Referee #1

Summary:
The manuscript describes the analysis of secondary organic aerosol (SOA) samples generated from diesel fuel vapours, concentrating on observations of liquid-liquid phase separation and viscosity. This continues a sequence of publications on similar topics by the authors examining a variety of SOA systems, expanding the coverage of atmospheric aerosol surrogate systems that can improve our understanding of ambient particles. The authors should consider my specific comments below in revising their manuscript.

Concerns:
[1] Collection of samples on glass slide for liquid-liquid phase separation and viscosity measurements: It would be helpful if the authors could say something about the possible changes in composition (particularly partitioning of semi-volatile and more volatile components) that result – how reflective of the actual aerosol composition in the Teflon chamber are the particles once deposited and then analyzed on the surface? This may be discussed in previous work but should be reiterated here. For example, the viscosity measurements are made in a flow-cell and necessarily this will presumably drive the composition to lower volatility and higher viscosity components over time. These changes in composition are not accounted for in the predictions of viscosity based on mass spectrometry measurements of the SOA composition.

[A1] This is a good question, and we have addressed it in previous publications, but we agree that we should also address this question in the current manuscript. To address the referee's comments we will add the following to the revised manuscript (Sect. 2.3).

"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."

Reference:
Song, M., Liu, P. F. F., Hanna, S. J., Zaveri, R. A., Potter, K., You, Y., Martin, S. T., and Bertram,

A. K.: RH-dependent viscosity of secondary organic material from toluene photo-oxidation and possible implications for organic particulate matter over megacities, Atmos. Chem. Phys., 16, 8817-8830, 10.5194/acp-16-8817-2016, 2016a.

[2] Page 8: The authors state "The increase in the range of RH values over which LLPS occurs is likely related to the spread in O:C values within the organic particles – as the spread in O:C values increases, the RH range for LLPS is also likely to increase." In itself, the spread is not a reason, is it? Can the authors provide some rationale for why increasing chemical complexity leads to an increase in the LLPS RH range?

[A2] We will re-write this section for clarity (Sect. 3.1). Specially the following will be added to the manuscript in place of the discussion on spread in O:C. "The increase in the range of RH values over which LLPS occurs is likely related to distribution of the polarities (or hydrophilicities) of the organics molecules within the SOA (Renbaum-Wolff et al., 2016; Gorkowski et al., 2019). When the organic molecules are hydrophobic or moderately hydrophobic (and hence have small O:C values) the particles are expected to have a single organic-rich phase until close to 100% RH, at which point LLPS can occur. When the organic molecules are hydrophilic (and hence have large O:C values), the particles are expected to have a single water-rich phase, with no occurrence of LLPS. Alternatively, if the particles contain a mixture of hydrophobic and hydrophilic organic molecules, the particles are expected to have both an organic-rich phase and a water-rich phase over a relatively wide range of RH values. A significant amount of molecules with low and high O:C values in the diesel SOA studied here (Fig. S3) is consistent with LLPS being observed over a relatively wide range of RH values."
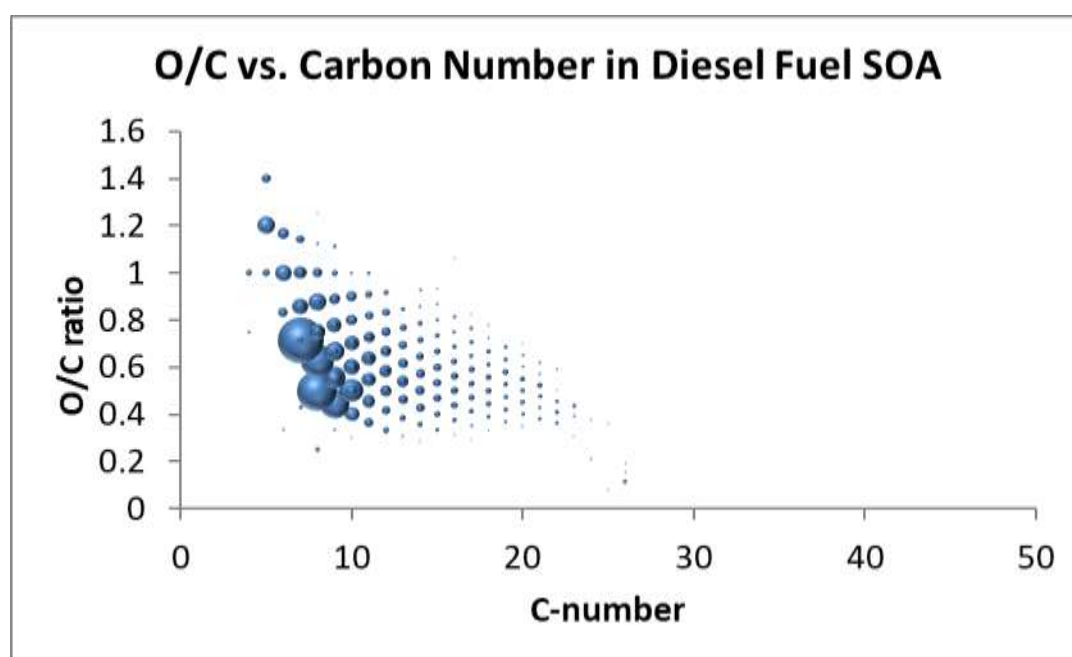

