

Thomas Koop
Editor of Atmospheric Chemistry and Physics
Bielefeld University, Faculty of Chemistry

Dear Thomas,

5 Listed below are our responses to the comments from reviewers 1 and 2. For clarity
and visual distinction, the referee comments are listed here in **black, bold, type, and are**
preceded by bracketed, italicised, numbers (e.g. [1]). Authors' responses are in red type
below each referee statement with matching italicised numbers (e.g. [A1]). Page and line
10 numbers refer to the online ACPD version of the manuscript. We thank the referees for
carefully reading our manuscript and for the excellent comments.

Allan Bertram
Professor of Chemistry
University of British Columbia

Reviewer 1

This short paper describes a nice addition to the literature on the viscosity of α -pinene particles. It follows and extends the group's 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 α -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 viscosity 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 (Hal-

lquist 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.

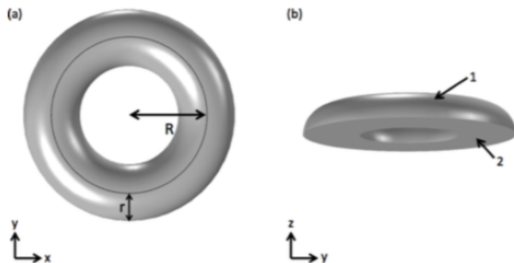


Figure 2. Details of half-torus model used to simulate the flow in experiments: (a) top view, where R and r are the notations used here to describe the dimensions of a half-torus geometry; (b) side view, where surface 1 represents the air–fluid interface, and surface 2 represents the fluid–substrate 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. It's 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 manufacturer's 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 I'm 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 isn't 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 don't 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 N₂ gas flow by assuming we have a two component system and using the equation for mixtures suggested by Arrhenius,

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

, 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 6.4×10^5 Pa s, and hence based on the Arrhenius mixing rule (equation S1, above) and the assumptions above, $\eta_a \leq 2.6 \times 10^6$ Pa s. Assuming $\chi_a = 1$ after 45 hours produces an upper limit for η_{mix} after 45 hours of 2.6×10^6 Pa s, consistent with the viscosity measured (1.0×10^6 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.

	$\eta_{mix} / \text{Pa s}$	χ_a	$\eta_a / \text{Pa s}$	χ_b	$\eta_b / \text{Pa s}$
After 1 hour	6.4×10^5 (measured)	≥ 0.935 (calculated)	$\leq 2.6 \times 10^6$ (calculated)	≤ 0.065 (calculated)	1.0×10^{-3} (assumed)
After 45 hours	1.0×10^6 (measured)	1.000 (assumed)	$\leq 2.6 \times 10^6$ (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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Effect of varying experimental conditions on the viscosity of α -pinene derived secondary organic material

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Abstract

Knowledge of the viscosity of particles containing secondary organic material (SOM) is useful for predicting reaction rates and diffusion in SOM particles. In this study we investigate the viscosity of SOM particles as a function of relative humidity and SOM particle mass concentration, during SOM synthesis. The SOM was generated via the ozonolysis of α -pinene at <5 % relative humidity (RH). Experiments were carried out using the poke-and-flow technique, which measures the experimental flow time ($\tau_{exp,flow}$) of SOM after poking the material with a needle. In the first set of experiments, we show that $\tau_{exp,flow}$ increased by a factor of 3,600 as the RH increased from <0.5 % RH to 50 % RH, for SOM with a production mass concentration of $121 \mu\text{g m}^{-3}$. Based on simulations, the viscosities of the particles were between 6×10^5 and 5×10^7 Pa s at <0.5 % RH and between 3×10^2 and 9×10^3 Pa s at 50 % RH. In the second set of experiments we show that under dry conditions $\tau_{exp,flow}$ decreased by a factor of 45 as the production mass concentration increased from $121 \mu\text{g m}^{-3}$ to $14,000 \mu\text{g m}^{-3}$. From simulations of the poke-and-flow experiments, the viscosity of SOM with a production mass concentration of $14,000 \mu\text{g m}^{-3}$ was determined to be between 4×10^4 and 1.5×10^6 Pa s compared to between 6×10^5 and 5×10^7 Pa s for SOM with a production mass concentration of $121 \mu\text{g m}^{-3}$. The results can be rationalised by a dependence of the chemical composition of SOM on production conditions. These results emphasise the shifting characteristics of SOM, not just with RH and precursor type, but also with the production conditions, and suggest that production mass concentration and the RH at which the viscosity was determined should be considered both when comparing laboratory results and when extrapolating these results to the atmosphere.

1 Introduction

Aerosol particles are ubiquitous in the Earth's lower atmosphere, of which a major source is the oxidation of volatile organic compounds (VOCs) (Andreae and Crutzen, 1997). VOCs are emitted from the Earth's surface by both human and natural sources and, once in the

atmosphere, are readily oxidised to form secondary organic material (SOM) that can condense to the particle phase (Hallquist et al., 2009). Aqueous-phase reactions also provide an important pathway to the production of SOM (Ervens et al., 2011).

Atmospheric particles containing SOM play an important role in governing the Earth's energy budget, both directly via the scattering or absorption of solar radiation (Yu et al., 2006) and indirectly by acting as cloud condensation nuclei (Solomon et al., 2007) and possibly as ice nuclei (Berkemeier et al., 2014; Choularton et al., 2007; Knopf and Rigg, 2011; Ladino et al., 2014; Wang et al., 2012b; Murray et al., 2010; Schill et al., 2014). SOM particles may also play a role in human health (Baltensperger et al., 2008) and the chemistry of the atmosphere by providing solid or liquid phases for reactions (Hallquist et al., 2009). Despite the importance of SOM particles, many of their physical properties, such as viscosity, are poorly understood.

The viscosity of SOM is important for a number of reasons. First, the viscosity of SOM governs the rate at which organic molecules can diffuse through particles, and knowledge of the viscosity is thus required to predict the mechanism, rate of growth, total mass, and size of modelled particles (Riipinen et al., 2011; Shiraiwa et al., 2011; Shiraiwa and Seinfeld, 2012; Shiraiwa et al., 2013; Zaveri et al., 2014). Viscosity is also important for predicting the long range transport of polycyclic aromatic hydrocarbons (Zelenyuk et al., 2012; Zhou et al., 2012), as well as rates of both heterogeneous and photochemical processes (Houle et al., 2015; Kuwata and Martin, 2012; Lignell et al., 2014; Zhou et al., 2013). In addition, if viscosities are high in particles containing SOM the optical properties of the particles may be altered (Adler et al., 2013; Robinson et al., 2014), and both the crystallization of inorganic salts (Bodsworth et al., 2010; Murray and Bertram, 2008; Song et al., 2012) and the ability of particles to uptake water (Bones et al., 2012; Hawkins et al., 2014; Lu et al., 2014; Price et al., 2014; Tong et al., 2011) may be inhibited. Furthermore, if SOM particles are solid or 'glassy' in phase under atmospheric conditions they may provide a surface for ice nucleation (Baustian et al., 2013; Berkemeier et al., 2014; Knopf and Rigg, 2011; Ladino et al., 2014; Wang et al., 2012b; Murray et al., 2010; Schill et al., 2014).

