Timothy Bertram
Co-Editor of Atmospheric Chemistry and Physics

Dear Tim,

Listed below are our responses to the comments from the reviewers of our manuscript. The reviewers' comments are in black text and our responses are in red text. We thank the reviewers for carefully reading our manuscript and for their helpful suggestions. Note, we would like to add an additional co-author to the manuscript, Y. J. Li, since he contributed significantly to the revised manuscript.

Sincerely,
Allan Bertram
Professor of Chemistry
University of British Columbia

"Relative humidity-dependent viscosities of isoprene-derived secondary organic material and atmospheric implications for isoprene-dominant forests" by M. Song et al.

Response to Referee #1 (Reviewer comments in black text)

This is an important study of viscosity of a mixture of organic compounds that could serve as a model for the organic material in isoprene derived secondary organic aerosol. The measurements have been carried out over a range of relative humidity values, and the results clearly show that the organic material in model isoprene derived aerosols is not as viscous as that in model aerosols produced from alpha-pinene. I have no major suggestions for improving this paper. Minor comments are listed below.

We thank Reviewer 1 for careful reading of the manuscript and the helpful comments and suggestions. Detailed responses are given below with their respective locations in the revised manuscript.

1134, line 1: for the benefit of the readers, please specify a typical size of an organic molecule for which the Stokes–Einstein equation should be applicable.

- ➔ This is a good point. We have now added the following text in Sect. 4.3.
  "The Stokes-Einstein relation should give a reasonable estimate of diffusion rates when the viscosity is lower than that of a glass and when the molecules undergoing diffusion are

roughly the same size or larger than the molecules in the SOM matrix. If we assume the SOM matrix is dominated by molecules similar to 2-methyltetrol and 2-methylerythritol ($C_5H_{12}O_4$), which have been identified as key oxidation productions of isoprene and have an isoprene skeleton, (Cleaeys et al., 2004; Carlton et al., 2009; Kleindienst et al., 2009) then the Stokes-Einstein equation should be applicable when the viscosity is lower than that of a glass (10^{12} Pa·s) and for organic molecules with a molecular weight approximately ≥ 136 g mol^{-1}, although additional work is required to confirm these assumptions."

1136, SOM preparation section: please estimate the contribution of ozone to SOA production. With 15 ppm ozone in the flow and k = 1.3E-17 cm3/(molec*s), the lifetime of isoprene should be about 3.6 minutes. The volume of the oxidation flow reactor is not specified in this paper and it is also not specified in the cited papers by Liu et al. (2013 and 2014). However, the Liu et al. (2014) paper quotes a residence time of 110 s at the same flow rate as used in this study. Therefore as much as 50 % of isoprene could potentially be oxidized by ozone instead of OH. Is this an issue considering that ozone-driven oxidation is also capable of producing aerosol from isoprene, e.g., Ref.[1]?

- ➔ To address the referee's comment we have added the following text to the revised manuscript (Sect. 2.1):

"The volume of OFR was 13.3 L and the OFR was operated at a flow of 7.0 and 9.5 L min^{-1}, resulting in residence times of 114 s and 84 s, respectively. Although the OH concentration was not measured in the OFR in this study, an OH concentration in the OFR in the range of 2×10^{8} to 2×10^{10} molec cm^{-3} was expected based on previous experiments under similar conditions (Lambe et al., 2011a). This OH concentration corresponds to a lifetime of isoprene between 0.5 and 50 seconds. For comparison, the O_3 concentrations used in these experiments correspond to a lifetime of isoprene of approximately 3.6 min. The OH concentration in the OFR was adjusted by changing the power of the UV lamps as described in Lambe et al. (2011a). For the experiments in this study, the lamp power was always full; therefore, the OH concentration in this study should have been close to 2×10^{10} molec cm^{-3}, and the OH pathway should have dominated the oxidation of isoprene."

Related to this, the authors should probably mention in this section that the high concentrations used in the oxidation flow reactor results in an unrealistically high contribution of the RO2+RO2 reaction products and Criegee intermediate reaction products to the SOA formation. The authors do mention the caveat to the conclusions resulting from high mass concentrations on page 1147; all I am suggesting is to explain it to the readers what could go wrong when using high concentrations.

