[A0] 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]***). Page and line numbers refer to online ACPD version.

Reviewer 1

This short paper describes a nice addition to the literature on the viscosity of a-pinene particles. It follows and extends the groups previously reported poke-and-flow technique. Several significant conclusions are reached that highlight the importance of relative humidity and SOA production conditions. The paper is well written, of appropriate length and easy to read. I recommend publication once the following comments and questions have been addressed satisfactorily.

We thank the referee for their helpful comments

Major comments

[1] **The first line of the abstract is too strong. Aerosol viscosity is not currently used in predictions of the impact of SOA on climate, visibility and health. Potentially it could be in the future but it is not obvious what benefits it will bring.**

[A1] The sentence "To predict the role of secondary organic material (SOM) particles in climate, visibility, and health, information on the viscosity of particles containing SOM is required." has been altered to "Knowledge of the viscosity of particles containing secondary organic material (SOM) is useful for predicting reaction rates and diffusion rates in SOM particles.

[2] **The laboratory conditions need to be related to atmospheric conditions. How does the range of SOA mass concentrations used compare to atmospheric concentrations? What does this suggest the viscosity of atmospheric a-pinene will be? A similar discussion should be provided for the O3 concentrations used.**

[A2] The SOM mass concentrations used when producing the SOM in the experiments are higher than in the atmosphere. Given the relationship observed between viscosity and production concentration of SOM in this paper the vis-

cosity results are likely a lower limit to the viscosity of α-pinene derived SOM in the atmosphere. To incorporate this into the manuscript P32983 L2-5 has been edited from ”Finally, the studies here are carried out at production mass concentrations greater than those found under ambient conditions (Hallquist et al., 2009; Slowik et al., 2010), and studies carried out using material produced under ambient conditions would provide further useful information.” to read ”Finally, the studies here are carried out at production mass concentrations greater than those found under ambient conditions (Hallquist et al., 2009; Slowik et al., 2010). Studies carried out using material produced under ambient conditions would provide further useful information. The inverse relationship between viscosity and production mass concentration suggests the results determined here likely represent a lower limit of viscosity for SOM produced by the ozonolysis of α-pinene in the atmosphere.”, and the sentence ”These studies were carried out at production mass concentrations greater than those found under ambient conditions. The inverse relationship between viscosity and production mass concentration suggests the results determined here likely represent a lower limit of viscosity for SOM produced by the ozonolysis of α-pinene in the atmosphere.” has been added to the conclusions at P32985 L20.

In the flow tube the O_3 concentration was 12 ppm and the reaction time was 38 s, giving an O_3 exposure (O_3 concentration x time) of 456 ppm s. In the chamber the O_3 concentration was 64-72 ppb and the reaction time was 4800 s, giving an O_3 exposure (O_3 concentration x time) of 300-350 ppm s. For comparison purposes the background concentration of O_3 in the atmosphere is 30 ppb, and assuming a reaction time of one hour an exposure of 110 ppm s is calculated (30 ppb x 3600 s).

To incorporate this into the manuscript, the text at P32973 L11 has been edited from ”Residence time in the flow tube was 38 ± 1 s” to ”Residence time in the flow tube was 38 ± 1 s, giving an O_3 exposure (O_3 concentration x time) of 456 ppm s. For comparison purposes the background concentration of O_3 in the atmosphere is 30 ppb, and assuming a reaction time of one hour an exposure of 110 ppm s is calculated.”. Additionally, the text at P32974 L19 has been edited from ”After 80 minutes of reaction, the...” to ”After 80 minutes of reaction, giving an O_3 exposure of 300-350 ppm s, the...”.

***[3]* Another recent study, Hosny et al. 2015, investigated the differences between water soluble fractions and whole SOM samples.**

The results between the two studies should be contrasted.

[A3] We agree, a paragraph discussing the results of Hosny et al. is now included following P32984 L29, reading "Hosny et al. (2016) recently studied the viscosity of SOM generated from the ozonolysis of myrcene and observed a difference in viscosity between the water soluble fraction and the whole SOM samples. In their case similar viscosities were observed at the lowest RH values studied (<40 %) but the whole SOM samples had a higher viscosity than the water soluble fraction at the highest RH values studied (>70 %). The reason for the difference between the results here and those of Hosny et al. is not clear."