5 Researchers have traditionally assumed particles containing SOM to be of low viscosity when modelling particle growth (Hallquist et al., 2009). However, recent measurements have suggested that this may not be the case under certain conditions. Measurements that have suggested SOM can have high viscosities include (1) direct measurements of viscosity
10 of SOM or proxies for SOM (Booth et al., 2014; Renbaum-Wolff et al., 2013; Pajunoja et al., 2014; Song et al., 2015; Zhang et al., 2015), (2) measurements of diffusion rates and mixing times in SOM (Abramson et al., 2013; Loza et al., 2013; Perraud et al., 2012), (3) bounce measurements off surfaces (Bateman et al., 2015; Kidd et al., 2014; Saukko et al., 2012; Virtanen et al., 2010, 2011), (4) measurements of the flatness of particles after impaction
15 (O'Brien et al., 2014), (5) measurements of rates of evaporation from SOM (Cappa and Wilson, 2011; Vaden et al., 2011), and (6) measurements of reactivity of SOM (Kuwata and Martin, 2012; Wang et al., 2012a, 2015). Nevertheless, the viscosities and diffusion rates of SOM are still a matter of debate (Saleh et al., 2013; Robinson et al., 2013; Yatavelli et al., 2014; Price et al., 2015).

15 Recently we investigated the viscosity of the water-soluble component of SOM produced from the ozonolysis of α -pinene in an environmental chamber (Renbaum-Wolff et al., 2013). The current manuscript is an extension of the work by Renbaum-Wolff et al. (2013). Similar to Renbaum-Wolff we study the viscosity of SOM particles derived via the ozonolysis of α -pinene; however, in contrast, the current study focuses on particles consisting of the whole
20 SOM, meaning both the water-soluble fraction and water-insoluble fraction.

In the first set of experiments, we investigated the viscosity of the whole SOM as a function of the 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
25 measurements at RH values between <0.5 % and 50 % RH, using SOM with production mass concentrations of 520 and 121 $\mu\text{g m}^{-3}$. The results add to the few existing measurements of the effect of RH on the viscosity of SOM produced via the ozonolysis of α -pinene (Renbaum-Wolff et al., 2013; Bateman et al., 2015; Kidd et al., 2014; Zhang et al., 2015). Understanding the effect of RH on the viscosity of SOM is important as RH in the boundary

layer regularly varies between roughly 20 % and 100 % RH with varied time and location in the planetary boundary layer (Hamed et al., 2011).

In the second set of experiments, we investigated the effect on viscosity of the production mass concentration of SOM particles (in units of micrograms of SOM per m³ of gas) used when generating SOM. Experiments have shown that the composition of SOM particles can change with production mass concentration (Shilling et al., 2009), possibly affecting the viscosity of the SOM particles. The production mass concentrations of the SOM in the current study ranged from 121 to 14,000 $\mu\text{g m}^{-3}$.

2 Experimental

SOM particles were produced either in a flow tube (particle mass concentrations of 520 to 14,000 $\mu\text{g m}^{-3}$) or a chamber (particle mass concentrations of 121 and 230 $\mu\text{g m}^{-3}$) at <5 % RH and collected on hydrophobic substrates with an impactor (Section 2.1 and 2.2). The poke-and-flow technique in conjunction with simulations of fluid flow was used to determine the viscosity of the SOM (Sections 2.3 and 2.4).

2.1 Production and collection of SOM generated at production mass concentrations from 520 to 14,000 $\mu\text{g m}^{-3}$

For the production of SOM at production mass concentrations from 520 to 14,000 $\mu\text{g m}^{-3}$, a previously described flow tube was used (Shrestha et al., 2013) to generate the SOM. Alpha-pinene (Sigma-Aldrich, ≥ 99.5 % purity, 97 % enantiomeric excess) and 2-butanol (Sigma-Aldrich, ≥ 99.5 % purity; used as an OH scavenger) were introduced into the flow tube at an α -pinene:2-butanol ratio of 1:49, using a dry air flow rate of 0.50 sLpm. Ozone was produced prior to the inlet of the flow tube by passing dry air through an ozone generator (Jetlight, Model 600) at a rate of 3.0 sLpm, resulting in an ozone concentration of 12 ppm at the inlet of the flow tube, as measured by an ozone sensor (Ecosensors, UV-100). Residence time in the flow tube was 38 ± 1 s, giving an O₃ exposure (O₃ concentration x time) of 456 ppm s. For comparison purposes the background concentration of O₃ in the

atmosphere is 30 ppb, and assuming a reaction time of one hour an exposure of 110 ppm s is calculated.

The concentration of the α -pinene entering the flow tube was varied to produce samples at a total of five different particle mass concentrations (as measured using an SMPS; TSI, model 3934), with the ozone concentration being kept in constant excess.

Table 1 shows the mass concentrations and collection times used in the flow tube experiments, as well as the mean geometric size of the particles produced in the flow (Sample names Flow tube #1 - Flow tube #5).

After exiting the flow tube the 2 Lpm of dry flow was diluted with an 8 Lpm flow of humidified air, giving a total airflow of 10 Lpm with a humidity of 68 ± 2 % RH, as measured using an RH meter (Rotronic, HC2-S). The airflow then passed through a single stage impactor (MSP Corp.), within which a hydrophobic glass substrate was mounted. Over the course of an experiment sub-micron sized SOM particles impacted on a hydrophobic glass substrate, with the humidified gas serving to reduce the fraction of particles that bounced in the impactor. Over time the particles coagulated to form super-micron sized particles.

The loss of some volatile components during the humidification 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).

The production mass concentration, mode diameter, geometric standard deviation, and collection times are detailed in Table 1. After collection, the samples were stored at 253 K until use. All samples were used within 4 weeks of production. To determine the impact of storing samples at 253 K, the viscosity of one sample (produced using a mass concentration of $6,000 \mu\text{g m}^{-3}$) was measured first after four days of storage and again after 24 further days of storage. The measured lower and upper limits of viscosity differed by <20 % (which is within experimental uncertainty) when measured at both 30 % and <0.5 % RH.