- ➔ We have now added the following text in Sect. 2.1.

> “The concentration of the major oxidants (O_3, OH, and HO_2) in the OFR is higher than in environmental chambers or the atmosphere, but the ratios of O_3 to OH and OH to HO_2 are similar to those encountered in the atmosphere and in environmental chambers. As a result, the OFR is used to simulate oxidation processes in the atmosphere and environmental chambers. Recent measurements with an aerosol mass spectrometer have shown that the composition of isoprene-derived SOM produced with an OFR is the same, within the uncertainty of the measurements, as isoprene-derived SOM produced with an environmental chamber (Lambe et al., 2015).”

Section 4.2: It may be worth mentioning the study of O’Brien et al. (2014), who looked at how much different types of particles flatten upon impact with an impactor substrate [2]. Their measurements suggest that laboratory models of isoprene derived particles are less viscous than those of alpha-pinene derived particles, and less viscous still than ambient aerosols.

- ➔ We have now mentioned the study of O’Brien et al. in Sect. 4.2 of the revised manuscript as suggested by the referee.
  “This conclusion is consistent with work by O’Brien et al. (2014) who also concluded that the viscosity of isoprene-derived particles is lower than the viscosity of α-pinene-derived particles based on the how much the particles flattened after impaction on a substrate.”

M. Shiraiwa (Referee)

In this study the authors have determined relative humidity-dependent viscosities of isoprene SOA. Viscosity is a key property of SOA, but measurements of viscosity of SOA materials are not easy and there have been only a few measurements for a-pinene SOA. The authors achieved the viscosity measurements of isoprene SOA successfully by combining two unique experimental approaches of a bead-mobility technique and a poke-flow technique. Based on RH-range observed in Amazon, they concluded that SOA particles in Amazon are liquid. I found that the study was conducted well and the manuscript is written clearly. I support publication in ACP and I have three specific comments that the authors should consider.

We thank M. Shiraiwa for the helpful comments and suggestions. Below are detailed answers to the reviewer comments with the locations of the incorporated changes in the revised manuscript.

Specific comments:

1. Please justify/discuss how well OFR-generated SOA particles represent ambient SOA. What was O:C ratio of isoprene SOA? Is chemical composition of OFR-generated isoprene SOA expected to be similar to that generated in a larger reaction chamber or in ambient conditions? How long was the reaction time in an OFR and how does exposure (time * concentration) correspond to atmospheric aging time?

- ➔ We have now discussed in detail these points in Sect. 2.1 of the revised manuscript.

> “Although the OH concentration was not measured in the OFR in this study, an OH concentration in the OFR in the range of 2×10^8 to 2×10^{10} molec cm^{-3} was expected based on previous experiments under similar conditions (Lambe et al., 2011a). This OH concentration corresponds to a lifetime of isoprene between 0.5 and 50 seconds. For comparison, the O_3 concentrations used in these experiments correspond to a lifetime of isoprene of approximately 3.6 min. The OH concentration in the OFR was adjusted by changing the power of the UV lamps as described in Lambe et al. (2011a). For the experiments in this study, the lamp power was always full; therefore, the OH concentration in this study should have been close to 2×10^{10} molec cm^{-3}, and the OH pathway should have dominated the oxidation of isoprene.
>
> Based on the flow tube residence times and the expected OH concentrations, OH exposures were expected to be in the range of 2.0×10^{10} to 1.8×10^{12} molec cm^{-3}. If one assumes an average atmospheric OH concentration of 1.5×10^6 molec cm^{-3}, this range of exposures is equivalent to ~0.15 to ~15 days of atmospheric oxidation by OH (Lambe et al., 2011a).
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> The concentration of the major oxidants (O_3, OH, and HO_2) in the OFR is higher than in environmental chambers or the atmosphere, but the ratios of O_3 to OH and OH to HO_2 are similar to those encountered in the atmosphere and in environmental chambers. As a result, the OFR is used to simulate oxidation processes in the atmosphere and environmental chambers. Recent measurements with an aerosol mass spectrometer have shown that the composition of isoprene-derived SOM produced with an OFR is the same, within the uncertainty of the measurements, as isoprene-derived SOM produced with an environmental chamber (Lambe et al., 2015).
>
> In the current study, the O:C ratio of the isoprene-derived SOM was not measured. However, in previous studies using the Harvard OFR, an O:C value of 0.82 for isoprene-derived SOM was measured using lower concentrations of isoprene (700 ppb). In these previous studies the O:C was calculated using the explicit approach described by Chen et al. (2011). In addition, the average O:C values of isoprene-derived SOM was found to be 0.64 to 0.79 by Chhabra et al. (2010) and 0.75 to 0.88 by Chen et al. (2011) in environmental chamber studies and 0.64 to 1.1 by Lambe et al. (2011b; 2015) in explicit studies using a similar OFR. The O:C values reported here for Chhabra et al. (2010) and Lambe et al. (2011b) have been scaled up by a factor of 1.27 as suggested by Canagaratna et al. (2015). Based on this information, we estimate that the O:C of isoprene-derived SOM in the current experiments was in the range of 0.64 to 1.1.”

