

We thank the reviewers for the thoughtful comments. We address each comment individually below, with the reviewers' initial comment in **black** and our responses in **blue**.

Response to Reviewer #1

The authors explored the heterogeneous oxidation of secondary organic aerosols (SOA) by OH radicals as a function of relative humidity. A difference was observed between heterogeneous oxidation at 25% compared to 80%, and a model was developed to explain the results. This manuscript is easy to follow and clear. The science is also of high quality and provides significant insight. I recommend the manuscript for publication after the authors have had a chance to address the following comments.

Comments:

In this study it was assumed that the oxidation of SOA by OH occurred only in the condensed phase. How did the authors rule out the possibility of gas-phase oxidation of semi-volatile organics that partition between the condensed-phase and gas-phase after the generation of SOA. This is likely a question that has been addressed in previous studies, but for the uninformed reader, it would be beneficial to discuss in the current manuscript as well.

The reviewer raises an important point. After forming the aerosol particles in the first flow tube the air stream is passed through a charcoal denuder to remove the vast majority of gas-phase organic species. It is possible that the SOA evaporates to some extent due to scavenging of the charcoal. However, previous experiments have shown negligible mass loss for SOA simply from scavenging of vapors in denuders on the time scales relevant to our experiment (Cappa and Wilson, 2011).

We already had indicated that a denuder was used, but we have expanded the discussion in Section 2.1 to make clearer the issue raised by the reviewer as:

“Downstream of the flowtube was a Carulite 200 (Carus) denuder followed by a Charcoal denuder to remove residual hydrocarbons and oxidants in the gas phase. Previous experiments have shown negligible mass loss of SOA particles due to scavenging of vapors in denuders on the time scales relevant to our experiments (Cappa and Wilson, 2011). Therefore, the gas-phase oxidation of semi-volatile organics in the second flowtube is limited.”

Page 13, lines 7-9. At this point in the manuscript (without the modelling) the implications to the atmosphere is not completely clear since the reaction time in the laboratory was seconds, while the reaction time in the atmosphere can be days. Because of this difference in reaction times, diffusion limitations can be more important in the laboratory compared to the atmosphere. Hence, at this point in the manuscript, the authors may want to change the wording to “These observations may have implications for the lifetime of SOA with respect to heterogeneous oxidation in the atmosphere”.

We have made this change.

As pointed out by the authors, mass concentrations of SOA was 1000 microgram/m³, which is higher than ambient concentrations. Can the authors speculate on how their results may change with mass concentration? Two recent studies have explored the effect of mass concentration on the viscosity of SOA. 1,2

The reviewer raises an important point. Recent studies explored the effect of mass loadings on the viscosity of SOA under dry conditions (<5%-20% RH) and demonstrated an increase in viscosity with a decrease in mass concentration (Grayson et al., 2016; Jain et al., 2018). While this indicates ambient aerosols are more viscous than lab aerosols generated here under low RH, we focus on the difference of viscosity of SOA between low and high RH. Renbaum-Wolff et al. (2013) have shown that SOA of ambient concentrations (<10 $\mu\text{g m}^{-3}$) are liquid-like ($D_{org} > 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) when RH > 70%, which is consistent with our model prediction for the D_{org} of SOA of 1000 $\mu\text{g m}^{-3}$. Given that, the difference of viscosity between low and high RH is likely similar or more substantial for ambient SOA than for lab generated SOA. This is because we find that there is a critical point below or above which additional variability in viscosity has only a minor influence on the oxidation behavior. Thus, even if the viscosity of the particles is higher at lower concentrations we would expect to observe similar behavior. Therefore, our results reported here can be applied to smaller mass loadings of SOA and the effect of RH on volume loss and compositional change of aerosols is important to SOA of ambient concentration.

We have added the following discussion in Section 4 to make this point clear.

“Our observations suggest that the lifetime of SOA with respect to heterogeneous OH oxidation is significantly shorter at high RH and that this loss mechanism should be considered in regional and global models. Although the mass concentrations of SOA we use here are 1 – 3 orders of magnitudes higher than ambient concentrations, the above conclusions are likely to hold true. Recent studies have demonstrated an increase in SOA viscosity with a decrease in mass loadings under low RH conditions (Grayson et al., 2016; Jain et al., 2018). However, under high RH conditions the SOA particles are likely to stay liquid-like independent of mass concentration. Thus, the difference in particle viscosity of several orders of magnitude between low and high RH conditions will almost certainly persist—and perhaps increase—at typical ambient SOA concentrations. Consequently, the influence of RH on SOA aging is likely important even at ambient SOA concentrations.”

References:

(1) Grayson, J. W.; Zhang, Y.; Mutzel, A.; Renbaum-Wolff, L.; Boege, O.; Kamal, S.; Herrmann, H.; Martin, S. T.; Bertram, A. K. Effect of varying experimental conditions on the viscosity of alpha-pinene derived secondary organic material. *Atmospheric Chemistry and Physics* 2016, 16, 6027-6040. (2) Jain, S.; Fischer, K. B.; Petrucci, G. A. The Influence of Absolute Mass Loading of Secondary Organic Aerosols on Their Phase State. *Atmosphere* 2018, 9, 14.

Cappa, C. D., and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, *Atmos Chem Phys*, 11, 1895-1911, <https://doi.org/10.5194/acp-11-1895-2011>, 2011.

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