[4] **What is the effect of different particle sizes on the experimental flow time? The particles studied were in the size range of the 50-70 microns, the corresponding changes in particle surface area and volume will be larger. Should the experimental flow time scale with diameter, surface area, or volume? Or is it size independent? If it is dependent on size has a correction been applied to the reported experimental flow time to account for the different sized particles?**

[A4] In cases where a half torus geometry was formed after poking, $\tau_{exp,flow}$ is expected to be (somewhat) proportional to R^2/r based on simulations, where R and r are defined as per Figure 2a in Grayson et al. (2015) and reproduced following this paragraph. The reported experimental flow times are the raw data (i.e., no corrections have been applied to take account of particle dimensions). When determining viscosities via simulations the measured dimensions of each particle were used. The sentence "Though the value of $\tau_{exp,flow}$ is also dependent on physical properties other than viscosity, such as particle size, the values reported here are the raw values (i.e., no corrections have been applied to take account of particle dimensions)." has been added on P 32976, L2 to clarify this.

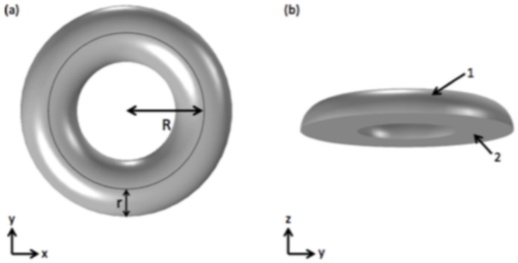

Figure 2. Details of half-torus model used to simulate the flow in experiments: **(a)** top view, where *R* and *r* are the notations used here to describe the dimensions of a half-torus geometry; **(b)** side view, where surface 1 represents the air–fluid interface, and surface 2 represents the fluid–substrate interface.

Minor comments

P32970 L16 - insert "many of" into position # in "Despite the importance of SOM particles, # their physical properties..."

This has been amended

P32972 L8 - understanding the effect of RH on viscosity. Its not obvious how the RH is affecting the viscosity. Is the water acting as a gas phase reactant? Maybe reacting with Criegee intermediates? Or is acting in the particle phase affecting the ageing of the particles? Previous work has shown that RH can have a significant effect on particle phase processing e.g. Gallimore et al. (2011). Here the water can act as both a reactant and phase modifier. A small discussion should be included.

The experiments here were all performed using SOM produced under dry conditions. As such, the experiments do not consider or explore the change in SOM properties as a function of RH at which the SOM is produced, which can lead to a difference in the properties of SOM (per, e.g., Kidd et al., 2014). The text "in the first set of experiments, we investigated the effect of relative humidity on the viscosity of the whole SOM. SOM was generated via the ozonolysis of α-pinene. Reported here are viscosity measurements as a function of RH between" on P32972 L1-3 has been edited to "In the first set of experiments, we investigated the viscosity of the whole SOM as a function of relative humidity at which the viscosity was measured. In all cases the SOM was generated via the ozonolysis of α-pinene under dry conditions, and hence the effect of relative humidity on the SOM chemistry was not explored.

Reported here are viscosity measurements at RH values between" to clarify that the focus of the experiments here is not on the RH at which the SOM is produced.

P32975 L24 - Fig 4 not Fig 3

This has been amended.

P32976 L9 - how long were the particles re-equilibrated with the flow cell temperature after coming out of the freezer? Was the time sufficient to ensure that the particle was at equilibrium?

The sentence "Each sample of particles on a substrate was allowed to equilibrate in the flow cell for 30 minutes prior to poke-and-flow experiments to ensure the particles reached thermal equilibrium with their surroundings after removal from storage at 253 K." has been added after P32975 L16 to clarify.

P32976 L15 - a one point calibration for relative humidity seems risky? Provide more details.

A one point calibration was performed at an RH close to the RHs used in these studies. The sensor was observed to have an offset of <0.1 °C, which was within the accuracy range suggested by the manufacturer (± 0.2 °C for dewpoints/frostpoints from -35 to +25 °C, or RH values ranging from 1.5 to 100 %). Based on this information, we assumed the manufacturers stated accuracy was valid for the entire RH range studied here.

P32976 L21 - oligomerization what would be the mechanism for this under a non-oxidising atmosphere?

The mechanism could potentially be condensation. The text ", such as condensation (e.g. Reinhardt et al., 2007), " has been added between "polymerisation" and "could" on P32976 L21 to address this point.

P32981 L20 - "are not inconsistent" change to "consistent" if it is.

