Professor Nga Lee (Sally) Ng
Co-Editor of Atmospheric Chemistry and Physics

Dear Sally,

Listed below are our responses to the comments from the reviewers of our manuscript. We thank the reviewers for carefully reading our manuscript and for their very helpful suggestions! For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. ***[1]***). Authors' responses are in red below each referee statement with matching numbers (e.g. ***[A1]***).

Sincerely,

Allan Bertram
Professor of Chemistry
University of British Columbia

Anonymous Referee #1

Maclean et al. has estimated mixing times of organic molecules within secondary organic aerosol particles. In chemical transport models SOA particles are often assumed to be homogeneously well-mixed on the timescale of <1h, which could be in question if SOA particles adopt glassy or amorphous semisolid states. Combining laboratory data, meteorological conditions, and chemical transport modeling, this study predicted that mixing times should be indeed within <1h in the planetary boundary layer. They concluded that the assumption of well-mixed SOA in chemical transport models seems reasonable for biogenic SOA in most locations in the PBL. This is a very interesting study, the method seems reasonable, and the manuscript is clearly written and easy to follow. I have several comments as below, which should be implemented in the revised manuscript before publication in ACP.

[1] The analysis is focused on 200nm-diameter particles and I agree that this may be most frequent size to be observed in ambient environments. Aged particles can have much larger diameters of up to 1 um, as observed for example in remote areas or Tokyo (see Fig. 7 in Takegawa et al., J. Geophys. Res., 111, D11206, 2006). Thus, I would suggest that the same analysis should be conducted with a larger diameter, say 500 nm-diameter particles. Then same figures of Fig. 3 could be presented and lines can be added in Fig. 4 (if the results are too similar with 200 nm, then they can be placed in the supplement/appendix). Mixing times should be larger for larger particles and I would be curious to know if mixing timescales would be still below 1 h. This should be easy and straightforward to do for authors and it will certainly strengthen their conclusion.

[A1] To address the referee’s comments we will calculate mixing times for 500 nm-diameter particles as suggested and add the results to the revised manuscript.

[2] It is very interesting to compare Fig. 6 in this study with Fig. 3d in Shiraiwa et al. (Nat. Communn., 8:15002, 2017). Shiraiwa et al. predicted the glass transition temperatures of SOA in a global model and estimated mixing timescales using annual average of RH and T for 2005-2009, while this study considers seasonal dependence, but did not simulate Tg or viscosity directly but viscosity was parameterized based on a-pinene viscosity measurements. I think there should be some discussion with a paragraph or two comparing these two studies. General trends seem to be consistent: longer timescales in west US, Sahara, and Mideast and shorter timescales in Europe and higher latitudes (Why there are no information over some places, such as Europe in panel a and over Amazon in both panels?). However, this study seems to estimate mixing timescales shorter in general. Please add some discussions.

[A2] In the revised manuscript, we will add discussion comparing our studies with the studies by Shiraiwa et al. as suggested.

[3] - Abstract, L23: “SOA concentrations are significant.” is ambiguous. I suggest being specific here (> 0.5 ug m-3).

[A3] this change will be made as suggested.

[4] - P2, L4: I suggest replacing “the lowest” to “low”. Not only the lowest ones, but low and semivolatile products would also condense.

[A4] This change will be made as suggested.

[5] - P5, L3: “under predict” should be “underpredict”.

[A5] This change will be made as suggested.

[6] - Figure 6 is not very easy to read and I feel this is because of overlapping yellow lines, arrows, and letters. Can you just remove these yellow things, and just put colors for places with SOA concentrations above 0.5 ug m-3? This would improve accessibility of this important figure.

[A6] Changes will be made as suggested.

[7] - It may be good and helpful for readers to have a summary/conclusion section in the end of the manuscript.

[A7] A summary/conclusion section will be added as suggested.

[8] - I suggest combining Section S1 with the main text, or include it as Appendix (particularly bring eq S1 and S2).

[A8] This change will be made.

[9] - I would suggest moving Fig. S3, S4 (also S5?) in the main text (maybe in Appendix?). There seem to be non-negligible cases with mixing timescales >1 h for anthropogenic SOA (given that sucrose is a good proxy for that).

[A9] If possible, we would prefer to keep these figures in the Supplement to avoid making the main document too long. However, we can move these figures to the main text if the Editor prefers.

Anonymous Referee #2

[10] The authors report on mixing timescales within SOA particles using a parameterization that is developed based on literature data. They conclude that within the planetary boundary layer biogenic SOA particles can usually be considered well-mixed, having mixing timescales < 1h. Their work has potentially important implications for thinking about how air quality and climate models treat SOA formation and addresses an important topic. My major concerns relate to the robustness of the parameterization and how this might impact the conclusions here, especially in the context of (i) the exceptionally different, and still unexplained, viscosities between the Grayson et al. and Zhang et al. studies, the key ones for this work and (ii) the uncertainty within an individual study of SOA viscosity. I do not find that the current work sufficiently addresses the question of robustness, even with the sensitivity test that is included. Associated, I have concerns that their statement that none of their conclusions are significantly impacted by data uncertainty is not sufficiently justified. Specific comments are below.

[A10] Thank you for raising these important and excellent questions/comments. We have addressed these questions/comments below.

[11] Fig. 1: Given that the parametrization depends on RH and T, it would be useful if Fig. 1 were augmented with additional panels showing the average PBL RH and T as a function of lat/lon.

[A11] As suggested, we will add a figure to the revised manuscript that shows global maps of the average RH and T for January and July.