2.2 Production and collection of SOM generated at production mass concentrations of 121 and $230 \mu\text{g m}^{-3}$

For production mass concentrations $<500 \mu\text{g m}^{-3}$ the time required to collect enough material for the poke-and-flow experiments was >12 hours using the flow tube setup described

above. As a result, to collect SOM using production mass concentrations less than $500 \mu\text{g m}^{-3}$ we used the Leipzig Aerosol Chamber (LEAK), a cylindrical 19 m^3 Teflon bag (Linuma et al., 2009). The LEAK chamber could be sampled at higher flow rates than the flow tube (16 Lpm as opposed to 2 Lpm), reducing the required collection time.

5 First, ozone was introduced into LEAK, which was operating under dry conditions ($<5 \%$ RH). The ozone concentration was held between $64\text{--}72 \text{ ppb}$ (ozone monitor; 49c Ozone Analyzer, Thermo Scientific, USA). Afterwards α -pinene (Sigma-Aldrich, $\geq 99.5 \%$ purity, 97% enantiomeric excess) was injected into LEAK, and the formation and growth of SOM particles within LEAK was monitored using an SMPS (TROPOS-type). No OH scavenger
10 was used during experiments. After 80 minutes of reaction, giving an O_3 exposure of $300\text{--}350 \text{ ppm s}$, the submicron sized particles were collected by pumping air from the chamber at a flow rate of 16 Lpm . At the exit of LEAK the air passed through a humidifier unit (FC300-1660-15-LP-01, Perma Pure LLC, NJ, USA), and upon exiting the humidifier unit the air was determined to be at $91 \pm 2.5 \%$ RH, as measured using a handheld RH meter (RH85,
15 Omega, USA). The airflow then passed through a single stage impactor, as described in Section 2.1. Particles collected and coagulated on a hydrophobic slide located with the impactor. 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. After collection, the samples were stored at 253 K until use.
20 All samples were used within 10 weeks of production. The production mass concentration, mode diameter, geometric standard deviation, and collection times are detailed in Table 1 (Samples named Chamber sample #1 and Chamber sample #2)

2.3 Poke-and-flow technique

25 A schematic of the setup for the poke-and-flow experiments is shown in Figure 2. The technique builds upon the qualitative technique described by Murray et al. (Murray et al., 2012) and has been described in detail previously (Grayson et al., 2015; Renbaum-Wolff et al., 2013). In short, a hydrophobic glass slide, containing super-micron sized particles, was placed in a flow cell, and the flow cell mounted to a microscope. Experiments were

performed at 293-295 K, with the temperature of the cell being monitored throughout by a thermocouple located directly beneath the slide surface. A flow of gas was passed through a bubbler located in a temperature controlled water bath prior to entering the cell, allowing control over humidity in the cell. The dewpoint of the gas was measured by a dewpoint monitor (General Eastern; Model 1311DR), which was positioned at the exit of the flow cell. The dewpoint monitor was calibrated using the deliquescence dewpoint of potassium carbonate, and found to give readings within 0.1 K of the expected value at 43 % RH. 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.

A sharp, sterilized needle was attached to a micromanipulator, which could move the needle in the x, y, and z, axes. The needle was aligned vertically above a particle, typically 50-70 μm in diameter, and then moved downwards along the z-axis, passing through the particle and impacting the substrate surface. Upon removal of the needle the behavior of the particle was observed via reflectance optical microscopy and recorded using a charge coupled device (CCD).

In the majority of cases the penetration and removal of the needle resulted in the material of the particle forming a half-torus geometry (see Figure 4, panel a2 for an example). Over time the material flowed, and the area of the hole at the centre of the half-torus decreased. Ultimately, the depression filled and the particle re-attained its initial, energetically favourable, roughly hemi-spherical geometry. From the images the area A of the depression was determined. An equivalent area diameter d was determined from the equation $d = (4A/\pi)^{1/2}$. The experimental flow time, $\tau_{exp,flow}$, was the time at which the equivalent area diameter decreased to half its original size. 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).

During poke-and-flow experiments the SOM was exposed to a dry or humid gas flow over a period of 3-15 h. During this time semi-volatile components of the SOM may un-

dergo evaporation. If the semi-volatile components were behaving as plasticizers within the SOM, the viscosity of the SOM may change. To determine whether this process occurred here and, if so, whether it had a significant effect on the results, the volumes of particles consisting of whole SOM and produced with a mass concentration of $6,000 \mu\text{g m}^{-3}$ were determined for up to 45 h while exposed to a dry (<0.5 % RH) flow of nitrogen gas (see Section S1 for further experimental details). Within experimental uncertainty the volume of the particles remained unchanged (Fig. S1).

In addition, the viscosity of particles consisting of whole SOM and produced with a mass concentration of $6,000 \mu\text{g m}^{-3}$ were determined after both 1 h and 45 h of exposure to a dry (<0.5 % RH) flow of nitrogen gas. The mean lower and upper limits of viscosity were determined to be roughly double after 45 h of exposure compared to their values after 1 h of exposure (Table S1 in the Supplement). **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 the evaporated material being** below the detection limit of the measurements of particle volume, but enough to result in a small increase in viscosity. Alternatively, oligomerisation or polymerisation, **such as via condensation (e.g. Reinhardt et al., 2007),** could occur within the samples at room temperature, with the products of this process being of higher viscosity than their precursors. This doubling in viscosity should be considered as a conservative upper limit to the effect of evaporation in the rest of the experiments reported here, which were carried out on a time scale of 3-15 h.

Two or three samples were analyzed per set of conditions, and the results of the three samples combined to give the values reported here. In total, this study contains the results from experiments on a total of 436 particles.

2.4 Simulations of fluid flow

Limits of viscosity were determined via simulation for each particle using the microfluidics module of COMSOL, a multiphysics program. Particles that exhibited flow were simulated using a half-torus geometry. Full details are shown in Figure 2 of Grayson et al. (2015). The

top and sides of the half-torus geometry, which represented the air-SOM interface, were allowed to undergo free deformation in all directions. The bottom of the half-torus geometry, which represented the SOM-hydrophobic glass interface, was allowed to undergo free deformation only in the horizontal plane. In the simulations the material flowed to minimize the surface energy, as was observed to occur in the experiments. For the simulations a mesh consisting of ≈ 5800 elements and a mesh spacing of 3.92-337 nm was used, with the range in values of mesh spacing being required to accurately model the shape of the half torus, as well as track its movement over time. The model flow time, $\tau_{model,flow}$, was determined to be the time at which the diameter of the hole at the centre of the half-torus decreased to half its original size, with simulations performed until $\tau_{model,flow}$ was within 1 % of $\tau_{exp,flow}$. Based on prior observations of Newtonian behaviour in sucrose-water solutions Hosny et al. (2013); Saggin and Coupland (2004), which are commonly used as proxies for SOM, the SOM was assumed to be Newtonian in nature for simulations.