O/C vs. Carbon Number in Diesel Fuel SOA

Figure S3. Distribution of O:C values and carbon numbers of the organic molecules in the diesel fuel SOA studied here. The size of the symbols indicates the relative amount of the organic molecules in the SOA based on the ion current in the mass spectrum.

References:

Gorkowski, K., Preston, T. C., and Zuend, A.: RH-dependent organic aerosol thermodynamics via an efficient reduced-complexity model, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-495, in review, 2019.

Renbaum-Wolff, L., Song, M., Marcolli, C., Zhang, Y., Liu, P. F., Grayson, J. W., Geiger, F. M., Martin, S. T., and Bertram, A. K.: Observations and implications of liquid-liquid phase separation at high relative humidities in secondary organic material produced by α-pinene ozonolysis without inorganic salts, Atmos. Chem. Phys., 16, 7969–7979, https://doi.org/10.5194/acp16-7969-2016, 2016.

[3] Figure 1: Are (a-c) just three different particles prepared under the same reaction chamber conditions? Similarly, in Figure 2, the different poke-flow measurements are made on different particles?

[A3] Yes, Fig. 1 and Fig. S2 show six different particles prepared under the same reaction chamber conditions. Also, a different particle, prepared with the same reaction conditions, was used for each poke-and-flow measurement. To address the referee's comments, this information will be added to the revised manuscript (Sect. 3.1) and the caption for Fig. 3.

[4] Page 8 onwards: Lower and upper limits to viscosity could clearly be dependent on any changes in composition that occur during the conditioning period. It would be helpful if the authors could show how the measured viscosity changes during the conditioning period, does it tend to a limit as the conditioning time increases? Is this conditioning based solely on adjustment to RH or is there some change in composition/partitioning of components into the gas phase during this time period (given the high concentrations in the reactor chamber)?

[A4] See response to [A1] above.

[5] Page 9: To what extent is it appropriate to even represent the viscosity by a single value given that could be multiple phases/heterogeneities with within the particle with different viscosities? For example, the method for recording the "upper limit" could presumably be a measure of the viscosity of one phase, providing sufficient mobility for the shape recovery, with a more viscous phase moving within the more mobile phase.

[A5] This is a good point. When calculating the viscosity, we did not take into account the heterogeneity of the particle (i.e. the presence of both an organic-rich and water-rich phase). The viscosity measurements were carried out at RH values ≲ 58 % RH. For this RH range, the amount of the water-rich phase was small but still detectable in most cases. Assuming the

water-rich phase is less viscous than the organic-rich phase, due to the plasticizing effect of water, the viscosity of the organic-rich phase will be greater than the calculated (i.e. reported) viscosities. To address the referee's comments, we will add this caveat to the revised manuscript (Sect. 3.3).

[6] Page 12: The authors state "At 30 % RH τ_{mixing} is $\gtrsim$0.4 h, and at 38 to 50 % RH τ_{mixing} is in the range of ~0.01 h to ~50 h (Fig. 5a). These results provide important constraints on τ_{mixing} values within anthropogenic SOA." Given the viscosity goes down with increasing RH, this sentence is confusing. The scales on Figure 5(a) are confusing, partly because it is very hard to read values due to the extremely large range. I recommend the authors only show a viscosity range from 10^4 Pa s to ~10^9 Pa s. Lower and higher viscosities are to a large extend superfluous and there are no data in these arranges.

[A6] To address the referee's comments, the statement mentioned above will be changed to the following: "At 38 − 50 % RH τ_{mixing} are in the range ~0.01 h to ~50 h (Fig. 5a). These results provide important constraints on τ_{mixing} values within anthropogenic SOA." In addition, we will decrease the range of viscosities shown in Fig. 5a, for clarity.