The text "shows that most of these previous studies (Cappa and Wilson, 2011; Perraud, 2012; Saleh, 2013) are not inconsistent with those presented here" has been amended to "shows the viscosities measured or inferred from these prior studies (Cappa and Wilson, 2011; Perraud, 2012; Saleh, 2013) overlap with those measured here" to clarify.

Reviewer 2

The paper presents very interesting results on how the viscosity of complex aerosol produced from a given precursor is likely to depend on total mass loadings. This fits in well with other chamber studies that suggest approaching atmospheric loadings is important to embed relevant compositional dependent properties. There are many methods now presenting work to infer or directly measure viscosity. The poke flow technique offers a nice angle to those systems for which inferring diffusion from shrinkage might be prone to errors introduced from phase separation/solubility considerations. I found the paper very well written. In fact, raising points for discussion is relatively hard as the authors are careful in inferring potential for solid conclusions and artefacts from experimental conditions. The paper should be published in ACP. My points below are aimed at continuing the interesting discussions raised and would value the response of the authors to clarify a few issues.

We thank the referee for their helpful comments.

[1] **Section 2.1 2.2: This is likely covered in previous publications, so apologies in advance, but how much confidence is there that the method does not force a given face state by virtue of impaction of the suspended droplets, ignoring any semi-volatile loss? I guess Im asking if there is any evidence that a meta stable liquid state in a suspension, left for long enough on an impacted filter, would change phase state by virtue of impaction? Atomising droplets from mixtures for which inferred viscosity is different between suspension and bulk methods would easily test this.**

[A1] Good question. Something like this could potentially occur for particles such as sucrose-water. When sucrose-water droplets are suspended, they can be metastable with respect to crystalline sucrose. Impaction upon a surface may induce nucleation followed by crystal growth. It seems unlikely that a process like this could happen for SOM particles since the concentration of any one organic in the SOM is unlikely to get high enough to crystallize (Marcolli et al., J. Phys Chem. A, 2004). In fact, we have not seen any evidence for the crystallisation of SOM in our experiments.

[2] **Would it be possible to pass your collected samples through**

a differential scanning calorimeter (DSC) perhaps to infer any expected phase change with temperature rate dependency?

[A2] Quite possibly for the samples collected using the higher production concentrations. For example the material collected from the flow tube at a SOM production concentration of 14,000 g m-3 produced 5x10-2 mg of SOM in approximately 20 minutes. Since DSC can be performed on samples as small as 0.5 mg, simply increasing the collection time would make this possible.

***[3a]* Section 2.3 One angle to add to this, that is interesting and you discuss in page 32976 (section 2.3) and throughout, is also the prospect of losing any semi-volatile material during collection. The idea you discuss is that if we can very roughly associate an increased plasticiser effect with increased volatility of compound (take water as an example), there also a chance that loss of that material from collected particles over 4 days, for example, might alter results. Your viscosity increase from very high to high mass loadings would suggest that the impact of plasticisers would be expected to roughly correlate with viscosity. The same might be true for techniques including bounce measurements where vigorous drying of the particle could perhaps force loss of key semi-volatile species. With typical mixing rules used to correlate composition change to diffusion coefficients, one might expect a relatively small amount of plasticiser loss to have a larger subsequent effect on viscosity. As before, have you characterised systems for which a range of volatilities, and viscosities, are known in pre-defined mixtures?**

[A3a] We have not characterized systems for which a range of volatilities and viscosities are known in pre-defined mixtures, although this would indeed be interesting.

We cannot rule out the loss of some volatile components during humidification in our experiments. The sentence ”The loss of some volatile components during humidification prior to collection cannot be ruled out. Loss of volatile components in the impactor should be relatively minor since the impactor used for collection has a small pressure drop (20 % or less).” has been added at P 32973 L 25 and the sentence ”As for before, the loss of some volatile components during humidification prior to collection cannot be ruled out, whilst the loss of volatile components in the impactor are expected to be relatively minor." added at P 32974 L26 to acknowledge this.

[3b] **In this paper you study this potential from a system with a mass concentration of 6000 micrograms. This is still high for atmospheric systems and it isnt clear to me whether the chemical mechanisms present under such conditions are impacting on the expected physical properties. Of course, one could argue that at lower mass loadings, say <100 micrograms, the volatility and products required to maintain mass loadings might have higher viscosities (non liquid perhaps), but it would still be interesting to confirm this.**

[A3b] Unfortunately we are currently not setup to investigate how the chemical mechanism could change with the mass concentration used to produce the secondary organic material. However, we hope that our response to Question 2 from Referee #1 at least partially addresses Question 3b from Referee #2.