Simulations were performed using estimates of the physical properties of SOM (i.e., particle-substrate slip length, surface tension, particle-substrate contact angle, and density) (Table S3). In addition images of each experiment were used to determine the dimensions of each particle and its value of $\tau_{exp,flow}$. Contact angles were determined using 3-D images of the super-micron particles suspended on hydrophobic surfaces using a confocal fluorescence microscope (Leica SP5 II, with an excitation wavelength of 458 nm) with a 20x objective, a schematic of which is shown in Fig. S2a. A z-stack series of images with a step size of 0.5 μm , was acquired for each particle. Contact angles were subsequently measured from the 2-D cross-sections in the y-z plane using the LB-ADSA plugin for ImageJ (Fig. S2b). Contact angles were determined by measuring multiple particles from each sample and are reported in Table S4. The values used during simulations of a given particle are those determined for particles of the corresponding sample.

The main source of uncertainty in the viscosity of the SOM arises from uncertainty in the physical properties of SOM that are used in simulations, including the slip length, the particle-substrate contact angle, and the surface tension at the particle-gas interface. The

variability in viscosity from particle to particle was only a small component of the overall uncertainty (discussed further in Section S2).

3 Results and Discussion

3.1 Effect of relative humidity on the viscosity of SOM

5 The effect of relative humidity on the viscosity of SOM was determined for SOM produced with production mass concentrations of $520 \mu\text{g m}^{-3}$ and $121 \mu\text{g m}^{-3}$. Shown in Figure 2 are images of SOM produced in the flow tube with a production mass concentration of $520 \mu\text{g m}^{-3}$ and studied at $<0.5\%$ and 50% RH. Shown in Fig. 2a (Panels a1-a3) is SOM being studied at $<0.5\%$ RH. Prior to poking the SOM is in a hemispherical geometry (Fig. 2, Panel a1). The act of poking the SOM with the needle led to the formation of a half-torus geometry (Fig. 2, Panel a2). Upon removal of the needle the material flowed and the hole began to close, with a $\tau_{exp,flow}$ of 1,074 s (Fig. 2, Panel a3). Shown in Fig. 2b (Panels b1-b3) is SOM being studied at 50% RH. As for the SOM in Fig. 2a, the SOM was hemispherical in geometry prior to being poked (Fig. 2, Panel b1), and the act of poking the SOM also lead to the formation of a half-torus geometry (Fig. 2b, Panel b2). However in this case the flow rate was clearly faster, and the SOM was determined to have a $\tau_{exp,flow}$ of 4.3 s (Fig. 2, Panel a3).

Figure 3 summarizes the RH dependent studies. For SOM produced at a production mass concentration of $520 \mu\text{g m}^{-3}$ the mean $\tau_{exp,flow}$ value was a factor of 460 lower at 50% RH than at $<0.5\%$ RH (Fig. 3a). By comparison, SOM produced at a production mass concentration of $121 \mu\text{g m}^{-3}$ the mean $\tau_{exp,flow}$ value was a factor of 3,600 lower at 50% RH than at $<0.5\%$ RH (Fig. 3b).

Based on simulations of the poke-and-flow experiments the viscosities of SOM produced at a production mass concentration of $520 \mu\text{g m}^{-3}$ the viscosity was between 3×10^5 and 2×10^7 Pa s at $<0.5\%$ RH and between 4×10^2 and 3×10^4 Pa s at 50% RH (Fig. 3c). The viscosity of SOM produced at a production mass concentration of $121 \mu\text{g m}^{-3}$ was

determined to be between 2×10^6 and 6×10^7 Pa s at <0.5 % RH and between 1.8×10^2 and 1.4×10^4 Pa s at 50 % RH. The results suggest the viscosity of both samples was between that of window putty and tar pitch at <0.5 % RH and that of ketchup and window putty at 50 % RH. The RH-dependent results are consistent with previous work that has shown that the viscosity of SOM can depend strongly on RH (Saukko et al., 2012; Renbaum-Wolff et al., 2013; Bateman et al., 2015; Song et al., 2015; Zhang et al., 2015), with the dependence of the viscosity on RH likely being a combination of water behaving as a plasticiser and the fraction of water present in a particle increasing with RH (Koop et al., 2011).

3.2 Effect of production mass concentration used when generating the SOM on the viscosity of SOM

Viscosity of SOM as a function of production mass concentration used to generate SOM was studied at 30 % RH and <0.5 % RH. Figure 4 shows examples of SOM generated at production mass concentrations of 14,000, 520, and $121 \mu\text{g m}^{-3}$ being poked at <0.5 % RH. In all cases the SOM exhibited flow, and there is a trend of increasing experimental flow time with decreasing production mass concentration.

A summary of the $\tau_{exp,flow}$ and viscosity values as a function of production mass concentration at <0.5 % RH is shown in Figure 5. Considering all the data together, as the production mass concentration decreases from $14,000 \mu\text{g m}^{-3}$ to $121 \mu\text{g m}^{-3}$, the mean $\tau_{exp,flow}$ values increase by a factor of 45 (Fig. 5a). Based on simulations of the poke-and-flow experiments the viscosities of the SOM samples are between 4×10^4 and 1.5×10^6 Pa s for SOM produced at a production mass concentration of $14,000 \mu\text{g m}^{-3}$ and between 6×10^5 and 5×10^7 Pa s for SOM produced at a production mass concentration of $121 \mu\text{g m}^{-3}$ (Fig 5b).

The inverse relationship between viscosity and production mass concentration is consistent with results of Shilling et al. (2009), who observed an inverse relationship between production mass concentration and the oxidation level of the resulting SOM. As previously

mentioned, higher oxidation levels are linked to higher glass transition temperatures and an increased likelihood that a particle rebounds from an impactor surface.

The results for SOM produced in the flow tube (production mass concentrations of 14,000 to 520 $\mu\text{g m}^{-3}$) and produced in the chamber (production mass concentrations of 230 and 121 $\mu\text{g m}^{-3}$) each exhibit the same trend: $\tau_{exp,flow}$ increases as production mass concentration decreases. However, the data are not in perfectly aligned. If the data from the flow tube are extrapolated to lower particle mass concentrations, slightly higher $\tau_{exp,flow}$ values are predicted compared to observations using samples from the chamber (roughly a factor of 2-3 higher). This difference could be due to some differences in experimental conditions. For example, the flow tube studies were carried out in the presence of an OH scavenger, 2-butanol, whereas no OH scavenger was used in the chamber studies. The presence of 2-butanol decreases the SOM yield from a given amount of precursor (Jonsson et al., 2008; Henry and Donahue, 2011). The reaction of OH with both α -pinene, as well as first generation products of α -pinene ozonolysis, can alter the chemical composition of the SOM produced (Vereecken and Peeters, 2012). Another difference in experimental conditions between the flow tube and the chamber studies was the RH at which the SOM was collected - $68 \pm 2 \%$ in flow tube studies and $91 \pm 2.5 \%$ in chamber studies. The increased humidity while SOM was being collected during the chamber studies may have resulted in a larger fraction of the more volatile components being present in the particle phase as material was collected, possibly explaining the lower than expected viscosity of the samples collected during chamber studies.

