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Interactive comment on "Mixing times of organic molecules within secondary organic aerosol particles: a global planetary boundary layer perspective" *by* Adrian M. Maclean et al.

Anonymous Referee #2

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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

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Discussion paper

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.

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.

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).

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%.

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.

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.

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?

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?

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