Response to the comments of Anonymous Referee #1
(Referee comments in black, our responses in blue)

Referee general comment 1:

DeRieux et al. present an extension of their recent model that predicts the viscosity of organic aerosol particles as a function of their simplified chemical composition, using elemental ratios. They have extended the model, largely using data recently compiled by Rothfuss and Petters (2017), to include organics with a molar weight up to ~1100 g/mol, from the original 450 g/mol. The motivation for this work is to predict the diffusivity of organic aerosol, as this /may/ have important limitations for vapor uptake and growth, water uptake and CCN activation, equilibration timescales, etc. It is important to note that this model only estimates the glass transition temperature, from which viscosity can in turn be estimated, and from this an estimate of diffusivity can be made. So, there are many critical steps along to way to deriving the actual property of interest, and the uncertainties involved in each of these steps needs to be discussed fully in this manuscript. Following the careful clarification and further discussion of several important aspects in this manuscript it should be acceptable for publication in ACP. The topic is within scope though personally I think there has been an over-abundance of effort spent recently on viscous organic aerosols. The significance and novelty of the research presented here is quite low by ACP standards, as it merely extends a recent model, and the model's predictions involve an important series of significant assumptions and estimations, and yet the actual diffusivity is still not arrived at. If I was interested in predicting viscosity or diffusivity I personally would turn to Rothfuss and Petters' functional group-based method. It provides deeper chemical insight, since viscosity and diffusivity are created by the interactions between molecules and their functional groups/dipoles. Still, if the major issues with this method and manuscript are satisfactorily addressed, there is nothing technically wrong with this paper to prevent its publication. I do think the authors could be addressing this topic in a deeper and more comprehensive way, and I hope my comments can be used to improve the paper. Referee #2 also raised several excellent points that also need to be fully addressed.

Thank you for your comments. While we acknowledge the importance of the diffusion coefficient, the primary purpose of this paper is to predict the glass transition temperature and viscosity for SOA mixtures using a bottom up approach (as specified in title, abstract and throughout the text) that can be used to make predictions of viscosity from soft-ionization high-resolution mass spectrometry data and be incorporated into atmospheric models. We are fully aware that estimations of bulk diffusivity involve multiple steps and that the Stokes-Einstein equation can be used for conversion of viscosity to bulk diffusivity for first-order approximation, but this relation may break down in highly viscous systems (Power et al., Chem. Sci., 2013; Marshall et al., Chem. Sci., 2016; Chenyakin et al., 2017). Bulk diffusion of small molecules such as water and ozone should be treated separately, for example using obstruction theory or percolation theory (e.g., Shiraiwa et al., PNAS, 2011; Bones et al., PNAS, 2012; Berkemeier et al., ACP, 2014; Price et al., ACP, 2015). In this study, we focus on estimations of T_g and viscosity. Estimations of bulk diffusivity in the SOA material are beyond the scope of this study.

We agree that the functional group model by Sastri and Rao (1992), as used by Rothfuss and Petters (2017), is a valuable method to predict the viscosity of a single pure organic compound when the chemical structure is known. Rothfuss and Petters (2017) demonstrated the influence of functional groups on viscosity of pure organic compounds, but did not provide a method to predict viscosity of complex multi-component SOA mixtures. In addition, the chemical structures of SOA components are often not known, whereas their elemental formulae can be determined in HR-MS measurements, and our method is able to provide practical estimates of T_g, making use of these measurements. Also, there are not yet any regional or global air quality models that explicitly treat functionality of SOA compounds. On the other side, the viscosity estimation method presented in our work is applicable in a global model (e.g., Shiraiwa et al., 2017) and the T_g prediction method developed in this study can be practically applied for example in the SOM model (Cappa and Wilson, 2012; Jathar et al., 2015). Thus, we are confident that this study is valuable and it would merit publication in ACP.

Comment 2: Introduction (page 3-4): The potential importance of viscous organic aerosol phases is really over stated here. As many other papers have done, most of the important implications of viscous organics are predicted but few have actually been demonstrated through laboratory or ambient experiments using real complex atmospheric aerosol or reasonable proxies. The authors are cherry picking the results to motivate their work. For example, the slow evaporation of SOA referred to is observed after a significant fraction of the SOA promptly evaporated. The slowly evaporating SOA remaining cannot be distinguished from the effects of diffusional limitations or just being too darn low in volatility. The viscosity of alpha-pinene SOA was recently studied in a more direct manner using optical tweezers and no significant limitations to diffusion were reported (Gorkowski et al., 2017). The authors are also ignoring highly relevant novel experiments from Neil Donahue's group where they use aerosol population experiments to evaluate the very condensation growth limitations that these authors posit are an important consequence of viscous SOA. Yet Ye et al. did not observe impediments to mixing expect at quite low RH (Ye et al., 2016). Scot Martin's group has approached this topic from a different perspective (Liu et al., 2016). And I see Ye et al. has extended these experiments to study toluene and some other systems as well: Ye, Q., Upshur, M. A., Robinson, E. S., Geiger, F. M., Sullivan, R. C., Thomson, R. J. and Donahue, N. M.: Following Particle-Particle Mixing in Atmospheric Secondary Organic Aerosols by Using Isotopically Labeled Terpenes, Chem, doi:10.1016/j.chempr.2017.12.008, 2018. The authors need to present the motivation behind studying viscous aerosol phases in a more precise and balanced manner, distinguishing between those effects that have been speculated, and those for which there is actual significant experimental evidence (especially from realistic atmospheric aerosol). Here for example is an interesting documented effect of phase state causing differential growth of aerosol particles: Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Liu, J., Bell, D. M., D'Ambro, E. L., Gaston, C. J., Thornton, J. A., Laskin, A., Lin, P., Wilson, J., Easter, R. C., Wang, J., Bertram, A. K., Martin, S. T., Seinfeld, J. H. and Worsnop, D. R.: Growth Kinetics and Size Distribution Dynamics of Viscous Secondary Organic Aerosol, Environ. Sci. Technol., 52(3), 1191-1199, doi:10.1021/acs.est.7b04623, 2018.

Following the reviewer's suggestion, we have extended the introduction to discuss previously missed relevant studies as indicated below:

Lines 56-59: "SOA particles were observed to evaporate unexpectedly slowly (Cappa and Wilson, 2011; Vaden et al., 2011), and recent modeling studies have evaluated the contributions of low diffusivity and volatility to slow evaporation rates (Roldin et al., 2014; Yli-Juuti et al., 2017)."
Lines 79-88: "Partitioning of semi-volatile compounds into viscous particles may result in kinetically-limited growth in contrast to quasi-equilibrium growth (Perraud et al., 2012; Shiraiwa and Seinfeld, 2012; Booth et al., 2014; Zaveri et al., 2014; Mai et al., 2015; Liu et al., 2016), which also affects the evolution of particle size distribution upon SOA growth (Shiraiwa et al., 2013; Zaveri et al., 2018). Chamber experiments probing mixing timescales of SOA particles derived by oxidation of various precursors such as isoprene, terpene, and toluene have observed strong kinetic limitations at low RH, but not at moderate and high RH (Loza et al., 2013; Ye et al., 2016; Ye et al., 2018). Gorkowski et al. (2017) did not observe significant diffusion limitations for glycerol and squalene in α-pinene SOA. Quasi-equilibrium versus kinetically-limited or non-equilibrium SOA growth remains an open issue and warrants further investigations. "

Comment 3: Page 3: Particle bounce measurements are not a reliable assessment of viscosity, and certainly not of diffusivity. These measurements may have started the focus on viscous phases but the measurement methods have advanced considerably since then. What we really need are measurements of the diffusivity of different types of molecules in atmospheric aerosols.

Even though bounce experiments do not provide robust viscosity measurements, they can give useful insights into the particle phase state and provide rough estimates of viscosity (Bateman et al., 2014; Bateman et al., 2015). As such, the results from these studies are represented with shaded boxes in our figures to represent the estimated viscosity. Additionally, we strongly agree that direct measurements of bulk diffusivity are needed (Chenyakin et al., 2017).

Comment 4: Line 59: Truly direct measurements of viscosity are difficult to achieve with the small mass loadings of aerosol available. Were these truly "direct" measurements of viscosity? More likely they were inferred from poke-flow or bead transport measurements.

In the references cited at Line 59, viscosities were inferred from measurements, such as poke-flow measurements, beam mobility measurements, and fluorescence lifetime imaging measurements. To address the referee's comment, "direct" will be removed from Line 59.

Comment 5: Line 70: It is odd that the important plasticization effects of water vapor uptake are not mentioned anywhere near this section on retarded water vapor uptake. Water uptake will reduce viscosity and these transport limitations.

We are fully aware of the plasticizing effect of water and we consider hygroscopic growth and use the Gordon-Taylor approach to account for this effect. We have clarified this point in the revised manuscript by adding the following text:

Lines 50-51: "The phase state is also strongly affected by relative humidity, as water can act as a plasticizer to lower viscosity (Mikhailov et al., 2009)."

