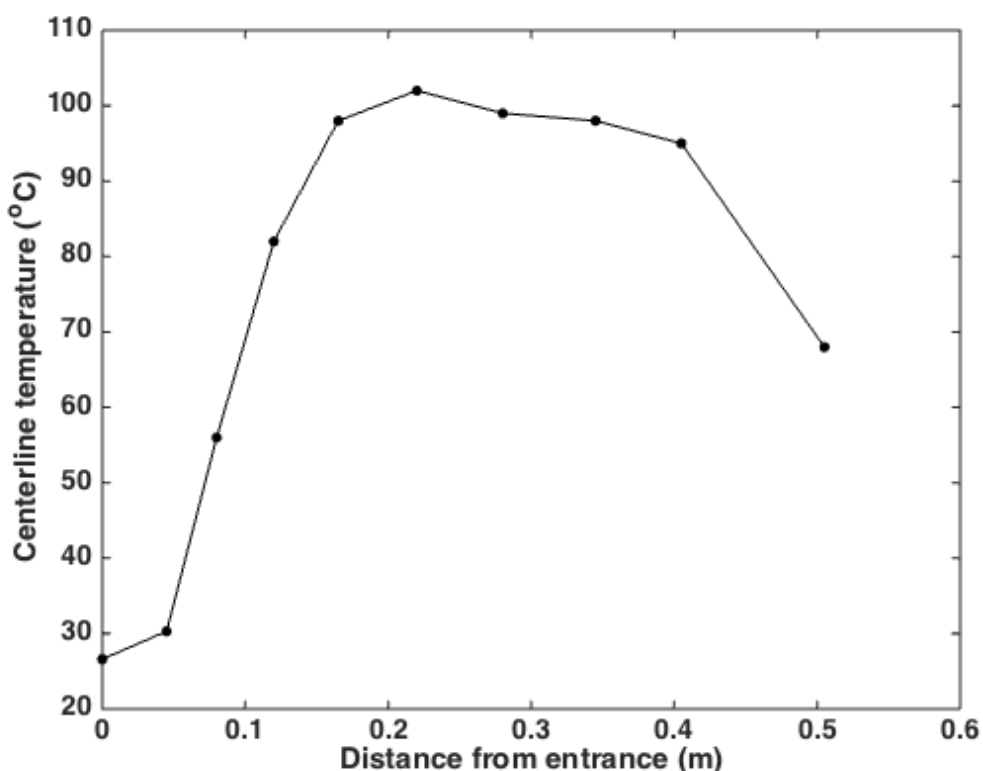


Fig.1. Temperature profile along the axis of the heating section at a flow rate of 2 L/min.

Reference:

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Tong, H.-J., Reid, J. P., Bones, D. L., Luo, B. P., and Krieger, U. K.: Measurements of the timescales for the mass transfer of water in glassy aerosol at low relative humidity and ambient temperature, *Atmos. Chem. Phys.*, 11, 4739–4754, doi:10.5194/acp-11-4739-2011, 2011.