[12] P3/L19: Looking at Fig. 2, it is difficult to fully understand the parameterization that has been developed. It seems apparent that the viscosity of the a-pinene SOA measured at 293 K at a given RH differs dramatically between studies, with the reported values varying over orders of magnitude. (I'm comparing the "brown" circles to the more red "stars and pentagons.") In fact, the authors acknowledge this fact in section 3.4 ("Sensitivity analysis..."), and attempt to address it. However, I have substantial

concerns, nonetheless. First, it is evident from Fig. 3 that the vast majority of the observations are in the T-range 290-300 K. This is the range of both the Grayson and Zhang observations. The Zhang et al. observations indicate that the viscosity at 293 K and 58% RH is 1 x 10ˆ7 Pa s, which translates to a mixing time of 5 h for a 200 nm diameter particle. A condition of 58% RH and T = 293 K is very close to the high probability region in Fig. 2B (July). Thus, it would seem that the probability of having mixing time scales >1 h in July (based on Zhang et al.) would be substantial, much more than indicated by the authors in Section 3.4. Most likely, this is because of the incorporation of the Jarvinen et al. low-T data, which appears to have a similar viscosity as the SOA from Zhang et al. at the same RH but a much lower temperature. Including the Jarvinen data, which is at temperatures well-below the most probable range, leads to the parameterized viscosity at this most probable (July) condition being underestimated relative to if only the Zhang et al. observations were used. (This is difficult to assess because the authors do not provide a Figure similar to Fig. 2 that shows the Grayson-excluded parameterization, nor do they provide their best fit parameters.) I suggest that the inclusion of histograms for the alternative (sensitivity) case, similar to Fig. 4, is necessary. Additionally, I strongly suggest that a sensitivity case that excludes the pure water observations in developing the parametrization is needed. With this, the Grayson et al. and Zhang et al. results should be considered separately. This would require ignoring any T-dependence, but as most of the RH/T pairs overlap with these data sets, and the variability in RH is much greater than the variability in T, it would be a reasonable approximation. The authors must show the contours associated with their alternative parameterizations (as they do in Fig. 2 for their reference case).

[A12] To address the referee’s concerns, in the revised manuscript, we will first focus on a parameterization that just includes the room-temperature and low-temperature viscosity data from Grayson et al. and Jarvinen et al., which corresponds to SOA generated at high mass concentrations. Then, we will focus on a parameterization that just includes the SOA room-temperature viscosity data from Zhang et al., which corresponds to SOA generated under low mass concentrations.

[13] Further, while I appreciate the sensitivity test that was done, it should be noted that the reported uncertainty in the Zhang et al. measurements is +/- 2 orders of magnitude. At the high end, this would imply that SOA in much of the atmosphere would not mix on a 1 h time scale. On the low end, nearly all SOA would always be well mixed. This is because a 1 h mixing time scale corresponds approximately to a viscosity of 2e6 Pa s, and thus variability around this value can have a large impact on the conclusions; the uncertainties on the Zhang et al. measurements overlap this critical value up to an RH of 58%.

[A13] In the revised manuscript, uncertainties in the viscosity data we be considered in the sensitivity analysis.

[14] Continuing with this, the results from Grayson et al. also suggest that the viscosity increases as the mass concentration decreases; this is offered as a potential (although

not demonstrated) explanation for the substantially larger viscosities in Zhang et al. and in Renbaum-Wolff et al. The Zhang et al. measurements are still at SOA concentrations above ambient. Isn't it possible that the viscosity of SOA at ambient concentrations is even higher than that reported in Zhang et al.? Or, doesn't it suggest that the "sensitivity" case is actually the better base case, since the concentrations in Zhang et al. are closer to ambient than in Grayson et al.? Overall, I have substantial concerns that the authors are under-emphasizing the potential uncertainty in their estimates in a manner that may influence their conclusions. I think that these issues need to be explored further before this work should be published.

[A14] To address the referee's comments we will add a section to the revised manuscript that discusses the effect of mass concentration used to generate the SOA on viscosity.

[15] Fig. 2 and Eqn. 4: Regarding the translation between viscosity and mixing time scale, I have some concerns about the authors' illustration. Based on Fig. 2, a viscosity of ~ 2e7 Pa s corresponds to a mixing time scale of 1 h for a 200 nm particle. Using the stated hydrodynamic radius (0.38 nm), the calculated diffusion coefficient for viscosity = 2e7 Pa s is 2.8e-20 mˆ2/s and the mixing timescale for a 200 nm particle is 10 h. Thus, the yellow line in Fig. 2b seems to delineate between >10 h and <10 h, not >1 h and <1 h. My assessment seems consistent with the color scale in Fig. 2b. Similarly, the lines in Fig. 3a and 3b are incorrectly labeled: the line labeled >< 1 h is actually for 10 h. This should not materially affect any conclusions, but should be fixed.

[A15] Yes, this was a mistake. The mistake will be fixed in the revised manuscript.

[16] The authors choose 0.5 micrograms/m3 as their dividing line between what to consider and what not to consider. While reasonable, this is nonetheless an arbitrary choice. Therefore, I suggest that it would be useful if the authors were to graph calculated viscosity vs. mass concentration. Is there any sort of trend that can be used to justify this dividing line?

[A16] We chose a mass concentration of 0.5 µg m^{-3} for filtering because the mass concentration of organic aerosol at the surface was > 0.5 µg m^{-3} in all but one of the previous field measurements of organic aerosol at remote locations (Spracklen et al. 2011). To address the referee's comment this information will be added to the revised manuscript.

[17] Fig. 5: Do the authors not find it surprising that RH and T are not less variable with altitude within the PBL during the period shown (13:00-15:00 local time)? I typically think of the PBL as "well mixed" with respect to e.g. RH in the afternoon when mixing is vigorous. Is this a result of averaging over many months.

[A17] Fig. 5 was calculated using a dry adiabatic lapse rate and assuming the mixing ratio of water is independent of height in the PBL. In the revised manuscript we will clarify this point.