Lines 226-228: "SOA particles contain a number of organic compounds as well as a variable amount of liquid water, which has low T_g (136 K) and can act as a plasticizer (Mikhailov et al., 2009; Koop et al., 2011)."

Comment 6: Line 73: Effects of slow water uptake on ice nucleation properties is one of those effects that has been proposed but I do not think there is direct evidence for this. Certainly not in realistic complex aerosol particles.

Direct experimental evidence for the effect of slow water uptake on ice nucleation properties has been reported by multiple groups for model organic compounds (Murray et al., 2010; Schill et al., 2014), laboratory generated SOA (Wang et al., 2012a; Ignatius et al., 2016; Charnawskas et al., 2017), and ambient SOA particles (Wang et al., 2012b). A comprehensive review on this topic was published very recently (Knopf et al., 2018). We have added additional references in the revised manuscript.

Comment 7: Line 89: The highly related study by Rothfuss and Petters really warrants much further discussion here. Their paper significantly advanced the methods we can use to understand and predict viscosity and diffusivity, and did this from a function group perspective. This manuscript also borrows heavily from the extensive dataset compiled by Rothfuss and Petters, and that paper deserves more credit for enabling the modeling presented in this manuscript under consideration. Later in this paper there also needs to be a solid comparison of this model to the functional group based one of Rothfuss and Petters.

We agree that the functional group model by Sastri and Rao, as used by Rothfuss and Petters, is a valuable method to predict the viscosity of single pure organic compound when the functional groups and structure of that compound are known. However, such an approach does not include a method for determining T_g or viscosity of multi-component mixtures (Rothfuss and Petters, 2017). To direct readers to their valuable work, we have added the following statement to our manuscript.

Lines 89-91:"Group contribution methods have been used to predict the viscosities of pure compounds when the functionality and molecular structure are known (Sastri and Rao, 1992; Rothfuss and Petters, 2017)."

Lines 98-99:"These studies provide important insights in estimating the viscosity of individual organic compounds."

Comment 8: Line 98: This is an inaccurate statement; we are getting more and more molecular-level understanding of organic aerosols and their vapor precursors, such as

from CIMS, and also FT-IR, Raman, and other analysis methods. While molecular-based analysis is more challenging than just reducing the measurements to simple elemental ratios, molecules can still be measured, they are what matter, and this is not a valid justification for relying on HCO ratios. You could refer to the large existing datasets from the AMS for example that only reduce the organic aerosol to its elemental ratios as a motivation for an atomic ratio-based model.

We have deleted this sentence in the revised manuscript.

Comment 9: Section 2: I have a series of concerns regarding how viscosity is measured here. The uncertainties in the various parameters and estimates involved need to be properly discussed, and these uncertainties propagated to provide an uncertainty range for the actual estimate of viscosity. The parameterization begins with an estimate of the melting point, Tm, from the EPA EPI Suite. Then the glass transition point, Tg, is estimated from Tm. How accurate are these estimates, especially for the types of molecules relevant for atmospheric aerosol? Was the EPA model trained on these sorts of models? Or you not use Tm in this new model since Eqn. (2) does not depend on Tm? In the end you state that Eqn. (1) can only be used for M < 450 g/mol but Eqn (2) is not suitable for use in common models such as the VBS. Since Eqn (1) will still be used these important aspects regarding the uncertainties in Tm and Tg need to be clarified.

Please note that both Eq. (1) and (2) are developed based on experimental T_g data. Eq. (1) is developed based on 178 CH and CHO compounds with measured T_g compiled by Koop et al. (2011) plus 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA), an atmospheric oxidation product of α-pinene with its measured T_g of 305 ± 2 K (Dette et al., 2014). Eq. (2) is developed based on the above 179 compounds plus the experimental T_g data compiled in Rothfuss and Petters (2017).

As measurements of T_g for atmospheric SOA components are scarce (Dette et al., 2014), as shown in Fig. 1c in the manuscript, we validate our parameterization by comparing the T_g predicted by Eq. (2) (referred as "predicted T_g") with both measured T_g (Koop, et al., 2011; Dette et al., 2014; Rothfuss and Petters 2017) as well as estimated T_g for 654 SOA components following the Boyer-Kauzmann rule with their melting temperature T_m (referred as "estimated T_g" in our manuscript), which has been validated by Koop et al. (2011). Thus, the Boyer-Kauzmann rule is used with an attempt to validate the ability of Eq. (2) applied in atmospheric organic components. The new figure Fig. A2(a) shows that the Boyer-Kauzmann rule works well to estimate T_g. For the 654 SOA components (Shiraiwa et al., 2014), as shown in Fig. 1c in the manuscript, even though T_m from the EPI Suite is adopted (because the measured T_m are not always available), Eq. (2) can constrain those compounds reasonably well. Regarding the uncertainty in T_g predictions, as we wrote in the manuscript, T_g of individual compounds can be predicted within ±21 K as indicated by the prediction band (dotted lines in Fig. 1c).

In short summary, both Eq. (1) and (2) are developed based on experimental T_g and the Boyer-Kauzmann rule estimating T_g by T_m is only used for comparison with Eq. (2) predictions. We agree with the reviewer's note that Eq. (1) can be applied in the VBS more easily. As we wrote in the manuscript, regarding the application in aerosol models, Eq. (2) may be suitable for coupling with the statistical oxidation model which

characterizes the SOA evolution as a function of n_C and n_O (Cappa and Wilson, 2012; Jathar et al., 2015). Eq. (2) is more flexible than Eq. (1) to bring in the compounds containing hetero-atoms (e.g., nitrogen or sulfur) in future studies.

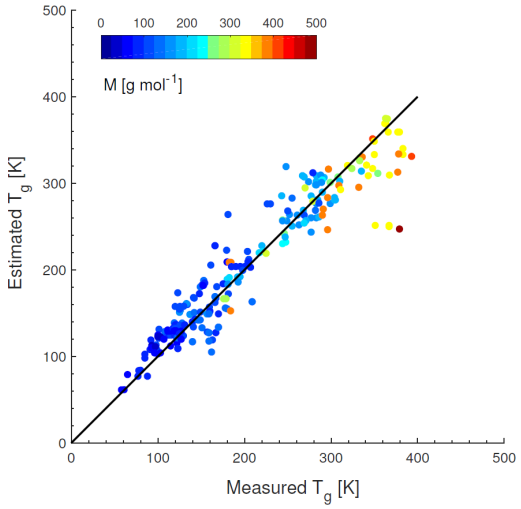


Figure A2(a). Comparison of measured and estimated T_g by the Boyer-Kauzmann rule for 251 organic compounds (Koop et al., 2011; Dette et al., 2014; Rothfuss and Petters 2017) with their measured T_m available. The markers are color-coded by molar mass.

Comment 10: Line 200: Please explain the free volume theory and topological constraint theory. Line 288: Please explain and justify the free volume assumption.

We have further explained these concepts by revising our manuscript as follows:

Lines 200-207: "The correlation between T_g and the number of carbon atoms is consistent with the free volume theory, in which molecular motion is restricted by the difference between the space required for a molecule to vibrate versus the space in which the molecule resides (i.e. the free volume) (White and Lipson, 2016). The correlation between T_g and the number of OH groups is more consistent with the topological constraint theory where the primary influence is the three dimensional structure of the molecule as determined by such factors as molecular bonds and hydrogen-bonding networks (Nakanishi and Nozaki, 2011; van der Sman, 2013).

Comment 11: Page 240: "Water mass fraction can be estimated using the effective hygroscopicity parameter". This likely will not capture the small but important mass fraction of water uptake at low RH that leads to significant plasticization and reduction of viscosity. You need to discuss if there is experimental evidence supporting the use of growth factor derived water uptake measurements to describe the effects of water on Tg and viscosity.

We have added the following discussion in the revised manuscript as follows:
Lines 245-249: "Pajunoja et al. (2015) found that water uptake in subsaturated conditions is inhibited until RH is high enough for dissolution of water in SOA particles with relatively low O:C ratios. As oxidation of SOA increases, solubility of water

increases and dissolution occurs at lower RH values. In both cases, the use of subsaturated hygroscopicity measurements was supported."
Lines 227-229: "SOA particles contain a number of organic compounds as well as a variable amount of liquid water, which has low T_g (136 K) and can act as a plasticizer (Mikhailov et al., 2009; Koop et al., 2011). Under humid conditions, SOA particles take up water by hygroscopic growth in response to RH, lowering T_g and viscosity of SOA particles."

Comment 12: Line 259: Another estimate, dependence of viscosity on temperature, requiring an estimate of the fragility constant, D. Sensitivity calcs are provided in Section 3 for the value of D, but no discussion of the accuracy of Eqns. 4 & 5 are presented. Giving the fragility parameter the symbol "D" is an unfortunate choice since diffusivity is usually represented by D as well, and isn't the diffusivity of molecules in aerosol particles the parameter that really matters, not the viscosity?