Also included in Figure 5 are previous measurements of the viscosity of α -pinene derived SOM measured under dry conditions. Zhang et al. (2015) studied material produced in the same flow tube as the material used here using a production mass concentration of $\approx 70 \mu\text{g m}^{-3}$, and Renbaum-Wolff et al. (2013) studied the water-soluble component of SOM produced at a production mass concentration of $\approx 50 \mu\text{g m}^{-3}$ in an environmental chamber. The results of Zhang et al. (2015) are consistent with the results obtained here. The results from Renbaum-Wolff et al. are not inconsistent with the current results due to the observed inverse relationship between viscosity and production mass concentration.

Other researchers have measured diffusion rates (Cappa and Wilson, 2011; Perraud et al., 2012; Abramson et al., 2013), or mixing times under dry conditions Robinson et al. (2013); Saleh et al. (2013) within SOM produced via the ozonolysis of α -pinene. In the supplemental material we have converted these measurements to viscosities using the Stokes-Einstein relationship. It should be kept in mind that the Stokes-Einstein relationship may break down for small molecules (Bones et al., 2012; Price et al., 2015) and for large molecules when the viscosity is high and near the glass transition temperature (Champion et al., 1997; Corti et al., 2008). Further discussion on the conversion of reported diffusion coefficients or mixing times to viscosities for each of these studies is given in Section S3. Figure S3 shows that most of these previous studies (Cappa and Wilson, 2011; Perraud et al., 2012; Saleh et al., 2013) are not inconsistent with those presented here. Some of the results are outside of the range reported here (Abramson et al., 2013; Robinson et al., 2013) suggesting factors beyond just a simple relationship between viscosity and production mass concentration are required to explain previous measurements. Differences may be due to invalid assumptions made when using the Stokes-Einstein relationship or other factors.

The effect of production mass concentration on viscosity was also studied at 30 % RH (Figure S4). At this RH, the effect of particle mass concentration was not as dramatic. For the samples produced in a flow tube, as the production mass concentration decreases from $14,000 \mu\text{g m}^{-3}$ to $520 \mu\text{g m}^{-3}$, the mean $\tau_{exp,flow}$ values increase by a factor of 5 (Fig. S4a). For the samples produced in the chamber, as the production mass concentration decreased from $230 \mu\text{g m}^{-3}$ and $121 \mu\text{g m}^{-3}$, the mean $\tau_{exp,flow}$ values increase by a factor of 1.5. Similar to the experiments at <0.5 % RH, if the results from the flow tube are extrapolated to lower particle mass concentrations, they predict larger $\tau_{exp,flow}$ values than observed from the chamber studies. As mentioned above, these differences may be due to small differences in experimental conditions between the flow tube and chamber.

Based on simulation the viscosity of the SOM at 30 % RH is between 1.0×10^3 and 9×10^4 Pa s at a production mass concentration of $14,000 \mu\text{g m}^{-3}$ and between 1.2×10^3 and 1.2×10^5 Pa s at a production mass concentration of $121 \mu\text{g m}^{-3}$ (Fig S4b). The smaller dependence of viscosity on production mass concentration at 30 % RH compared to <0.5

% RH can be explained by the dependence of the viscosity on the water content of the SOM. Under dry conditions the measured viscosity is due only to the viscosity of the SOM. However as RH is increased the SOM uptakes water, and the viscosity of the different SOM samples become increasingly dependent on the viscosity of water and converge, finally approaching the viscosity of water, $\approx 10^{-3}$ Pa s, at 100 % RH.

Also included in Fig S4b are viscosities of α -pinene-derived SOM measured at 30 % RH by Zhang et al. (2015) and Renbaum-Wolff et al. (2013). As mentioned above Zhang et al. (2015) studied material produced in the same flow tube as the material used here, and Renbaum-Wolff et al. (2013) studied the water-soluble component of SOM produced in an environmental chamber. One possible explanation of the results shown in Figure S4b is a very strong dependence of viscosity on production mass concentration in the range of 50 and 121 $\mu\text{g m}^{-3}$. To determine if a strong dependence of viscosity in the range of 50 and 121 $\mu\text{g m}^{-3}$ shown in Fig S4b exists or due to other factors, additional studies are needed. More importantly, additional studies are needed to determine if the viscosity of the water-soluble component of SOM is the same as the viscosity of the whole SOM (water-soluble and water insoluble components) produced at production mass concentrations around 50 $\mu\text{g m}^{-3}$. In addition, further comparison studies using the technique introduced by Zhang et al. (2015) and the poke-and-flow technique used here would be beneficial. 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.

3.3 Effect of the water-insoluble component on the viscosity of SOM

To better understand the difference between the viscosity of water-soluble SOM and SOM containing both the water-soluble and water-insoluble components, additional measurements were carried out using just the water-soluble component of SOM generated by the

5 ozonolysis of α -pinene at a production mass concentration of $14,000 \mu\text{g m}^{-3}$. Particles were generated using the flow tube as discussed in Section 2.1, and particles from the outlet of the flow tube were collected on a Teflon filter. After collection, SOM was extracted from the Teflon filter by placing it in a clean glass jar and immersing the filter in 10 mL of
10 Millipore ($18.2 \text{ M}\Omega \text{ cm}$) water. The jar was shaken for 1.5 h, with the filter being flipped over half way through, after which the filter was removed from the jar, resulting in a solution of the water-soluble component of the SOM. The solution was then nebulized and sprayed onto a hydrophobic glass substrate, producing super-micron sized particles. The particles were then studied using the poke-and-flow technique and their viscosities determined using
15 simulations of fluid flow as described in Sections 2.3, 2.4, and S4.

Shown in Figure 6 are images of a particle comprised of the water-soluble fraction of SOM (Fig. 6a) and a particle comprised of the whole SOM, both the water-soluble and water-insoluble fractions (Fig. 6b). Both were produced at a production mass concentration of $14,000 \mu\text{g m}^{-3}$ and studied at $<0.5 \%$ RH. Although the production of both the water-soluble SOM and the whole SOM took place using equivalent flow tube conditions, the images of the SOM during the poke-and-flow experiments were clearly different, with the water-soluble SOM cracking and showing no observable flow over the course of 14 hours (Fig. 6a, Panels a2 & a3), whilst the whole SOM exhibited flow, with a $\tau_{exp,flow}$ of 1074 s (Fig. 6b, Panels b2 & b3).

