

Interactive comment on “Relative humidity-dependent viscosity of secondary organic material from toluene photo-oxidation and possible implications for organic particulate matter over megacities” by M. Song et al.

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Received and published: 7 May 2016

The authors have measured relative humidity-dependent viscosity of toluene SOA after a series of publications on viscosity measurements of α -pinene and isoprene SOA. This group is currently one of the only groups that can achieve such challenging measurements by combining two different unique experimental methods of a bead-mobility technique and a poke-flow technique. Based on viscosity measurements and RH observations in major urban cities in the world, they estimated whether anthropogenic SOA particles in these cities would be well-mixed or not. The experiments seem to

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be conducted well and the manuscript is written clearly, but some analysis/discussions should be deepened/expanded as below. I have several major comments that should be addressed and implemented in the revised manuscript before publication in ACP.

Major comments:

[1] Toluene is assumed to be a good proxy of anthropogenic precursors (P10, L28, without references). While this assumption might be fine, more justifications would be necessary: emission and ambient concentrations of toluene and other anthropogenic precursors are missing and not discussed sufficiently. Thus, general conclusion of phase state of OA in megacities (last sentence of abstract) sounds not convincing to me. The authors could look into emission inventories to check whether toluene is indeed a major precursor in selected major cities. Alkane, alkene and other aromatic compounds may be also important anthropogenic precursors and SOA generated by these precursors may have different viscosities. For example, a recent study showed that dodecane SOA may be less viscous and naphthalene SOA may be more viscous, compared to pinene and isoprene SOA (Berkemeier et al., ACP, 14, 12513, 2014). Please expand discussions on this issue.

[A1] To address the referee's comment, we have modified the first paragraph in section 5. The modified paragraph is reproduced below: "Several caveats should be kept in mind when applying the mixing times discussed earlier to particles over megacities. First, organic particulate matter over megacities are most likely more complicated than toluene-derived SOM. Toluene and other aromatics can account for a large fraction of nonmethane hydrocarbon emission in urban environments (Singh et al., 1985; Na et al., 2005; Suthawaree et al., 2012) and toluene and aromatics are thought to be one of the main sources of SOM particles in urban environments (Odum et al., 1997; Schauer et al., 2002a; 2002b; Vutukuru et al., 2006; Velasco et al., 2007; de Gouw et al., 2008; Velasco et al., 2009; Gentner et al., 2012; Liu et al., 2012; Hayes et al., 2015). Nevertheless, large alkanes and unspciated nonmethane organic gases also likely play a role in SOM formation in urban environments. Second, the toluene-derived SOM was

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generated using relatively large mass concentrations of particles (60 – 1000 $\mu\text{g m}^{-3}$). The good agreement between our results and the results from Bateman et al. (2015) and Li et al. (2015), which were carried out with a mass concentration of 30 – 1000 $\mu\text{g m}^{-3}$, suggests that for toluene-derived SOM the viscosity is not strongly dependent on the mass concentration of organics used to generate the SOM, but additional studies are needed to confirm this. Third, as mentioned above, the Stokes-Einstein equation was used to estimate diffusion coefficients and hence mixing times, and this equation can underestimate diffusion coefficients close to the glass transition temperature. Due to these caveats, the analysis below should be considered as a starting point for understanding the mixing times of large organic molecules in organic particulate matter over megacities. Additional studies are needed to explore the implications of the caveats discussed above.”

[2] Moreover, as the authors also mentioned in P12, L15-20, I think that the temperature effect on viscosity is so important and probably as large as the RH effect (e.g., Koop et al., PCCP, 2011) that it is not easy to draw general conclusions of anthropogenic SOA phase state by measurements of toluene SOA only at room temperature. As shown in Fig. 6, most cities (except tropics) have lower temperatures than 20 °C in winter.

[A2] Here the referee is raising the issue of temperature effect on viscosity of aerosol particles. To address the referee's comments in the revised manuscript we have limited the analysis to months when the median afternoon temperature is within 5 K of the temperatures used in the viscosity measurements (i.e. 290 to 300 K). The following text has also been added to the manuscript: “In addition to relative humidity, viscosity can depend strongly on temperature (Champion et al., 1997; Koop et al., 2011). For example, the viscosity of solutions of sucrose and water may increase by two to three orders of magnitude for a 10 K decrease in temperature close to the glass transition temperature (Champion et al., 1997). However, the effect of temperature on the viscosity of toluene-derived SOM has not been quantified. As a result, we have limited the current analysis to months when the median afternoon temperature is within 5 K

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of the temperatures used in the viscosity measurements (i.e. 290 to 300 K). The fact that the median afternoon temperature is often below 290 K, highlights the need for low-temperature viscosity measurements.”