These equations are well established in the glass community as detailed in cited references (Angell, 1995, 1997). The symbol for fragility strength, D, is used by the glass community and we have chosen to maintain this convention. In our previous publications, we used 'D_b' for bulk diffusivity. Please note that diffusivity estimations are beyond the scope of this study (see our response to the first comment).

Comment 13: Line 288: Please briefly discuss this more "profound meaning" of the Vogel temperature. There are a lot of concepts and terms used here that are not familiar to the atmospheric chemistry audience.

We have revised the manuscript to clarify this concept as follows:
Line 288-295: "For the WLF equation, T_g is the reference temperature and there is a linear dependence assumed between temperature and free volume (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007). For the VTF equation, the reference is the Vogel temperature (T_0)–a hypothetical temperature at which all non-vibrational motion ceases and viscosity becomes infinite and the theoretical foundation of the VTF equation includes both thermodynamic and kinetic considerations (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007)."

Comment 14-16: Line 305: There are highly relevant measurements of viscosity of SOA, or of its impacts (or lack thereof) on mixing timescales that are missing here, such as the papers by Ye, Gorkowski, and Liu mentioned above. Line 317: Up to what RH values is the viscosity of alpha-pinene SOA significant? My understanding of the literature is that above a rather low RH threshold of 20-30%. I think the importance of viscosity is again being overstated here, and again the mixing experiments are a better direct probe of how viscosity might affect vapor uptake and growth. This needs to be discussed more quantitatively than referring to "low RH". Sect. 3.2: Refer to the recent mixing experiments involving toluene by Ye et al. Fig. 10 would be much more meaningful if the estimated mixing/equilibration timescale was added to the right y-axis. Just plotting it as viscosity is not meaningful to most readers. The important effect is how viscosity affect

diffusivity, which determines equilibration timescales. You will need to discuss the important issues of converting between viscosity and diffusivity.

The goal of this section is to compare our viscosity estimation method with viscosity measurements—estimations of bulk diffusivity and mixing timescales are beyond the scope of this study. We also do not discuss the effects of viscosity on vapor uptake and particle growth. Equilibration timescale is not only a function of viscosity and bulk diffusivity, but it also depends strongly on other factors including accommodation coefficient, particle number concentration, and particle size (Shiraiwa and Seinfeld, 2012). Thus, even though we agree that equilibration timescales would be highly important, they are beyond the scope of this study. The suggested references are included in the introduction (see our response 1).

Comment 17: Line 307: "The wide range of viscosities reported for α-pinene SOA may indicate that the O:C values may be different in different experiments." This frankly is quite sloppy. The average O:C value will change just with changes in aerosol mass concentration, as the less volatile components are typically more oxidized. And then there are all the important effects of using different chemical aging mechanisms to form the SOA. Not to mention the interesting effects of water vapor itself on the chemical composition of SOA. How is this accounted for? The plasticization effect of increased water vapor is important but it also changes the reaction products, as these authors recently reported: Hinks, M. L., Montoya-Aguilera, J., Ellison, L., Lin, P., Laskin, A., Laskin, J., Shiraiwa, M., Dabdub, D., and Nizkorodov, S. A.: Effect of relative humidity on the composition of secondary organic aerosol from the oxidation of toluene, Atmos. Chem. Phys., 18, 1643-1652, https://doi.org/10.5194/acp-18-1643-2018, 2018.

Even though the O:C ratio can affect the phase state, the O:C ratio of SOA were unfortunately unavailable for most studies, with the exception of Zhang et al (2015) which reported O:C =~0.46. We agree that RH upon SOA formation can affect chemical composition and phase of SOA particles (Kidd et al., 2014; Hinks et al., 2018). We have revised the manuscript to clarify this point as follows:
Lines 307-314: "The wide range of experimentally measured viscosities reported for α-pinene SOA, particularly from 30-60% RH is most likely a consequence of the different experimental approaches, mass loadings and O:C ratios for each experiment. For instance, Grayson et al. (2016) used mass loadings of 121 to 14000 μg m^{-3} and observed that viscosity decreased as mass loading increased. Higher mass loadings would lead to greater partitioning of semi-volatile and lower molar mass compounds into the particle phase, which would lead to the decrease of T_g and viscosity of the resulting SOA mixture. They concluded that their results should be considered a lower limit for viscosity of α-pinene SOA in the atmosphere."

Comment 18: Line 351: The high sensitivity of predicted viscosity to Tg is really concerning considering that Tg is estimated from Tm, which is also estimated from the EPA EPI Suite model. The effect of varying D and kappa is briefly discussed, but what is critically missing is an assessment of the accuracy and uncertainty in the predicted viscosity. When you consider how many steps are taken to calculate viscosity, and how

sensitive it is to Tg, I am left with little confidence in this model's predictions.

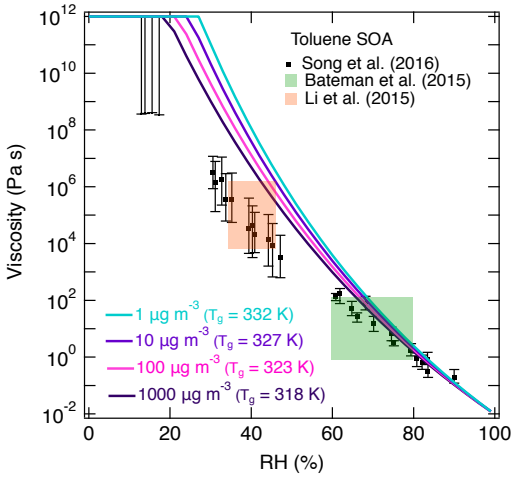
Please refer to response 9. Our T_g parameterization is developed from experimental T_g and the Boyer-Kauzmann rule using T_m is used only for comparison. Note that the T_g of isoprene and α-pinene SOA used in Figs 4-6 are adopted from Table A1 in Berkemeier et al. (2014) who showed the T_g of isoprene and α-pinene SOA varied with O:C. We did not use Eq. (1) or (2) to predict the T_g of isoprene and α-pinene SOA here because elemental composition of SOA for different experiments was unavailable. Thus, the performance of viscosity predictions of isoprene and α-pinene SOA shown in Figs 4-6 has no relation to Eq. (1) or (2). For viscosity predictions, VTF and WLF equations are established and validated in the glass community. In fact, these equations have also been widely used in the atmospheric community to predict the viscosity of SOA mixtures (Berkemeier et al., 2014; Wang et al., 2015; Schill et al., 2013; Maclean et al., 2017; Rothfuss and Petters, 2017a, 2017b; Pratap et al., 2018). Figure 4 in our manuscript shows that the VTF predictions assuming D of 10 agree well with the WLF predictions.

Comment 19: Line 329: See comment above for Line 307. The important roles of aerosol mass loading and other experimental conditions can be discussed in a much more meaningful and quantitative manner. We have a pretty good grasp of how the aerosol mass loading affects partitioning, volatility, O:C, and thus predicted viscosity, yet here it is presented as some nebulous unconstrained factor.

We agree that mass loading can affect viscosity, as it affects the chemical composition of SOA particles. Grayson et al. (2016) observed a decrease in α-pinene SOA viscosity when mass loading increased, with a factor of 45 decrease in viscosity observed when mass loading increased from 121 to 14000 μg m^{-3} at <0.5% RH. Song et al. (2016) investigated this effect for toluene SOA produced at two different mass loadings (60-100 and 600-1000 μg m^{-3}) and compared their results to previous studies on toluene SOA by Bateman et al. (2015) (30-50 μg m^{-3}) and Li et al. (2015) (44-125 μg m^{-3}). They did not observe a significant effect of mass loading on viscosity, concluding that toluene SOA mixtures are not very sensitive to mass loading effects.
To follow up on this issue, we carried out a sensitivity study of mass loadings on viscosity of toluene SOA using HR-MS data. The saturation mass concentration (C^0) was predicted for each component using the molecular corridor approach (Li et al., 2016). Assuming that the mass signal intensity is proportional to the total mass of the compound in the mixture, and applying the absorptive partitioning theory (Pankow, 1994), particle-phase concentrations of each compounds were estimated at different mass loading values (1-1000 μg m^{-3}) followed by T_g and viscosity estimations for each mass loading using the scaled particle-phase concentrations. Mass loading effects on viscosity can be clearly observed in new Fig. A3: as mass loading increases, the glass transition temperature of the SOA mixture and the viscosity decrease. At low RH, the predicted viscosities span up to two orders of magnitude, while at high RH they have little difference. The mass loading effect is smaller than that observed when model parameters ($T_{g,org}$, κ, k_{GT} and D) are varied and its overall effect is not large, which is consistent with Song et al. (2016). Mass loading effects may warrant further investigations with dedicated experiments

combined with modeling partitioning and viscosity predictions. We have added the following text to our manuscript:

