

## ***Interactive comment on “Lower than expected volatility of secondary organic aerosols formed during $\alpha$ -pinene ozonolysis” by Kei Sato et al.***

**Anonymous Referee #1**

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The authors investigated volatility of secondary organic aerosol (SOA) from  $\alpha$ -pinene oxidation using measurements of chemical composition of particles, evaporation upon heating and evaporation upon dilution. The topic is important in the field of atmospheric aerosols and well suited in Atmospheric Chemistry and Physics. The experimental work coupling different methods for investigating the volatility of SOA seems valid. I find that there are few aspects in the analysis and discussion of the results which should be improved/clarified before the manuscript can be published. Please find below my specific comments.

Specific comments:

1. How large fraction of compounds are actually detected with PTR-MS? Is sticking of molecules on the filter affecting uncertainty of the resulting  $C_{sat}$ ?

C1

2. Particles were formed in different chambers in dry and 40% RH case: one with Teflon-coated walls and the other made of fluorinated ethylene polyethylene. At least Teflon walls are found previously to take up organic vapors. This can affect the composition (i.e. volatility distribution) of the particles and reduce the comparability of the dry and 40% RH experiments. Also, the SOA formation conditions have not been same in both types of experiments. The authors should discuss the effect of such possible sources of uncertainty in context of comparing the dry and 40% RH experiments. Also, please make it clear what was the RH in the evaporation section of the set-up when the particles formed at 40% RH were studied. I assume it was 40% (P4, L126).

3. LC/MS measurements of composition: A. Can the SOA evaporate or react during the treatment of the filter sample? How much uncertainty does this cause to the measured composition? Especially, one would expect some of the semi-volatiles to evaporate when the filter extract is concentrated in nitrogen stream. If such effects are possible, the effect on the inferred SOA composition and VBS should be discussed. B. How large fraction of SOA compounds are expected to be detected with the method and do the compounds that are not detected cause uncertainty to the results? The ionization and transmission efficiencies are discussed on page 6 related to  $C_{sat}$  distribution. Were the same efficiencies assumed when analyzing carbon number distributions? C. Based on Figure 3 there are rather large differences between runs 1 and 6 and between 7 and 8 although the oxidation conditions have been similar. This should be addressed in the discussion of the results.

4. Authors present the  $C_{sat}$  distributions as sum of particle and gas phase (Figure 4) where particle phase is based on measured composition and gas phase is calculated assuming gas-particle equilibrium. Based on Figure 3, O/C is continuing to change at the end of the experiment suggesting that the system is not in equilibrium. Based on text on page 6 it's not clear if this was considered in the analysis when estimating abundance of gas phase compounds.

5. The volatility distributions in Fig. 4 a-b have different shape compared to Fig. 4 c.

C2

Do authors have any ideas on what causes this?

6. Heat induced evaporation (Figure S3 and P7 L248-260): The variation of MFR at T=50C seem rather large for cases with OH scavenger (black markers). Did the authors look into what could cause this variation? Authors state that “Although the effects of OH scavengers, photochemical aging, and relative humidity on particle volatility were studied, the thermograms showed that all SOA results were similar to each other, within experimental uncertainties.” Can the variation between the black markers be something else than experimental uncertainty? In that case there could be some effect of OH scavenger, aging and RH hidden in the data points.

7. “The present results indicate that gas/particle partitioning was virtually irreversible even though the VFR continued to decrease after 3 h.” (P7, 282) This is unclear. What do the authors mean by irreversibility here?

8. “To the best of our knowledge, this study is the first to arrive at the results described above.” (P8, L291) Please be more specific here. Not all the results described in the manuscript are as new as this suggests. Highly oxidized and/or long carbon chain compounds and slow evaporation are detected in earlier studies also, e.g. in the references of the current manuscript.

9. Please consider revising the title “Lower than expected volatility of secondary organic aerosols formed during  $\alpha$ -pinene ozonolysis”. The evaporation of particles was indeed slower than expected based on the yield experiments. However, considering Vaden et al. (2011, ACP) and other studies since then (which authors reference in the manuscript), I don't think “lower than expected” is anymore valid. With this I do not by any means suggest that the current study would not be important. It is definitely a topic which is worth of extensive research. However, the current title suggests that the authors find even lower volatility than Vaden et al. and other studies have found, which doesn't seem to be the case.

10. Figure S2 and Table S2. These include only a small number of compounds and

C3

different compounds for different methods. It is not clear why these specific compounds were chosen for these comparisons.

Technical comments:

P1, L22: “Atmospheric fine aerosols are believed to negatively affect climate (IPCC, 2013)...” Is this a typo? What do authors mean by ‘negatively affect climate’?

P1, L39: “Wilson et al., 2014” should probably be 2015.

P2, L41-43: “...however, later research showed that the evaporation process is strongly influenced by the particle phase state, and suggested that dilution results cannot be simply interpreted by gas/particle partitioning.” Please add reference to this statement.

P5, L179: “The highest relative abundance was observed in the photochemical aging experiment,...” Please specify which compounds you refer to.

P5, L191: “...that such dimerization will occur prior to the formation of the latter.” Please clarify this sentence.

P7, L271: “Although evaporation is assumed to occur instantaneously in VBS models,...” Did you mean equilibrium partitioning models? VBS is often used also for representing dynamics of condensation/evaporation.

P8, L297: “...and photochemical aging in gas phase would be slower than that expected in the model.” Please clarify this sentence. It is not clear how this conclusion was reached.

Figure S2. At the start of figure caption, please change “MW” to “Molecular weight (MW)” for clarity.

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