

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

M. Shiraiwa (Referee) (Reviewer comments in black text)

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 α -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).

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 (T_g) of isoprene and α -pinene SOA would be helpful. T_g 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 T_g indicates higher viscosity. As discussed in the text, molecular weight may be indeed primarily important for viscosity and T_g , 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 T_g .

→ 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 T_g 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”