Lines 1015-1021:



"Figure A3. *Effect of mass loading on predicted viscosity for toluene SOA. Solid lines represent the predicted viscosity with Eq.(2) using chemical composition of toluene SOA formed at low RH. Viscosity was predicted with different mass loadings ranging from 1-1000 µg m^{-3}. Markers and shaded boxes represent experimentally measured viscosity values. Song et al. (2016) mass loadings were 60-100 and 600-1000 µg m-3. Bateman et al., (2015) and Li et al., (2015) mass loadings were 30-50 µg m^{-3} and 44-125 µg m^{-3}, respectively."*

Lines 307-314: "The wide range of experimentally measured viscosities reported for α-pinene SOA, particularly from 30-60% RH is most likely a consequence of the different experimental approaches, mass loadings and O:C ratios for each experiment. For instance, Grayson et al. (2016) used mass loadings of 121 to 14000 µg m^{-3} and observed that viscosity decreased as mass loading increased. Higher mass loadings would lead to greater partitioning of semi-volatile and lower molar mass compounds into the particle phase, which would lead to the decrease of T_g and viscosity of the resulting SOA mixture. They concluded that their results should be considered a lower limit for viscosity of α-pinene SOA in the atmosphere."

Lines 447-460: "In addition, different mass loadings may have affected viscosity. Song et al. (2016) measured viscosity at two different mass loadings (60-100 and 600-1000 µg m-3) and compared their results to Bateman et al. (2015) (30-50 µg m^{-3}) and Li et al. (2015) (44-125 µg m^{-3}), observing little impact of mass loadings on viscosity. We carried out a sensitivity study of mass loadings on viscosity using a set of compounds detected by HRMS. The saturation mass concentration was predicted for each component using the molecular corridor approach (Li et al., 2016). Assuming that the mass signal intensity is proportional to the total mass concentration of the compound in the mixture, and applying the absorptive partitioning theory (Pankow, 1994), particle-phase concentrations of each compound were predicted to estimate T_g at different organic aerosol mass loading values (1-1000 µg m^{-3}). The glass transition temperature of the

SOA mixture decreases as mass loading increases. Viscosity decreases up to two orders of magnitude at low RH, while at high RH they have little difference as shown in Fig. A3. Simultaneous measurements of viscosity and chemical composition with different mass loadings should be performed in future studies."

Comment 20: Line 390: Analyte solubility in the solvent used is also an important factor in the detection efficiency using DESI.

We agree that the choice of solvent is an important factor for this characterization method. We selected the solvent to maximize solubility and ionization efficiency of OA compounds in ESI. For SOA, acetonitrile or methanol represent a good choice because they extract all of the organics from the sample and provide stable ESI conditions (Hinks et al., 2017).

Comment 21: Line 387: The key role of aerosol loadings is again treated very vaguely. What were the mass loadings for these two different experiments? The OFR method typically works at much much higher loadings than in a large smog chamber. Please be specific here. There is no need to treat the aerosol loading as some unknown factor.

The mass loadings for the experiment are listed at the beginning of the section. We have also added them to the caption for Figure 7 in the revised manuscript:

Lines 974-975, Figure 7 caption: "Mass loadings were 23 μg m^{-3} for LRH and 8 μg m^{-3} for HRH (Hinks et al., 2017)."

Comment 22: Sect. 3.3: The analysis of biomass burning particles, while valiant, is really unsatisfying. First, why weren't experiments on BBA when AMS data is available to provide elemental analysis used? Surely there must be experiments on BBA where AMS and the other necessary measurements were made? If not I suggest this entire section be omitted, as the results are terrible, because the input data from the experiments does not properly constrain the model. The exclusion of CHOS and CHON compounds from the model is a problem for BBA, where organonitrates are common components, and organosulfates can be as well. It seems that applying the model to BBA is too pre-mature. The authors could move this to the SI if they think there is some value in the exercise.

The point of our analysis is to compare the predicted viscosity with HRMS data using two different ionization methods. Our intention was not to provide accurate estimates of viscosity of BBA especially since, as the referee also pointed out, we do not currently have equations to predict T_g for N and S containing compounds. The value of Section 3.3 is enabling a comparison of data from the ESI and APPI methods to discuss the variability in the modeling prediction. For this reason, we opted to include this section in the main manuscript. To clarify this point we added the following text:

Lines 478-480: "Please note that we do not intend to provide accurate estimates of ambient biomass burning particles (as inorganic components are also not included in this analysis), but we investigate how the use of different ionization methods would lead to

variations in our viscosity predictions."

Comment 23: Line 531: "Current Tg parameterizations do not consider functionality or molecular structure explicitly and further measurements of Tg and viscosity of SOA would allow us to refine the method presented in this study." This is precisely why the functional group-based approach of Rothfuss and Petters is vastly superior than the Tg based approach here, and yet this closely related alternate model is barely discussed here. As mentioned earlier, in the end you get an estimate of viscosity (following a series of steps with their own uncertainties), but the property that really matters is diffusivity, and unfortunately the Stokes-Einstein relationship between viscosity and diffusivity is inaccurate by more than one order of magnitude in high viscosity systems (Marshall et al., 2016). So it is not clear to me what this rather simplistic estimate of viscosity from T_g really tells us about important aerosol physicochemical properties in the end.

As we mentioned in the above responses, Rothfuss and Petters (2017) did not provide a method to predict viscosity of complex multi-component SOA mixtures. Diffusivity estimations are beyond the scope of this study and will be investigated in future studies (please see response 1).

Comment 24: As Referee 2 pointed out, there is little data > 500 g/mol plotted in Fig 3a to fit to.

Please see our response to Referee 2.

Comment 25: Fig. 4a: The slope of the experimental data is quite different from the predicted lines. Please discuss as this is concerning. The experimental data has a much shallower slope. A similar discrepancy is seen in Fig. 5. These issues give me even less confidence in the model.

As illustrated in Figures 5(d) and 6(d), the slope of the curve decreases at low RH if the values of k_{GT} or κ are lower at 1.0 or 0.05, respectively. However, the curve does not fit well at high RH with this value of k_{GT}. Available experiments indicate that k_{GT} should be around 2-3 (Dette et al., 2014; Dette and Koop, 2015). We acknowledge that our method has certain limits, which need to be investigated further.

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Response to the comments of Anonymous Referee #2
(Referee comments in black, our responses in blue)

Referee General Comment:
This ACPD article describes a modeling method to estimate the glass transition temperature and viscosity of organic mixtures and secondary organic aerosols (SOA) with molecular weight up to 1100 g mol-1. This work continues the work that the authors published before, but the difference is that previous work can only predict organics with molar masses up to 450 g mol-1 while this work extends the molar mass region twice as much as the previous work. The scientific significance of this study is that the current model is able to predict the glass transition temperatures and viscosities of oligomers instead of just small organic molecules, which can be applied those oligomer-rich SOA systems. I like that even though the paper focus on molecular mass>450 g/mol, the fitting equation still fit for molecular <450 g/mol, and the results are even better. This study describes the modeling process, and then utilizes experimental data to verify the model. The experimental data add credibility to the modeling results. Overall, the manuscript is sound and after addressing the following issues, it is suitable to be published on ACP.

Responses:
We thank Anonymous Referee #2 for the review and the positive evaluation of our manuscript. Based on your constructive suggestions for improvement, we will expand discussions in the revised manuscript as detailed below.

In Figure 1, it looks like there are only 8 compounds whose molar masses are larger than 450 g/mol, which is quite few compared with the number of compounds whose molar masses are below 450 g/mol. Would the limited number of compounds with higher molar masses causing a skew when modeling their viscosity and glass transition temperatures?

We share this concern as well. As pointed out in the manuscript, there are only eight experimental data points available on the glass transition temperatures of higher molar mass compounds (M > 450 g mol^{-1}) of atmospheric relevance, as compiled by Rothfuss and Petters. Including this dataset has enabled us to extend the molar mass range to which our method applies. We have been reviewing polymer data for glass transition values, but have found that the molar mass is often ill-defined for polymer distributions in these studies, making it hard to be incorporated in our method. We plan to continue to refine our method as additional glass transition data on high molar mass compounds becomes available. We have added the following sentences in the revised manuscript:

Lines 137-138: "Eight of these compounds are carbohydrates with M > 450 g mol^{-1}."
Lines 179-180: "We plan to continue to refine our method as additional glass transition data on high molar mass compounds become available."