20 Table 2 summarizes experimental results at $<0.5 \%$ RH for both the water-soluble SOM and the whole SOM produced at a production mass concentration of $14,000 \mu\text{g m}^{-3}$. The $\tau_{exp,flow}$ and viscosity of the water-soluble component were both at least a factor of 300 greater than the $\tau_{exp,flow}$ and viscosity of the whole SOM.

25 The difference in viscosity between the whole SOM and the water-soluble SOM may arise from differences in the extent of oxidation of the SOM. Water-soluble SOM is assumed to be composed of the more oxidized components of the whole SOM and literature suggests that higher oxidation is related to a warmer glass transition temperature (Koop et al., 2011; Berkemeier et al., 2014; Dette et al., 2014), implying that viscosity increases with oxidation level.

The results for Table 2 correspond to a high production mass concentration. At lower SOM particle concentrations such as concentrations used by Renbaum-Wolff et al. (2013) the difference between water-soluble SOM and whole SOM is likely smaller, since as the production mass concentration decreases, the extent of oxidation in the particle phase is expected to increase and hence the amount of water insoluble material in the particle phase should decrease. In addition, literature suggests that the SOM formed from the ozonolysis of α -pinene is largely composed of water-soluble organic compounds (Hall and Johnston (2011)) produced using a production mass concentration of $<500 \mu\text{g m}^{-3}$. Further, mass spectral analysis has revealed little difference in the chemical composition of SOM produced via the ozonolysis of α -pinene and extracted using either water or a methanol:water solution (Heaton et al. (2007)), and cloud condensation measurements suggest SOM generated via the ozonolysis of α -pinene is not limited by solubility of the organic material in water (King et al., 2009) for SOM produced at production mass concentrations of $<100 \mu\text{g m}^{-3}$. Based on these arguments the results shown in Table 2 should be considered as an upper limit to the difference between the viscosity of water-soluble SOM and whole SOM produced using production mass concentrations lower than $14,000 \mu\text{g m}^{-3}$.

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. (2016) is not clear.

4 Summary

The effect of various experimental parameters on the viscosity of SOM derived via the ozonolysis of α -pinene have been studied. First, the effect of relative humidity on the viscosity of the whole SOM was studied. For each sample studied the $\tau_{exp,flow}$ values were larger and the simulated viscosities higher as the RH was decreased from 50% to $<0.5\%$

(Figs. 2 & 3). Specifically, for SOM produced at a production mass concentration of $121 \mu\text{g m}^{-3}$, the $\tau_{exp,flow}$ increased by a factor of 3,600 as the relative humidity (RH) decreased from 50 % to <0.5 % RH. Based on simulations, the viscosities of the particles were between 3×10^2 and 9×10^3 Pa s at 50 % RH and between 6×10^5 and 5×10^7 Pa s at <0.5 % RH.

Second, the effect on viscosity of the production mass concentration used during the production of SOM was investigated at 30 % and <0.5 % RH. The measurements provide evidence of an inverse relationship between production mass concentration in the reaction vessel and viscosity of the SOM material (Figs. 4 & 5). The effect was most prominent at <0.5 % RH where $\tau_{exp,flow}$ increased by a factor of 45 as the particle mass concentration decreased from $14,000 \mu\text{g m}^{-3}$ to $121 \mu\text{g m}^{-3}$. From simulations of the poke-and-flow experiments, the viscosity of the SOM produced at a production mass concentration of $14,000 \mu\text{g m}^{-3}$ are between 4×10^4 and 1.5×10^6 Pa s and the viscosity of SOM produced at a production mass concentration of $121 \mu\text{g m}^{-3}$ are between 6×10^5 and 5×10^7 Pa s at <0.5 % RH (Fig. 5). **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.**

We also observed that $\tau_{exp,flow}$ and viscosity of the water-soluble component of SOM was at least a factor of 300 greater than the $\tau_{exp,flow}$ and viscosity of the whole SOM when using a production mass concentration of $14,000 \mu\text{g m}^{-3}$. This result should be considered as a upper limit to the difference between the viscosity of water-soluble SOM and whole SOM produced at production mass concentrations lower than $14,000 \mu\text{g m}^{-3}$.

Overall the results suggest that the RH at which the viscosity was determined and the mass concentration at which the SOM was produced should be considered when laboratory experiments are being compared or when used to infer viscosities of atmospheric particles.

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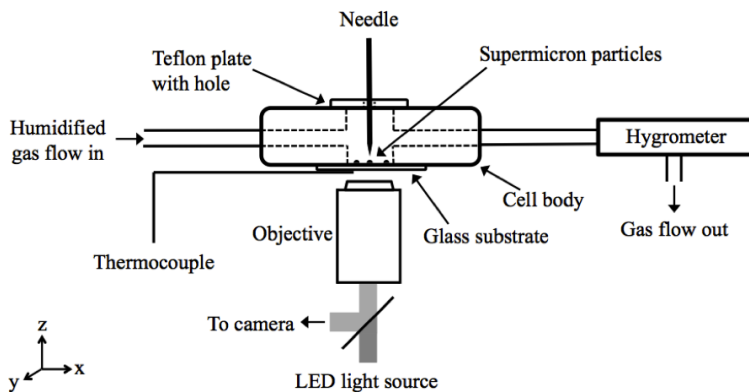


Figure 1. Schematic representation of poke-and-flow experimental setup.

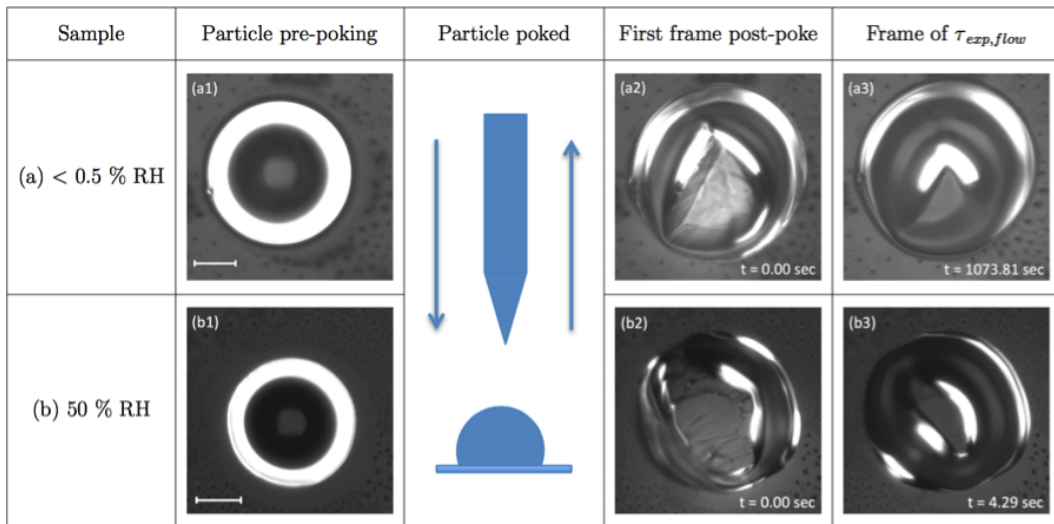


Figure 2. Optical images recorded during typical poke-and-flow experiments of whole SOM produced at a production mass concentration of $520 \mu\text{g m}^{-3}$ being poked at (a) <0.5 %, and (b) 50 %, RH. Images a1 and b1 correspond to SOM prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: $20 \mu\text{m}$.

