Professor Alexander Laskin
Co-Editor of Atmospheric Chemistry and Physics

Dear Alex,

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

The authors report about viscosity and diffusivity measurements of a brown carbon containing limonene SOA produced by ozonolysis under high mass loading conditions with subsequent exposure to ammonia. They report an increase in viscosity by 3-5 orders upon changing the water activity from 0.9 to dry and use the measured diffusion coefficient to deduce the mixing times for atmospheric particles. Their result suggest that mixing times are below 1 hour for PBL-conditions. This is in contrast to previous studies looking at SOA under low mass loading conditions which report significantly longer mixing times. The authors compare their viscosity data with their diffusivity data using the Stokes-Einstein relationship and conclude that it holds accurately for viscosities up to 10^4 Pa s.

This is a well-written manuscript and its topic is of core interest to the readers of ACP. It makes a very elegant use of the FRAP technique as it uses the BrC contained in the SOA as the fluorophore.

[1] However, the results suffer from being obtained under high mass loading conditions, which make them less relevant for direct applications to atmospheric SOA. As such the calculated mixing times likely provide a lower limit for atmospheric limonene SOA particles. I recommend to the authors to add a discussion whether it would be conceivable to use their technique also for brown LSOA produced at lower mass loading, so that the reader get a better feeling for the limits of the technique. I recommend publishing the paper as is.

[A1] The measurements reported in the original manuscript can be extended to lower mass loading conditions by using a multi-orifice impactor, which concentrates collected material into spots, and by collecting material for extended periods of time (e.g. 1-4 days) (Grayson et al.,

2016). In response to the referee's comment, this information will be added to the end of the summary and conclusions of the revised manuscript.

Minor comments:

[2] - Abstract: While the authors acknowledge the problem of high mass loading here, I feel they should state explicitly that the magnitude of the difference in mixing times to more realistic SOA may be 3 orders of magnitude.

[A2] As suggested, in the abstract we will explicitly state that the mixing times may be 3 orders of magnitude longer.

[3] - Line 211: I am not entirely convinced by this argument. I agree that thermal steady state will be reached much quicker than the characteristic diffusion time. However, equally important may be the steady-state temperature difference. If significant, such a temperature difference may cause a redistribution of water molecules to outside of the irradiated region changing water activity locally. From the power density and thermal conductivity in the experiments the authors may estimate the temperature increase of the illuminated region.

[A3] Based on the laser power density and heat capacity of the sample and assuming no heat loss, the temperature increase for one image scan in the FRAP experiments will be ~1 K. In addition, the characteristic time for thermal diffusion when imaging is 30 ms. Since this characteristic time is much less than the imaging time, the temperature increase during scanning is expected to be less than ~1 K.

[4] - Line 253: I assume in Fig. 4, these are all above continents, correct?

[A4] Correct. More specifically, above the oceans, organic aerosol (OA) concentrations are almost always ≤ 0.5 μg m^{-3} according to predictions from GEOS-Chem (Figure 1 in (Maclean et al., 2017)). Since we are only included conditions in Fig. 4 corresponding to when OA was > 0.5 μg m^{-3} at the surface, Fig. 4 shows conditions almost exclusive for above continents. We will modify the manuscript to make this clear.

[5] - Caption of Fig. 5: Does the uncertainty for the calculated diffusivity include the uncertainty of the fluorophore radius?

[A5] Yes, except for the calculated diffusivity from Hinks et al. In the revised manuscript, we will also include the uncertainty in the fluorophore radius in the calculated diffusivity from Hinks et al.

Anonymous Referee #2

Summary:

'Viscosities, diffusion coefficients, and mixing times of intrinsic fluorescent organic molecules in brown limonene secondary organic aerosol and tests of the Stokes-

Einstein equation' combines viscosity and diffusivity measurements across a range of water activities for brown limonene SOA, and characterizes the accuracy of Stokes-Einstein relation for this system. The brown limonene SOA was generated using dark ozonolysis of d-limonene and then collected with an impactor and exposed to ammonia.