[4] **How does the potential presence of non Newtonian fluids affect any inferred viscosity from your simulations? Would a variable poke rate infer this? I guess for atmospheric systems, we only really need to know the magnitude scale for viscosity but it is interesting nonetheless.**

[A4] Previous work has suggested that sucrose-water (Hosny et al., 2013, Saggin and Coupland, 2004) solutions are Newtonian fluids. As sucrose-water solutions have been used as proxies for SOM, we have assumed SOM to be a Newtonian fluid. The sentence "Based on prior observations of Newtonian behaviour in sucrose-water solutions, which are commonly used as proxies for SOM, the SOM was assumed to be Newtonian in nature during simulations." Has been added on P32977 L15.

A variable "poke rate" is a very interesting ideal, but at this point we dont have the capability to vary this rate. Definitely something to think about for the future!

[5] **On page 32976 you state that This result suggests it is possible that a small volume of semi-volatile material may have evaporated during the exposure to dry nitrogen, below the detection**

limit of the measurements of particle volume, but enough to result in a small increase in viscosity. One might expect this. Taking water as an example, the mixing rules used to predict changing diffusion coefficients with changing composition suggest a relatively small amount of water is needed to significantly alter equilibration timescales. Have you modeled this effect from your measurements assuming a simple mixing rule and loss of a range of semi-volatiles?

[A5] Based on the referees suggestions we have gone back and modelled this effect from measurements using the simple mixing rule suggested by Arrhenius. The following text has been added to Section S1 in the supplemental, as has Table S2.

"We estimate the maximum expected increase in viscosity of the SOM during exposure to a dry N_2 gas flow by assuming we have a two component system and using the equation for mixtures suggested by Arrhenius,

$\mathrm{Ln}(\eta_{mix}) = \chi_a \ln(\eta_a) + \chi_b \ln(\eta_b)$

, where a and b are the two components, χ represents the mole fraction of each component in the mixture (mix), and η represents viscosity. To take an extreme case, we assumed at a time of 1 hour (the start of the experiment) the first component, a, is non-volatile and the second component, b, is volatile and of viscosity similar to that of water (1e-3 Pa s). We assume at 45 hours (the end of the experiment) all of component b has evaporated, and therefore $\chi_a = 1$ and $\chi_b = 0$. We also assume that at 1 hour, $\chi_b \leq$0.065 (which is the maximum possible value of χ_b based on the uncertainty in the optical images and assuming component b had completely evaporated after 45 hours), making $\chi_a \geq$0.935 (1 - 0.065).

At a time of 1 hour, the measured viscosity (η_{mix}) was 6.4e5 Pa s, and hence based on the Arrhenius mixing rule (equation S1, above) and the assumptions above, $\eta_a \leq$2.6e6 Pa s. Assuming $\chi_a = 1$ after 45 hours produces an upper limit for η_{mix} after 45 hours of 2.6e6 Pa s, consistent with the viscosity measured (1.0e6 Pa s). Hence the evaporation of a semi-volatile component combined with the Arrhenius mixing rule during the 44 hours of exposure is consistent with the small increase in viscosity observed in the experiments. The values of η and χ discussed in this paragraph are summarised in Table S2."

Table S2: Values used during the calculations of viscosity in SOM using the Arrhenius equation.

	η_{mix} / Pa s	χ_a	η_a / Pa s	χ_b	η_b / Pa s
After 1 hour	6.4 x 10^5 (measured)	$\geq$0.935 (calculated)	$\leq$2.6 x 10^6 (calculated)	$\leq$0.065 (calculated)	1.0 x 10^{-3} (assumed)
After 45 hours	1.0 x 10^6 (measured)	1.000 (assumed)	$\leq$2.6 x 10^6 (calculated)	0.000 (assumed)	N/A

Additionally, the passage "This result suggests it is possible that a small volume of semi-volatile material may have evaporated during the exposure to dry nitrogen, below the detection limit of the measurements of particle volume, but enough to result in a small increase in viscosity." on P32976 L16 of the main text has been edited to read "In the Supplement (Section S1 and Table S2) we also show, using the Arrhenius mixing rule, that this small increase in viscosity could be due to evaporation of a small amount of semi-volatile material during the exposure to dry nitrogen, with the volume of evaporated material being below the detection limit of the measurements of particle volume, but enough to result in a small increase in viscosity.".

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