In Figure 4 (a), the author uses measured viscosity data of alpha-pinene SOA to model the viscosity trend with RH. The author seems to heavily rely on the data from Renbaum-Wolff because that set of data covers a wider RH. However, in Renbaum- Wolff et al. specified that their data was only the water-soluble part of SOA, while all the other measured data listed in the plot were based on the whole SOA. The model does not seem to distinguish these two differences and mix all the data together. Wouldn't this approach lead to inaccuracy to predict the viscosity of total SOA? Maybe it is better for the author to use the measured viscosity of total SOA to predict SOA's viscosity, and leave the water-soluble part of the SOA to another plot and estimate its viscosity individually.

Our viscosity predictions are based on four parameters (glass transition temperature of dry SOA mixture ($T_{g,dry}$), hygroscopicity (κ), fragility and Gordon-Taylor constant (k_{GT}). Especially $T_{g,dry}$ and κ may be different for water-soluble or total SOA. Moreover, different studies generated SOA in different conditions (e.g., flow tube vs. chamber, different oxidant concentrations, etc.) that would lead to variations in these parameters. While we agree that this approach would lead to inaccuracy/uncertainties in comparing our predictions with different experiments, there are insufficient data points to have separate panels. In accordance with your comment, we clarify this point in the revised manuscript as shown below and also make data points by Renbaum-Wolff in open markers in Fig. 4 and 5 to make it clear that these data points are for water-soluble components.

Lines 314-316:"It should also be noted that the viscosity measurements from Renbaum-Wolff et al. (2013) were for the water-soluble portion of the SOA."

Lines 944-945, added to caption for Figure 4: "Panel (a): Renbaum-Wolff et al. (2013) data represents viscosity for water-soluble portion of SOA;"

Figure 4(b) was based on Song et al. 2015 data and Bateman et al. 2015 data. I checked Song et al. 2015 and found out that their data was based on SOA condensation from the potential aerosol mass (PAM) reactor (Song, Liu et al. 2015). In the ambient environment, it has shown that the majority of the isoprene SOA is formed by heterogeneous reactions with the acidic sulfate particles, rather than condensation of semi-volatile species (Lin, Zhang et al. 2013, Surratt, Chan et al. 2010). Heterogeneous reactions of isoprene products will be able to form more oligomers and lead to a lower viscosity (Gaston, Riedel et al. 2014). Therefore the experimental data from Figure 4(b) may not represent the ambient isoprene SOA viscosity. At the very least the author should make it clear in the manuscript (both Figure 4(b) and Figure 10) about the limitation of this study so more motivation is put for others to perform experimental viscosity measurement

on ambient-like isoprene SOA particles generated from heterogeneous reactions.

Thank you for this insightful comment. We agree that laboratory-generated SOA may be different from ambient SOA. Following your comment, we have added the following discussion in the revised manuscript:

Lines 333-342:"In contrast to α-pinene SOA, there are limited viscosity measurements for isoprene SOA. While the predicted viscosity is consistent with the experimental data, comparison of our model predictions to additional measurements is strongly recommended. Song et al. (2015) prepared their samples in a potential aerosol mass (PAM) reactor while those investigated by Bateman et al. (2015) were generated in a smog chamber. It has been suggested that under ambient conditions the majority of isoprene-derived SOA can be derived through heterogeneous interactions with acidic sulfate particles forming oligomers (Lin et al., 2013; Surratt et al., 2010)(Gaston et al., 2014), which may increase viscosity. Further studies are warranted to compare laboratory-generated and ambient isoprene SOA, and to investigate the effect of the acidic seed on the viscosity."

In Figure 9 and 10, the author used ESI and APPI data to model the viscosity value of biomass burning aerosols. Biomass burning aerosols typically also contain inorganic components as well but the author neglects that part and only take the organic component into consideration. How would the inorganic components affect the viscosity of the total aerosols? Maybe the author should be a bit more specific when they mention biomass burning particles?

Please note that we do not intend to provide accurate estimates of ambient biomass burning particles in this study, but we investigate how the use of different ionization methods would lead to variations in our viscosity predictions. If the particles are well-mixed with the inorganic fraction (such as sulfate and nitrate, which have with lower T_g), that would lead to decrease of viscosity (Dette and Koop, 2015). A liquid-liquid phase separation is most likely to occur when the O:C ratio of the organic fraction is below 0.5 (You et al., 2014) and in this case the predicted viscosity would only apply to the organic phase. We have added the following text to Section 3.3:

Lines 478-480: "Please note that we do not intend to provide accurate estimates of ambient biomass burning particles (as inorganic components are also not included in this analysis), but we investigate how the use of different ionization methods would lead to variations in our viscosity predictions."

Editorial comments:

Lines 135-137: When the author says: " Specifically, data for 76 aliphatic alcohols, 39

carbohydrates and their derivatives...", do all these compounds have molar masses larger than 450 g/mol? It sounds like it because the way the author phrase the sentence. If not, the author may want to revise this sentence to make it more clear and indicate which compounds have molar masses > 450.

Thank you for this key comment. The eight compounds with M > 450 g mol^{-1} are all carbohydrates (Fig. 4 in Rothfuss and Petters, 2017). This could lead to a skew when applying our parameterization in high molar mass compounds containing multifunctional groups. We will continue to refine our method as additional glass transition data on high molar mass compounds becomes available, especially the compounds containing multifunctional groups. The following statement has been added to this section:

Lines 137-138: "Eight of these compounds are carbohydrates with M > 450 g mol^{-1}."

Table 1, nc(0) symbol is not centered in the table;

Symbol has been centered in its column.

Line 903, the parenthesis after 2014 is missing;

This was corrected.

Line 909, the letters are partially overlapping with the table.

This was fixed.

Predicting the glass transition temperature and viscosity of secondary organic material using molecular composition

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Abstract:

Secondary organic aerosols (SOA) account for a large fraction of submicron particles in the atmosphere. SOA can occur in amorphous solid or semi-solid phase states depending on chemical composition, relative humidity (RH), and temperature. The phase transition between amorphous solid and semi-solid states occurs at the glass transition temperature (T_g). We have recently developed a method to estimate T_g of pure compounds containing carbon, hydrogen, and oxygen atoms (CHO compounds) with molar mass less than 450 g mol^{-1} based on their molar mass and atomic O:C ratio. In this study, we refine and extend this method for CH and CHO compounds with molar mass up to ~1100 g mol^{-1} using the number of carbon, hydrogen, and oxygen atoms. We predict viscosity from the T_g-scaled Arrhenius plot of fragility (viscosity vs. T_g/T) as a function of the fragility parameter D. We compiled D values of organic compounds from literature, and found that D approaches a lower limit of ~10 (+/- 1.7) as the molar mass increases. We estimated viscosity of α-pinene and isoprene SOA as a function of RH by accounting for hygroscopic growth of SOA and applying the Gordon-Taylor mixing rule, reproducing previously published experimental measurements very well. Sensitivity studies were conducted to evaluate impacts of T_g, D, hygroscopicity parameter (κ), and the Gordon-Taylor constant on viscosity predictions. Viscosity of toluene SOA was predicted using the elemental composition obtained by high-resolution mass spectrometry (HRMS), resulting in a good agreement with the measured viscosity. We also estimated viscosity of biomass burning particles using the chemical composition measured by HRMS with two different ionization techniques: electrospray ionization (ESI) and atmospheric pressure photoionization (APPI). Due to differences in detected organic compounds and signal intensity, predicted viscosities at low RH based on ESI and APPI measurements differ by 2-5 orders of magnitude. Complementary

measurements of viscosity and chemical composition are desired to further constrain RH-dependent viscosity in future studies.

1. Introduction

Secondary organic aerosols (SOA) account for a large fraction of submicron particles in the atmosphere and they play an important role in climate, air quality and public health (Goldstein and Galbally, 2007; Jimenez et al., 2009). Traditionally, SOA particles were assumed to be liquid with dynamic viscosity η below 10^2 Pa s, but a number of recent studies have shown that they can also adopt amorphous semi-solid ($10^2 \leq \eta \leq 10^{12}$ Pa s), or glassy solid ($\eta > 10^{12}$ Pa s) states, depending on chemical composition and temperature (Zobrist et al., 2008; Koop et al., 2011; Huang et al., 2018; Reid et al., 2018). The phase state is also strongly affected by relative humidity, as water can act as a plasticizer to lower viscosity (Mikhailov et al., 2009). Ambient and laboratory-generated SOA particles have been observed to bounce off the smooth hard surface of an inertial impactor at low RH, implying a non-liquid state (Virtanen et al., 2010; Saukko et al., 2012; Bateman et al., 2015; Jain and Petrucci, 2015), whereas predominantly biogenic SOA particles in the Amazon basin did not bounce off the impactor surface at high RH, implying they are primarily liquid (Bateman et al., 2016). Upon dilution or heating, SOA particles were observed to evaporate unexpectedly slowly (Cappa and Wilson, 2011; Vaden et al., 2011), and recent modeling studies have evaluated the contributions of low diffusivity and volatility to slow evaporation rates (Roldin et al., 2014; Yli-Juuti et al., 2017). Measurements of viscosity of SOA bulk material derived from oxidation of α-pinene (Renbaum-Wolff et al., 2013; Zhang et al., 2015; Hosny et al., 2016), limonene (Hinks et al., 2016), isoprene (Song et al.,

2015), and toluene (Song et al., 2016a) have confirmed that SOA particles adopt a wide range of viscosities.

