Professor Annele Virtanen,
Co-Editor of Atmospheric Chemistry and Physics
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Dear Annele,

Below are our responses to the comment provided by reviewer #2. For clarity, the referee comments or questions are in black text, and are preceded by bracketed, italicized numbers (e.g. *[1]*). Our responses are in in blue text below each comment or question with matching italicized numbers (e.g. *[A1]*). We thank the referee for their time and care reading our manuscript and for their helpful comments and questions.

Sincerely,

Allan Bertram
Professor of Chemistry
University of British Columbia

Referee #2
Comments:

[1] To address my comment and the first comment by the referee 1 the authors have modified the manuscript by adding discussion on evaporation of compounds during conditioning. I have concerns regarding the calculations the authors present for this issue and the conclusions they draw from them. I recommend a revision before the manuscript is accepted.

Authors state: "In the poke-and-flow experiments (as well as the LLPS experiments), the particles are exposed to a constant flow of gas which can lead to a change in the composition of the particles by partitioning of semi-volatiles to the gas phase. For a 1 hr poke-and-flow experiment, the amount of gas exposed to the SOA is 30 L compared to 380 L collected from the environmental chamber. Exposing the SOA to this amount of gas can be considered equivalent to changing the mass loading used to generate the SOA from 550 µg m^{-3} to 510 µg m^{-3}. Exposing the particles to a constant gas flow for 27 hours (maximum amount of time a sample was exposed to a constant gas flow) can be considered equivalent to changing the mass loading from 550 µg m^{-3} to 175 µg m^{-3}. This should be considered a worse-case scenario since this estimation does not consider kinetic constraints to evaporation. Based on previous measurements, the viscosity of toluene SOA is independent of mass loadings ranging from ~800 µg m^{-3} to ~80 µg m^{-3} (Song et al., 2016a). Assuming that diesel fuel SOA behaves like toluene SOA, the viscosity of diesel fuel SOA should not be influenced by exposure to a constant flow of gas in our poke-and-flow experiments. Consistent with this discussion, we did not observe a relationship between particle viscosity and time the SOA was exposed to a constant flow of gas in our experiments.”

This does not seem valid reasoning. This would approximately hold if adding 30 L of clean air to a 380 L expansible chamber where mass loading where initially 550 μg m^{-3}. However, according to my understanding, in this study the authors collect the particles on a glass slide and then clean air is flowing above this glass slide during conditioning. In this case the equilibration calculation presented above does not hold and the system to consider is the particle phase formed by the particles on the glass slide and the organic-free clean gas flowing above them. As the particles are surrounded by the clean air continuously, they are evaporating. Given enough time they should actually evaporate completely. Therefore the presented calculation is not a worse-case scenario like the authors stated. The observed lack of a relationship between viscosity and the time the particles were exposed to the gas flow could be due to the relatively long exposure time even in the fastest case: 1 hour is enough time for semi-volatiles to evaporate considerably. Therefore the particle composition could be changing during the conditioning in all of the experiments to the extent that it does not represent the viscosity of the original particles. The issue of evaporating compounds and the resulting uncertainty or systematic error in viscosities should be discussed in the text.

[A1] Thank you for feedback. We do think our equilibrium calculations are useful to put in context the amount of “dilution” that occurs in our experiments, but we concede that the equilibrium calculations do not exactly represent our experiments. As suggested by the referee, we removed the equilibrium calculations from the manuscript and modified the manuscript to include the issue of evaporating compounds and the resulting uncertainty or systematic error in viscosities.

The following is the modified text in Section 2.3:

“We acknowledge that viscosity of the SOA could change between the time of its initial formation in the chamber and the time of the off-line viscosity and LLPS measurements. Such changes can be driven by both evaporative losses and slow chemical aging processes. During the MOUDI sampling, impacted particles are surrounded by the same gaseous products as in the chamber and should not evaporate. We expect the evaporation to be minimal when the collected particles are briefly exposed to ambient air, sealed in a storage container with a small head space volume (~ 2 cm^3), and frozen for storage and shipment. However, in the poke-and-flow experiments (as well as the LLPS experiments), the particles are exposed to a constant flow of purified air at room temperature for an extended period of time which can lead to a change in the composition of the particles by partitioning of semi-volatiles to the gas phase. For a 1 hr poke-and-flow experiment, the amount of gas exposed to the SOA is 30 L compared to 380 L collected from the environmental chamber. For a 27 hr poke-and-flow experiment (maximum amount of time a sample was exposed to a constant gas flow), the amount of gas exposed to the SOA was 810 L compared to 380 L collected from the environmental chamber. We did not observe a relationship between particle viscosity and time the SOA was exposed to a constant flow of gas in our experiments; however, semi-volatiles may still have evaporated in the experiments when the particles were conditioned to a known RH and during the poke-and-flow measurements. The loss of semi-volatiles would lead to an increase in viscosity of the SOA (Wilson et al., 2015; Yli-Juuti et al., 2017; Buchholz et al., 2019). Consequently, our results should be considered as upper limits to the viscosity of the SOA generated with a particle mass loading of 550 μg m^{-3}. The evaporation of semi-volatiles in the experiments as well as possible slow chemical aging reactions occurring during shipment and storage may in fact have resulted in the SOA being more similar to the chemical composition of SOA in the atmosphere, which are formed at particle mass loadings $<$ 550 μg m^{-3} and then chemically aged."

The following is the text added to Section 3.3:
"Second, some of the semi-volatiles may have evaporated from the diesel fuel SOA in the poke-and-flow experiments. If evaporation of semi-volatiles did occur, the viscosity of the diesel fuel SOA at (~500 μg m^{-3}) may be lower than reported here (Wilson et al., 2015; Yli-Juuti et al., 2017; Buchholz et al., 2019)."

References:

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Wilson, J., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation Kinetics of Laboratory-Generated Secondary Organic Aerosols at Elevated Relative Humidity, Environ. Sci. Technol., 49, 243-249, 10.1021/es505331d, 2015.

Yli-Juuti, T., Pajunoja, A., Tikkanen, O. P., Buchholz, A., Faiola, C., Vaisanen, O., Hao, L. Q., Kari, E., Perakyla, O., Garmash, O., Shiraiwa, M., Ehn, M., Lehtinen, K., and Virtanen, A.: Factors controlling the evaporation of secondary organic aerosol from alpha-pinene ozonolysis, Geophys. Res. Lett., 44, 2562-2570, 10.1002/2016gl072364, 2017.