[3] As pointed out in the text, organic aerosols are likely to be internally mixed with inorganics such as sulfate and nitrate (P11, L2). This and also other groups have shown by experimental and modeling studies that a liquid-liquid phase separation is expected if an O:C ratio of an organic-rich phase is low, whereas a mixed one phase may be likely for high O:C. Have you measured an O:C ratio of toluene SOA? Fig. 7 in Lambe et al. AMT, 4, 445, 2011 showed that O:C ratio of OFR-generated toluene SOA can be as high as 1.0. This issue should be discussed.

[A3] To address the referee’s comments the following text has been added to the revised manuscript: “Mass concentrations of SOM particles in the OFR were 60-100 $\mu\text{g m}^{-3}$ and 600-1000 $\mu\text{g m}^{-3}$ for the two different experimental conditions (see Table 1). For the mass concentration of 60-100 $\mu\text{g m}^{-3}$, the oxygen-to-carbon (O:C) ratio was 1.08, calculated from the AMS mass spectra following the approach of Chen et al. (2011). This value can be compared with the O:C values ranged from 0.9 to 1.3 measured for toluene-derived SOM generated in a similar OFR (Lambe et al., 2015).”

[4] What was RH in an OFR chamber during SOA formation? Was it all at the same RH? A recent study has shown that as the RH at which the α -pinene SOA is formed increases, there is a decrease in viscosity, and SOA that is formed dry and subsequently humidified remains solid to high RH (Kidd et al., PNAS, 111, 7552, 2014). This potential RH effect needs to be discussed.

[A4] To address the referee’s comment, the following text has been added to Section 2.1 of the revised manuscript.

“The relative humidity inside the reactor was held constant at 13 +- 3 %. A recent study has shown that the viscosity of α -pinene-derived SOM is dependent on the RH at which the SOM is generated (Kidd et al., 2014). Additional studies are needed to explore this

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potential RH effect on the viscosity of toluene-derived SOM.”

[5] Water acts as plasticizer and plays a key role in determination of phase state. It would be interesting to plot viscosity against water mass fraction in SOA, which can be estimated using a hygroscopicity parameter kappa (e.g., Lambe et al., AMT, 4, 445, 2011; Hildebrandt Ruiz et al., ACP, 15, 8301, 2015).

[A5] Thank you for the suggestion. To address the referee’s comment we have added V_{wet}/V_{dry} as a secondary x-axis to Fig. 5, where V_{dry} is the volume of SOM at 0% RH and V_{wet} is the volume of the SOM after taking up water at a given RH. In addition the text below has been added to the manuscript:

“The strong dependence of viscosity on RH shown in Fig. 5 can be understood by considering the hygroscopic nature of the SOM. To illustrate this point in Fig. 5 viscosity is also plotted versus V_{wet}/V_{dry} of the SOM (secondary x-axis), where V_{dry} is the volume of SOM at 0% RH and V_{wet} is the volume of the SOM after taking up water at a given RH. V_{wet}/V_{dry} was calculated with the following equation (Petters and Kreidenweis, 2008; Pajunoja et al., 2015):

$$V_{wet}/V_{dry} = \kappa / (100/RH - 1) + 1 \quad (\text{Eq. 1})$$

where κ is the hygroscopic parameter. A hygroscopic parameter of 0.15 was assumed, consistent with previous measurements for toluene-derived SOM (Ruiz et al., 2015). Equation (1) neglects the Kelvin effect, which is a reasonable assumption for the large particles used in our studies. Fig. 5 illustrates that the water content (top x-axis) of the particles plays a key role in regulating the viscosity. ”

Minor comments:

[6] P3, L11: The model used in Riipinen et al., 2011 did not treat bulk diffusion and they have rather emphasized an importance of gas diffusion and condensation. Thus, this reference seems not to be appropriate here. Instead, the authors could cite Shiraiwa et al., PNAS, 110, 11746, 2013.

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[A6] We have now corrected the reference.

[7] P4, L16: Loza et al., EST, 47, 6173, 2013 conducted also very similar experiments that may be worth included.

[A7] The paper has been added.

[8] P10, L7, L10: "However" is used twice in a row. Please refine.

[A8] It has been revised.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-14, 2016.

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