The particle phase state has been shown to affect gas uptake and chemical transformation of organic compounds due to kinetic limitations of bulk diffusion (Shiraiwa et al., 2011; Abbatt et al., 2012; Kuwata and Martin, 2012; Zhou et al., 2013; Slade and Knopf, 2014; Arangio et al., 2015; Davies and Wilson, 2015; Wang et al., 2015; Berkemeier et al., 2016; Marshall et al., 2016; Liu et al., 2018; Pratap et al., 2018; Zhang et al., 2018). Molecular motion can be hindered in a highly viscous matrix, slowing down photochemical reactions in particles (Lignell et al., 2014; Hinks et al., 2016). Water diffusion can be still fast even in an amorphous solid matrix under room temperature, but it can be hindered significantly under low temperatures (Mikhailov et al., 2009; Zobrist et al., 2011; Bones et al., 2012; Berkemeier et al., 2014; Price et al., 2014), affecting homogeneous vs. heterogeneous ice nucleation pathways (Murray et al., 2010; Wang et al., 2012a; Wang et al., 2012b; Baustian et al., 2013; Schill and Tolbert, 2013; Berkemeier et al., 2014; Schill et al., 2014; Lienhard et al., 2015; Ignatius et al., 2016; Knopf et al., 2018). Despite the substantial implications of the SOA particle phase state, its effects on gas-particle interactions have not yet been considered explicitly in current climate and air quality models (Shrivastava et al., 2017).

Partitioning of semi-volatile compounds into viscous particles may result in kinetically-limited growth in contrast to quasi-equilibrium growth (Perraud et al., 2012; Shiraiwa and Seinfeld, 2012; Booth et al., 2014; Zaveri et al., 2014; Mai et al., 2015; Liu et al., 2016), which also affects the evolution of particle size distribution upon SOA growth (Shiraiwa et al., 2013; Zaveri et al., 2018). Chamber experiments probing mixing timescales of SOA particles derived by oxidation of various precursors such as isoprene, terpene, and toluene have observed strong

kinetic limitations at low RH, but not at moderate and high RH (Loza et al., 2013; Ye et al., 2016; Ye et al., 2018). Gorkowski et al. (2017) did not observe significant diffusion limitations for glycerol and squalene in α-pinene SOA. Quasi-equilibrium versus kinetically-limited or non-equilibrium SOA growth remains an open issue and warrants further investigations.

Group contribution methods have been used to predict the viscosities of pure compounds when the functionality and molecular structure are known (Sastri and Rao, 1992; Rothfuss and Petters, 2017). Song et al. (2016) showed that estimations from group contribution approaches combined with either nonideal or ideal mixing reproduced the RH-dependent trends particularly well for the alcohol, di-, and tricarboxylic acid systems with viscosity of up to 10^4 Pa s. By contrast, model calculations overestimated the viscosity of more viscous compounds including mono-, di-, and trisaccharides by many orders of magnitude (Song et al., 2016b). A recent study compiled viscosity of organic compounds with atmospherically relevant functional groups, investigating the influence of the number and location of functional groups on viscosity (Rothfuss and Petters, 2017). These studies provide important insights in estimating the viscosity of individual organic compounds.

Particle phase state can be characterized by a glass transition temperature (T_g), which is a characteristic temperature representing a non-equilibrium phase transition from a glassy solid state to a semi-solid state as the temperature increases (Koop et al., 2011). Recently, we have developed a method to estimate T_g of pure organic compounds comprised of carbon, hydrogen, and oxygen (CHO compounds) with molar mass less than 450 g mol^{-1} based on their molar mass and atomic O:C ratio (Shiraiwa et al., 2017). It has been applied successfully in a global chemistry climate model to predict T_g and the phase state of atmospheric SOA, which indicated that SOA particles are mostly liquid or semi-solid in the planetary boundary layer, while they

should be glassy in the middle and upper troposphere (Shiraiwa et al., 2017). A recent study provided a consistent result, suggesting that mixing timescales of organic molecules within SOA are often < 1 h in a global planetary boundary layer (Maclean et al., 2017).

It has been shown that SOA particles contain oligomeric compounds with molar masses higher than 450 g mol^{-1} (Gao et al., 2004; Tolocka et al., 2004; Nizkorodov et al., 2011; Nozière et al., 2015), which makes the previously developed parameterization incomplete. In this study, we extend the parameterization of T_g to higher molar mass compounds, and apply it to high-resolution mass spectrometry data for toluene SOA and biomass burning particles. The Arrhenius approach and the Gordon-Taylor mixing rules were applied to estimate viscosity of SOA bulk materials to compare with the literature reported viscosity measurements. This method will be useful for estimations of viscosity of organic particles, for which high-resolution mass spectra are available. It can also be applied in global or regional models to evaluate impacts of the particle phase state on the role of SOA in climate and air quality.

2. Parameterization development

2.1 Glass transition temperature

Figure 1a shows the dependence of T_g on the molar mass (M) of organic compounds. Solid markers represent measured T_g of 258 CHO compounds (Koop et al., 2011; Dette et al., 2014; Rothfuss and Petters, 2017), while open markers represent 654 CHO compounds in SOA (Shiraiwa et al., 2014). Markers are color-coded by atomic O:C ratio. Their melting points (T_m) were estimated by the Estimation Programs Interface (EPI) Suite software version 4.1 (US-EPA, 2012) and their T_g were estimated using the Boyer-Kauzmann rule: $T_g = g \cdot T_m$ with $g = 0.7$ (Koop et al., 2011; Shiraiwa et al., 2017). This rule can provide good estimates of T_g, as has been

validated in previous work (Koop et al., 2011) and also shown in Fig. A2(a). A subset of data shown in Figure 1 was originally published in Shiraiwa et al. (2017) for compounds with $M <$ 450 g mol^{-1}. This version of the figure has been updated to include a number of experimentally measured T_g values of larger compounds with M up to 1153 g mol^{-1}, including aliphatic compounds containing OH and/or COOH groups. Specifically, data for 76 aliphatic alcohols, 39 carbohydrates and their derivatives, 4 carboxylic acids, and 4 hydroxy acids, as compiled by Rothfuss and Petters (2017), have been added to Figure 1. Eight of these compounds are carbohydrates with $M > 450$ g mol^{-1}. These updates are critical for reliable parameterization of T_g based on M. When M increases above ~500 g mol^{-1}, the slope of T_g decreases, making it challenging to extrapolate the low-M data from the original Shiraiwa et al. (2017) study to higher M values. When M increases to ~1000 g mol^{-1}, the corresponding T_g appears to level at around 420 K.

Such dependence on M has been described for polymers with the Fox-Flory equation: $T_g(M) = T_{g,\infty} - \frac{K_m}{M}$ (Fox Jr and Flory, 1950), where K_m is a constant and $T_{g,\infty}$ is the asymptotic value of T_g specific to the polymer. We conducted a literature search and found that most of the reported $T_{g,\infty}$ values fell below ~500 K (Fox Jr and Flory, 1950; Onder et al., 1972; Montserrat and Colomer, 1984; Polymer handbook, 1999; Papadopoulos et al., 2004; Matsushima et al., 2017). The Fox-Flory equation works very well for high molar mass compounds and is also generally applicable to smaller compounds (Koop et al., 2011), as supported by an approximately linear dependence of T_g on the inverse molar mass in Fig. A1(a). Figure 1b plots the values of T_g as a function of the atomic O:C ratio of organic molecules. Figures 1a and 1b clearly demonstrate that T_g depends primarily on the molar mass with a weak dependence on the atomic O:C ratio.

A parameterization for T_g calculation based on the molar mass and atomic O:C ratio was developed in our recent work, which is applicable to CH and CHO compounds with $M < 450$ g mol^{-1} (Shiraiwa et al., 2017):

$$T_g = A + BM + C^2M^2 + D\,(O{:}C) + E\,M\,(O{:}C) \quad (1)$$

where A = –21.57 (±13.47) [K], B = 1.51 (±0.14) [K mol g^{-1}], C = -1.7×10^{-3} ($\pm3.0\times10^{-4}$) [K mol^2 g^{-2}], D = 131.4 (±16.01) [K] and E = –0.25 (±0.085) [K mol g^{-1}], respectively. These values were obtained by fitting the measured T_g of 179 CH and CHO compounds with $M < 450$ g mol^{-1} with multi-linear least squares analysis. Note that application of Eq. (1) may provide unreasonable T_g values for compounds with $M > 500$ g mol^{-1} because it does not account for the strong curvature in the T_g vs. M dependence shown in Figure 1a.