For the viscosity characterization, the authors used the bead-mobility technique for water activities higher than 0.7. For lower water activities, previously published data using poke-flow techniques by Hinks et al. are used. For the diffusion coefficient and mixing time characterization, a nice aspect of the paper, the authors measure the diffusion coefficient of fluorescent molecules using 'rectangular area fluorescence recovery after photobleaching' (rFRAP). A thin film of brown LSOA was prepared between hydrophobic glass slides. A small area was then photobleached with a laser beam, and the fluorescence is allowed to recover by diffusion of fluorophores into the photobleached region. The measurements in the study were used to test the accuracy of Stokes-Einstein relation, which is commonly used to infer diffusivity from viscosity measurements. It was found that the Stokes-Einstein relationship gave good agreement with measured values over several orders of magnitude in viscosity. This paper is well-written and the experiments well executed, with results useful for the community. There are some minor questions/comments listed below that the authors could better address to improve the clarity of the paper.

Overall, I recommend publication in ACP.

Specific Comments"

[6] What is the chemical identity of the fluorophores (the "intrinsic fluorescent organic molecules") in brown limonene SOA? Are they present in other SOA? Can the diffusivity measurement used here be extended to other systems?

[A6] The exact molecular identities of the chromophores and fluorophores in brown LSOA is not known (see line 307-310 of the original version of the manuscript). It may be possible to extend these diffusion measurements to other systems that have intrinsic fluorescent organics, such as SOA produced from the photooxidation of aromatic compounds (Aiona et al., 2018). SOA from the photooxidation of aromatic compounds contain fluorescent molecules, but experiments are needed to determine how readily these molecules will photobleach in our experiments. Alternatively, to extend these measurements to other SOA, we can add fluorescent dyes to the SOA matrix, and use these fluorescent dyes for the FRAP measurements.

[7] Consider very briefly explaining the poke-flow technique for the uninitiated reader, with description of limitations and uncertainties, since the results are used at low water activities.

[A7] A brief description of the poke-flow technique will be added as well as limitations and uncertainties of the technique.

[8] A schematic of the rFRAP technique/set-up, central to this paper, would be appreciated in the SI. Additionally, the SI would be more instructive if it includes details of the thin-film preparation process, with illustrative images of the slides after preparation. Also, can the authors

comment on why 2D FRAP was used, instead of the more traditional 1D FRAP? Is there some advantage? If 2D is somehow better, why rectangular, and not circular (for symmetry, which would likely simplify the analysis).

[A8] A schematic of the rFRAP technique and slide after preparation will be included to the SI as requested. For 1D FRAP, I assume the referee is referring to measurements that include just temporal information. In this case, knowledge of the initial bleaching profile is needed, which can be difficult to determine accurately. For 2D FRAP, rectangular FRAP was chosen over circular FRAP since rectangular FRAP has a closed-form expression for the recovery process. To clarify, additional information will be added to the revised manuscript on the benefit of rectangular FRAP over circular FRAP.

[9] Line 178 - Why were the bleach and image sizes chosen based on water activity? Is there a calibration curve for water activity versus area bleached? Does changing the area affect the time of measurement?

[A9] The recovery time in rFRAP experiments is related to both the photobleaching area and diffusion rate. When the diffusion rate was fast (e.g. high water activities), we used a larger photobleaching area, and when the diffusion rate was slow (e.g. low water activities), we used a smaller photobleaching area to give experimentally accessible recovery times. To address the referee's comment, we will add this information to the revised manuscript.

[10] Line 28 of the abstract contains the abbreviation 'PBL' without first being defined (it is defined later in the introduction. Additionally, the term 'LSOM' has been used in the figures and SI, but LSOA is used in the main manuscript.

[A10] Thank you for catching these mistakes. They will be corrected in the revised manuscript.

References:

Aiona, P. K., Luek, J. L., Timko, S. A., Powers, L. C., Gonsior, M., and Nizkorodov, S. A.: Effect of Photolysis on Absorption and Fluorescence Spectra of Light-Absorbing Secondary Organic Aerosols, Acs Earth and Space Chemistry, 2, 235-245, 10.1021/acsearthspacechem.7b00153, 2018.

Grayson, J. W., Zhang, Y., Mutzel, A., Renbaum-Wolff, L., Boege, O., Kamal, S., Herrmann, H., Martin, S. T., and Bertram, A. K.: Effect of varying experimental conditions on the viscosity of alpha-pinene derived secondary organic material, Atmospheric Chemistry and Physics, 16, 6027-6040, 10.5194/acp-16-6027-2016, 2016.

Maclean, A. M., Butenhoff, C. L., Grayson, J. W., Barsanti, K., Jimenez, J. L., and Bertram, A. K.: Mixing times of organic molecules within secondary organic aerosol particles: a global planetary boundary layer perspective, Atmospheric Chemistry and Physics, 17, 13037-13048, 10.5194/acp-17-13037-2017, 2017.