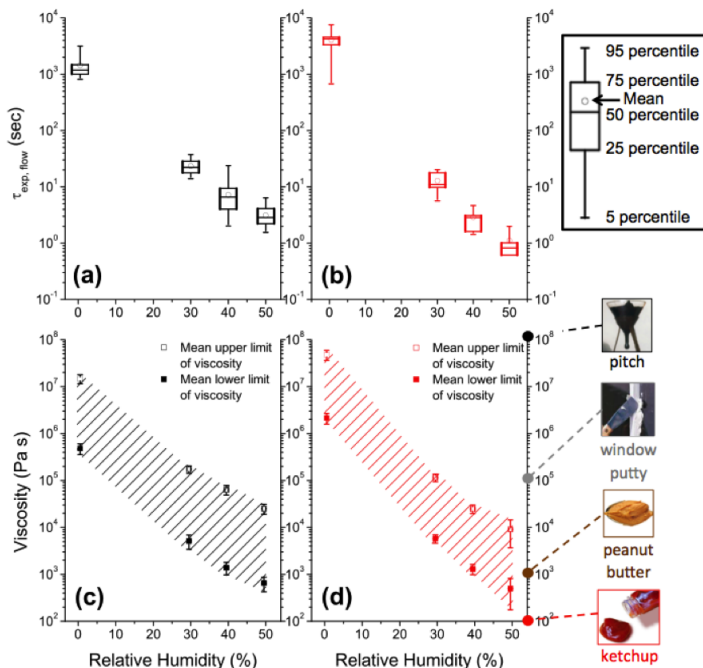


Figure 3. Summary of poke-and-flow experiments from $<0.5\%$ to 50% RH performed on samples of the whole SOM produced at mass concentrations of $520 \mu\text{g m}^{-3}$ (Panels (a) and (c)) and $121 \mu\text{g m}^{-3}$ (Panels (b) and (d)). Panels (a) and (b) show box plots of observed $\tau_{exp,flow}$ times for particles poked at different RHs. Panels (c) and (d) show the simulated lower (filled symbols) and upper (open symbols) limits of viscosity. Y-error bars represent 95 % confidence intervals, and x-error bars represent the range of RH at which measurements were made. The shaded regions are included to guide the eye of the reader. The viscosities of common substances at room temperature have been added to (a) to provide points of reference, as per Koop et al., 2011. The image of pitch is part of an image from the pitch drop experiment (image courtesy of Wikimedia Commons, GNU Free Documentation License, University of Queensland, John Mainstone).

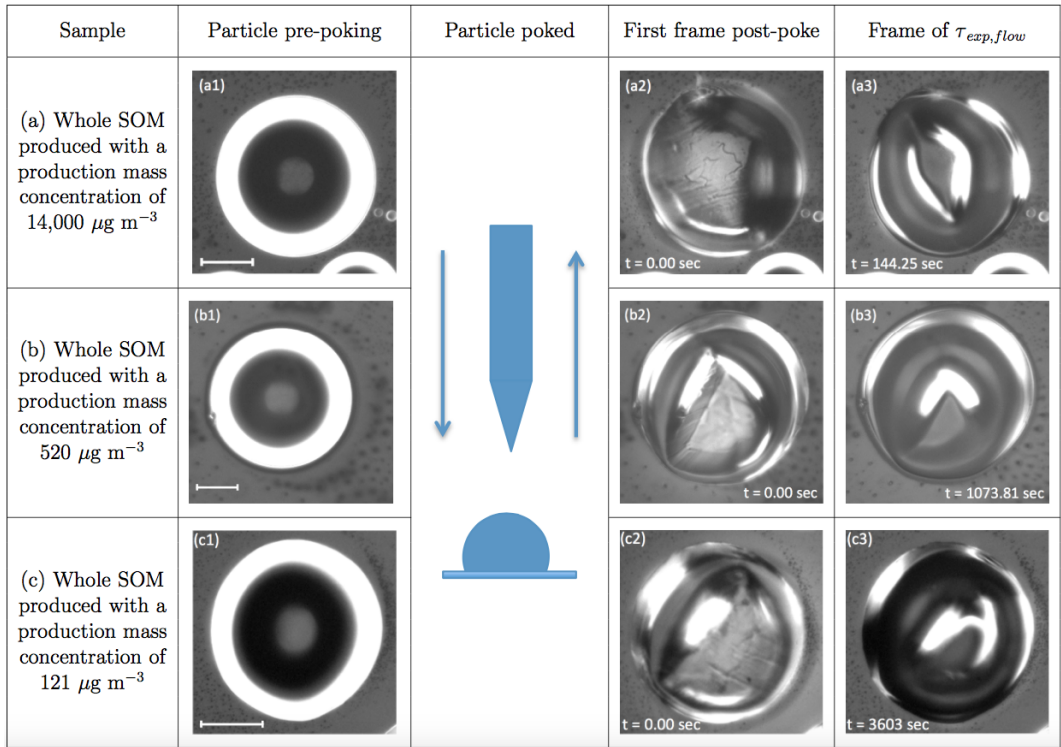


Figure 4. Optical images recorded during typical poke-and-flow experiments of particles of the whole SOM produced at production mass concentrations of (a) $14,000 \mu\text{g m}^{-3}$, (b) $520 \mu\text{g m}^{-3}$, and (c) $121 \mu\text{g m}^{-3}$ being poked at $<0.5\%$ RH. Images a1, b1 and c1 correspond to SOM prior to poking. Images a2, b2 and c2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3, b3 and c3 correspond to images of the experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1, b1 and c1: $20 \mu\text{m}$.