2. In the section 4.2, discussion on glass transition temperature (Tg) of isoprene and a-pinene SOA would be helpful. Tg of isoprene is predicted to be lower than the room temperature at low O:C ratio, and it tends to become higher at high O:C ratio (see Table A1, Berkemeier et al., 2014). Higher Tg indicates higher viscosity. As discussed in the text, molecular weight may be indeed primarily important for viscosity and Tg, but O:C ratio does affect them, too (Koop et al., 2011;

Saukko et al., 2012). In this sense, it would be great if you could specify O:C ratio of isoprene SOA, if possible, and discuss on Tg.

➔ The reviewer raises a good point. To address this comment we have added the following text to Sect. 4.2.
“The O:C ratio is also expected to affect the viscosity of the SOM, with higher O:C values leading to higher viscosities and glass transition temperatures (Koop et al., 2011; Berkemeier et al., 2014). However, O:C alone is unlikely to explain the difference in viscosity between isoprene-derived SOM and α-pinene-derived SOM since the O:C of isoprene-derived SOM in our experiments is expected to be between 0.64 and 1.1 (see Sect. 2.1) while the O:C of SOM from the ozonolysis of α-pinene is typically in the range of 0.3 to 0.5 (Chen et al., 2011).”

3. The phase state and viscosity are strongly affected not only by relative humidity but also by temperature. If the authors would like to make general conclusion on the phase state of Amazonian SOA, it would be better if some statistics were presented for temperature to make sure that the ambient temperature is usually higher than the predicted Tg of Amazonian SOA (see Fig. 9d, Koop et al., 2011).

➔ To address the referee’s comment we have included a discussion on the temperature range in the Amazon. Specifically we have added the following to Sect. 5:
“The second piece of information needed to assess τ_{mixing} for SOM is temperature. For the eight ground-based stations shown in Fig. 9, for both the wet and dry seasons, the median temperature was 300 K and the 10th and 90th percentiles were 297 K and 303 K, respectively. These temperatures are above the estimated glass transition of a generic SOM (Koop et al., 2011). The viscosities shown in Fig. 8a were determined using a temperature of 295 ± 1 K, which is at the lower end of the temperature range for the Amazon. As temperature increases the viscosity is expected to decrease for the same composition of water and SOM”

B. Wang
Bingbing Wang
Environmental Molecular Sciences Laboratory,
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There are a limited number of studies investigating the viscosity of secondary organic materials (SOM) and their RH and temperature dependence. This paper by Song et al. presents a nice work on the viscosity of isoprene-derived secondary organic materials as a function of RH at 295 K. In Section 4.2 and Figure 8, the authors also discussed and compared the viscosity of isoprene SOM to alpha-pinene SOM from previous studies.
Through this comment, I would like to draw the attention to our recent work reporting a method to derive and estimate the viscosity of SOM as a function of atmospheric relevant temperature and RH (Wang et al., JPCA 2014). In that study, we applied a set of parameters to derive the viscosity

of alpha-pinene SOM and the esitimated viscosity are consistent with the experimental determined values by Renbaum-Wolff et al. (2013).

We thank Bingbing Wang for the suggestions. We have included the viscosity results for α-pinene SOM shown in Wang et al. 2014 in the revised manuscript.