In this study we have developed an improved parameterization to predict T_g of CH and CHO compounds using the number of carbon (n_C), hydrogen (n_H), and oxygen (n_O) that can also be applied to higher molar mass compounds. Motivated by a good correlation between T_g and volatility (Fig. 1a in Shiraiwa et al., (2017)), we use an equation with a similar formulation to the equation used to predict the saturation mass concentration or volatility (Donahue et al., 2011; Li et al., 2016):

$$T_g = (n_C^0 + ln(n_C))\,b_C + ln(n_H)\,b_H + ln(n_C)\,ln(n_H)\,b_{CH} + ln(n_O)\,b_O + ln(n_C)\,ln(n_O)\,b_{CO} \quad (2)$$

where n_C^0 is the reference carbon number, b_C, b_H and b_O denote the contribution of each atom to T_g, and b_{CH} and b_{CO} are coefficients that reflect contributions from carbon-hydrogen and carbon-oxygen bonds, respectively. These values were obtained by fitting the measured T_g of 42 CH compounds and 258 CHO compounds with multi-linear least squares analysis with 68% prediction and confidence intervals. The best-fit parameters are summarized in Table 1.

176 Note that the evaluation dataset used to derive Eq. (2) contains CH compounds with $M <$
177 260 g mol^{-1} (see Fig. A2b for comparison of measured and predicted T_g). Thus, the application of
178 Eq. (2) to higher molar mass compounds may require further investigations when measured T_g
179 for higher molar mass compounds becomes available. We plan to continue to refine our method
180 as additional glass transition data on high molar mass compounds become available. Figure 1c
181 shows that the T_g values predicted using Eq. (2) are in good agreement with the T_g values
182 measured in experiments (see also Fig. A1(b)) or estimated by the Boyer-Kauzmann rule as
183 indicated by the high correlation coefficient of 0.95. T_g of individual compounds can be
184 predicted within ±21 K as indicated by the prediction band (dotted lines in Fig. 1c); however,
185 this uncertainty may be much smaller for multicomponent SOA mixtures under ideal mixing
186 conditions as indicated in the confidence band (dashed lines, almost overlapping with the 1:1
187 line).

188 These results are noteworthy given that the parameterization (Eq. 2) does not consider
189 either explicit molecular structures or functional groups. Previous studies have shown that T_g can
190 be especially sensitive to the number of OH groups, which interact strongly through hydrogen
191 bonding. For example, Nakanishi et al., (2011) found a direct relationship between T_g and the
192 number of hydroxyl groups in a molecule for sugar alcohols; T_g increases as the number of OH
193 groups increases. They reported that the correlation between T_g and the number of OH groups
194 was much stronger than the correlation between T_g and the number of carbons in a molecule.
195 Such a trend is implicitly included in Eq. (1) and (2), which contain the O:C ratio and number of
196 oxygen atoms as parameters, respectively. Recently, Rothfuss and Petters (2017) showed an
197 approximately linear relationship between the number of OH groups and T_g for compounds with
198 up to eight OH groups. Grayson et al. (2017) showed that addition of hydroxyl functional groups

199 increases viscosity, a conclusion supported by both the experimental data and quantitative
200 structure-property relationship model. The correlation between T_g and the number of carbon
201 atoms is consistent with the free volume theory, in which molecular motion is restricted by the
202 difference between the space required for a molecule to vibrate versus the space in which the
203 molecule resides (i.e., the free volume) (White and Lipson, 2016). The correlation between T_g
204 and the number of OH groups is more consistent with the topological constraint theory, where
205 the primary influence is the three dimensional structure of the molecule as determined by
206 molecular bonds and hydrogen-bonding networks (Nakanishi and Nozaki, 2011; van der Sman,
207 2013). Future experiments targeting more comprehensive T_g data, especially for higher molar
208 mass compounds, would lead to further refinements of our T_g parameterizations.

209 Comparing Eq. (1) and (2), the two parameterizations give similar performance for
210 compounds with $M < 450$ g mol^{-1} as shown in Fig. A2c. The statistical measures of correlation
211 coefficient (R), mean bias (MB), and root mean square error (RMSE) are 0.93, –6.45 K, and
212 25.64 K, respectively, for the performance of Eq. (1), while for Eq. (2), they are 0.95, 3.15 K,
213 and 21.11 K, respectively. It should be noted again that Eq. (1) cannot be used to predict T_g for
214 compounds with $M > 450$ g mol^{-1}. For example, T_g of stachyose ($M = 667$ g mol^{-1}) predicted by
215 Eq. (1) is 198 K, while that by Eq. (2) is 394 K, which agrees much better with the measured
216 mean T_g of 396 K (Rothfuss and Petters, 2017). Eq. (2) is more flexible than Eq. (1) and can be
217 potentially expanded to include compounds containing hetero-atoms (e.g., nitrogen or sulfur),
218 once substantial sets of experimental values of T_g for such compounds become available.
219 Regarding the application in air quality and climate models, Eq. (1) can be applied in the
220 volatility basis set (VBS) (Donahue et al., 2006; Donahue et al., 2011) and the molecular
221 corridor approach (Shiraiwa et al., 2014; Li et al., 2016) to predict the T_g of SOA particles

(Shiraiwa et al., 2017), while the new parameterization may be suitable for coupling with the statistical oxidation model which characterizes the SOA evolution as a function of n_C and n_O (Cappa and Wilson, 2012; Jathar et al., 2015).

These parameterizations (Eqs. 1, 2) calculate T_g based on the elemental composition of organic compounds. SOA particles contain a number of organic compounds as well as a variable amount of liquid water, which has low T_g (136 K) and can act as a plasticizer (Mikhailov et al., 2009; Koop et al., 2011). Under humid conditions, SOA particles take up water by hygroscopic growth in response to RH, lowering T_g and viscosity of SOA particles. Estimations of T_g for SOA-water mixtures were discussed by Shiraiwa et al. (2017), who applied the Gordon-Taylor equation validated for a wide range of mixtures of organics, polymer, and water (Roos, 1993; Hancock and Zografi, 1994; Zobrist et al., 2008; Dette et al., 2014; Dette and Koop, 2015). Briefly, T_g of mixtures of SOA compounds under dry conditions ($T_{g,org}$) were calculated assuming the Gordon-Taylor constant (k_{GT}) of 1 (Dette et al., 2014): $T_{g,org} = \sum_i w_i T_{g,i}$, where w_i is the mass fraction of organic compound i, which can be derived using mass concentrations of SOA products. The Gordon-Taylor equation can also be applied to calculate T_g of organic-water mixtures considering the mass fraction of organics (w_{org}) in SOA particles (Koop et al., 2011):

$$T_g(w_{org}) = \frac{(1-w_{org})T_{g,w} + \frac{1}{k_{GT}} w_{org} T_{g,org}}{(1-w_{org}) + \frac{1}{k_{GT}} w_{org}} \quad (3)$$

w_{org} can be calculated using the mass concentrations of water (m_{H_2O}) and SOA (m_{SOA}) as $w_{org} = m_{SOA} / (m_{SOA} + m_{H_2O})$. m_{H_2O} can be estimated using the effective hygroscopicity parameter (κ) (Petters and Kreidenweis, 2007):

$$m_{H2O} = \frac{\kappa \rho_w m_{SOA}}{\rho_{SOA}\left(\frac{1}{a_w} - 1\right)} \quad (4)$$

The density of water (ρ_w) is 1 g cm^{-3}, the density of SOA particles (ρ_{SOA}) is assumed to be 1.2 g cm^{-3} (Kuwata et al., 2012), m_{SOA} is the total mass concentrations of SOA, and a_w is the water activity calculated as a_w = RH/100. Pajunoja et al. (2015) found that water uptake in subsaturated conditions is inhibited until RH is high enough for dissolution of water in SOA particles with relatively low O:C ratios. As oxidation of SOA increases, solubility of water increases and dissolution occurs at lower RH values. In both cases, the use of subsaturated hygroscopicity measurements was supported.

2.2 Viscosity

Temperature dependence of viscosity (η) was predicted using the modified Vogel-Tammann-Fulcher (VTF) equation (Angell, 1991):

$$\eta = \eta_\infty e^{\frac{T_0 D}{T - T_0}} \quad (5)$$

where η_∞ is viscosity at infinite temperature; T_0 is the Vogel temperature; T is the ambient temperature. The fragility parameter, D, characterizes how rapidly the dynamics of a material slow down as T approaches T_g, reflecting to what degree the temperature dependence of the viscosity deviates from Arrhenius behavior. When T is close to T_g ($T_g/T \approx 1$), smaller D values indicate that viscosity is sensitive to temperature change (fragile behavior); while larger D values indicate that viscosity is less sensitive to temperature change (strong or Arrhenius behavior).