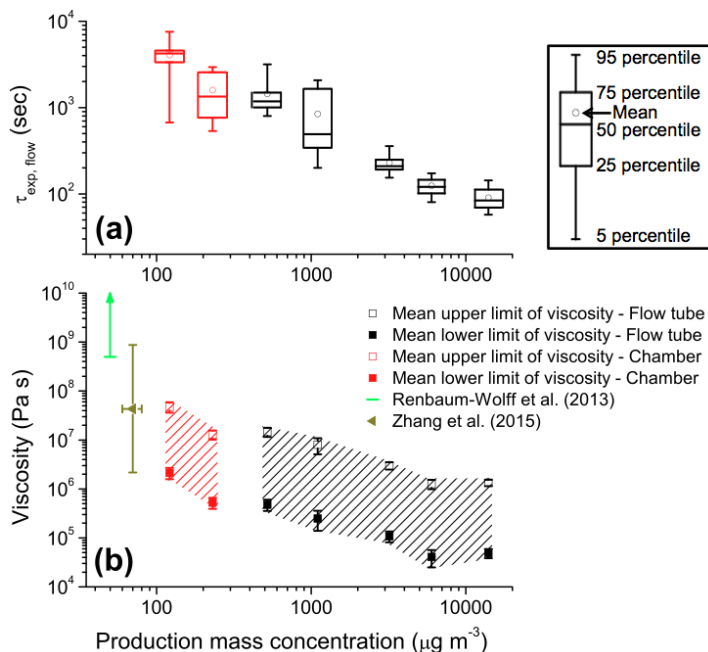


Figure 5. Summary of poke-and-flow experiments performed on samples of whole SOM at <0.5 % RH. Black symbols represent results from particles produced in a flow tube, whilst red symbols represent results from particles produced in a chamber. Panel (a) shows box plots of observed $\tau_{exp,flow}$ times at different production mass concentrations for particles poked <0.5 % RH. Boxes represent the 25, 50, and 75 percentiles, open circles represent median values, and whiskers represent the 5 and 95 percentiles. Panel (b) shows the simulated lower (filled squares) and upper (open squares) limit of viscosity for particles at each production mass concentration poked at <0.5 %. Symbols represent mean values. The y error bars represent 95 % confidence intervals. The shaded regions are included to guide the eye of the reader. Also included in (b) are literature viscosities for SOM produced via the ozonolysis of α -pinene (Renbaum-Wolff et al., 2013; Zhang et al., 2015).

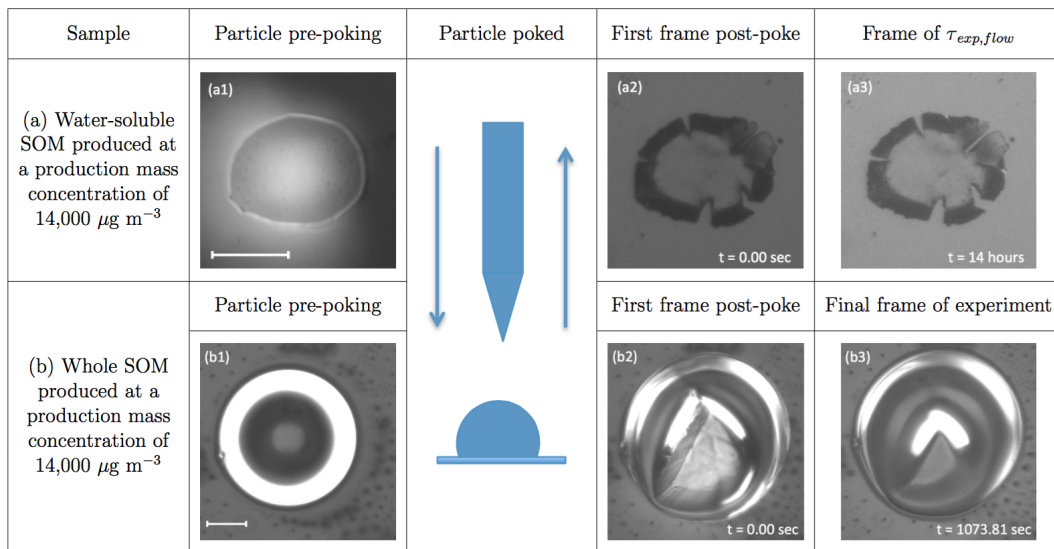


Figure 6. Optical images recorded during poke-and-flow experiments using particles consisting of (a) the water-soluble component of the SOM and (b) the whole SOM (i.e., both the water-soluble and the water-insoluble components). In both experiments the SOM was produced using a mass concentration of $14,000 \mu\text{g m}^{-3}$ and was poked at $<0.5\%$ RH. Images a1 and b1 correspond to the SOM prior to being poked. The brightness in Image a1 is due to reflection of the source light by the needle positioned just above the particle. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). The particle comprised of the water-soluble component of SOM exhibited cracking behaviour and, as shown in Image a3, no change in the size or shape of the cracks can be observed 14 hours after the particle has been poked. The particle comprised of whole SOM exhibited flow, and Image b3 corresponds to an image of the particle at its experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: $20 \mu\text{m}$.

Table 1. Conditions used for generating and collecting samples of SOM generated via the ozonolysis of α -pinene. The whole SOM (both water soluble and water insoluble component of the SOM) was collected.

Sample name	Samples studied	Production mass concentration ($\mu\text{g m}^{-3}$)	Mode diameter (nm)	Geometric standard deviation	Collection time (min)
Flow tube sample #1	3	$(1.4 \pm 0.1) \times 10^4$	265 ± 7	1.43	20
Flow tube sample #2	3	$(5.9 \pm 0.7) \times 10^3$	194 ± 5	1.47	90
Flow tube sample #3	3	$(3.4 \pm 0.1) \times 10^3$	163 ± 2	1.46	150
Flow tube sample #4	3	$(1.2 \pm 0.2) \times 10^3$	121 ± 8	1.46	450
Flow tube sample #5	3	$(5.2 \pm 0.2) \times 10^2$	132 ± 2	1.52	800
Chamber sample #1	2	$(2.3 \pm 0.1) \times 10^2$	181 ± 12		95
Chamber sample #2	2	$(1.2 \pm 0.1) \times 10^2$	169 ± 12		180

Table 2. Summary of $\tau_{exp,flow}$ times and viscosities of whole SOM and water-soluble SOM produced in the flow tube at a production mass concentration of $14,000 \mu\text{g m}^{-3}$ and studied at $<0.5 \%$ RH.

	$\tau_{exp,flow}$ ^a	Viscosity (Pa s) ^b
Water-soluble SOM	$>4.3 \times 10^4$	$>4.8 \times 10^8$
Whole SOM	90 (57, 144)	$3.8 \times 10^4 - 1.5 \times 10^6$

^a For the whole SOM, $\tau_{exp,flow}$ values represent experimental values in the form "mean (5th percentile, 95th percentile)". For the water-soluble SOM, the lower limit to $\tau_{exp,flow}$ represents the shortest experimental time that the particles were observed.

^b For whole SOM, the lower limit of viscosity represents the lower 95 % confidence interval of the lower limit of viscosity, whilst the upper limit of viscosity represents the upper 95 % confidence interval of the upper limit of viscosity. For water-soluble SOM the lower limit of viscosity was calculated for the particles observed over the shortest experimental time.