Assuming η_∞=10^{-5} Pa s (Angell, 1991):

$$\log \eta = -5 + 0.434 \frac{T_0 D}{T - T_0} \quad (6)$$

When $T = T_g$, η = 10^{12} Pa s, which leads to (Angell, 1991; Angell, 2002):

$$T_0 = \frac{39.17\, T_g}{D + 39.17} \quad (7)$$

As can be seen in Eq. (5), both T_g and D are required to calculate η from Eq. (4) at a given temperature.

Figure 2 shows the T_g-scaled Arrhenius plot of fragility (viscosity versus T_g/T) referred to as an Angell plot (Angell, 1995). D values of organic compounds are typically in the range of ~5–30 (Angell, 1997). To estimate D values that could be applied to SOA compounds, we compiled measured fragility values. Fragility was often measured in the form of the fragility steepness index (m), which represents the slope of the Arrhenius plot at the point where $T = T_g$ (Boehmer et al., 1993). Compounds with lower m exhibit higher D values, indicating stronger glass formers. The measured m of 95 organic compounds are included in the Supplement. m can be converted to D using the following equation (see the full derivation of this equation in Appendix A):

$$D = \frac{665.89}{m-17} \quad (8)$$

Figure 3 shows the measured D as a function of (a) molar mass and (b) atomic O:C ratio of organic molecules. The molar mass exerts a stronger effect on fragility, while there is little dependence of D on the O:C ratio. As molar mass increases, D approaches a lower limit of 10.3 (± 1.7), consistent with the value of 10 used in our recent study (Shiraiwa et al., 2017). To evaluate the impact of the variations of D on viscosity prediction, sensitivity calculations were conducted as described in Sect. 3.

Besides the VTF equation, another commonly used equation for describing the temperature dependence of viscosity is the Williams-Landel-Ferry (WLF) equation: $\log\frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T-T_g)}{C_2+(T-T_g)}$, where empirical parameters C_1 and C_2 are adopted as 17.44 and 51.6 K, respectively (Williams et al., 1955; Schill and Tolbert, 2013; Wang et al., 2015). The two equations are

mathematically equivalent, both defined with respect to a reference temperature, and their parameters are related through $C_1 = \frac{DT_0}{2.303(T_g - T_0)}$ and $C_2 = T_g - T_0$. For the WLF equation, T_g is the reference temperature and there is a linear dependence assumed between temperature and free volume (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007). For the VTF equation, the reference is the Vogel temperature (T_0)–a hypothetical temperature at which all non-vibrational motion ceases and viscosity becomes infinite and the theoretical foundation of the VTF equation includes both thermodynamic and kinetic considerations (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007). The calculations of viscosity in this study are based mainly on the VTF equation and the difference between calculated results from the two equations will be briefly discussed in the following section.

3. Comparison of predicted viscosity with measurements

3.1. SOA formed from α–pinene and isoprene

The purpose of this section is to demonstrate that viscosity of SOA material can be predicted over a broad range of RH values from four parameters: T_g of dry SOA ($T_{g,org}$), fragility (D), hygroscopicity (κ), and the Gordon-Taylor constant for mixing SOA and water (k_{GT}). Viscosity of α-pinene SOA has been measured as a function of RH by several groups using multiple experimental techniques as shown in Fig. 4(a) (Abramson et al., 2013; Renbaum-Wolff et al., 2013; Kidd et al., 2014; Pajunoja et al., 2014; Bateman et al., 2015; Zhang et al., 2015; Grayson et al., 2016). The wide range of experimentally measured viscosities reported for α-pinene SOA, particularly from 30-60% RH is most likely a consequence of the different experimental approaches, mass loadings and O:C ratios for each experiment. For instance,

Grayson et al. (2016) used mass loadings of 121 to 14000 μg m^3 and observed that viscosity decreased as mass loading increased. Higher mass loadings would lead to greater partitioning of semi-volatile and lower molar mass compounds into the particle phase, which would lead to the decrease of T_g and viscosity of the resulting SOA mixture. They concluded that their results should be considered a lower limit for viscosity of α-pinene SOA in the atmosphere. It should also be noted that the viscosity measurements from Renbaum-Wolff et al. (2013) were for the water-soluble portion of the SOA. These datasets suggest that viscosity of α-pinene SOA approaches very high values (~>10^8 Pa s) below 20-30% RH and decreases with an increase in RH reaching a value of ~10 Pa s at 80% RH. As can be seen in Fig. 4(b), isoprene SOA is less viscous with $\eta < 10^6$ Pa s even under dry conditions, undergoing a phase transition from a semi-solid phase to a liquid phase at ~55% RH (Bateman et al., 2015; Song et al., 2015).

The solid lines with the shaded areas in Figure 4 are viscosity values predicted using $T_{g,org}$, D, κ, k_{GT}. $T_{g,org}$ values were adopted by Berkemeier et al. (2014) who estimated $T_{g,org}$ with the Boyer-Kauzmann rule using the melting point of representative SOA oxidation products. Note that Eq. (1) or (2) were not used to estimate $T_{g,org}$, which should be done in future studies by obtaining their elemental composition using high resolution mass spectrometry. For α-pinene, $T_{g,org}$ was assumed to be 278 K corresponding to an O:C ratio of 0.5 (Berkemeier et al., 2014), which is a typical O:C ratio of α-pinene SOA (Aiken et al., 2008; Chen et al., 2011; Putman et al., 2012).

The $T_{g,org}$ selected for isoprene SOA was 255 K, corresponding to the O:C ratio of 0.6. Although no measurements of the O:C ratio for the experimental isoprene SOA data were reported, Song et al. (2015) estimated O:C of 0.64-1.1 based on literature values. As O:C ratios are useful in estimating $T_{g,org}$, we encourage the measurement of the O:C ratio of SOA when

conducting viscosity measurements. In contrast to α-pinene SOA, there are limited viscosity measurements for isoprene SOA. While the predicted viscosity is consistent with the experimental data, comparison of our model predictions to additional measurements is strongly recommended. Song et al. (2015) prepared their samples in a potential aerosol mass (PAM) reactor while those investigated by Bateman et al. (2015) were generated in a smog chamber. It has been suggested that under ambient conditions, the majority of isoprene-derived SOA can be derived through heterogeneous interactions with acidic sulfate particles forming oligomers (Lin et al., 2013; Surratt et al., 2010; Gaston et al., 2014), which may increase viscosity. Further studies are warranted to compare laboratory-generated and ambient isoprene SOA, and to investigate the effect of the acidic seed on the viscosity.

For both α-pinene and isoprene SOA, D was set to 10 based on the analysis presented in Fig. 3(a). κ was set to 0.1 based on field and laboratory measurements (Gunthe et al., 2009; Lambe et al., 2011b; Pajunoja et al., 2014; Petters et al., 2017) and k_{GT} was assumed to be 2.5 (Zobrist et al., 2008; Koop et al., 2011). Using these parameters, the predicted viscosities match well the magnitude and the RH-dependence of the measured viscosity of α-pinene and isoprene SOA. Figure 4 also shows predicted viscosities (dotted lines) using the WLF equation, which shows similar values as the VTF equation, but slightly underestimates the viscosity of α-pinene SOA at low RH and overestimates the viscosity of isoprene SOA at high RH.

Sensitivity studies were conducted to examine the effects of $T_{g,org}$, D, κ and k_{GT}, on the calculated viscosity. In these studies, $T_{g,org}$ of α-pinene and isoprene SOA were varied within 229-328 K and 255-316 K, respectively, representing $T_{g,org}$ of different oxidation states (Berkemeier et al., 2014). D was varied between 5 and 30, which is the range characteristic for organic compounds (see Fig. 3a). κ of 0.05-0.15 were used for α-pinene and isoprene SOA

356 (Lambe et al., 2011b; Pajunoja et al., 2015). For the Gordon-Taylor constant, values of 2.5±1.5
357 were considered (Zobrist et al., 2008; Koop et al., 2011; Dette et al., 2014; Dette and Koop,
358 2015).

359 The effect of varying each parameter on the calculated viscosity of α-pinene SOA is
360 illustrated in Fig. 5. Variations of ±50 K in $T_{g,org}$ result in 3-6 orders of magnitude difference in
361 calculated values at dry conditions, indicating that $T_{g,org}$ is a critical parameter for viscosity
362 estimations. Decreasing D from 10 to 5 led to a decrease of calculated values by more than one
363 order of magnitude. The calculated results were within the upper limit of measurements when
364 increasing D from 10 to 20, and the predicted values were only slightly enhanced when further
365 increasing D from 20 to 30. Calculated values with variations in κ from 0.05 to 0.15 and k_{GT}
366 from 1.0 to 4.0 were all within the measured ranges.

367 For isoprene SOA, an increase of $T_{g,org}$ to 287 K, which represents a higher oxidation
368 state (Berkemeier et al., 2014), led to calculated values to be several orders of magnitude higher
369 than the upper limit of measurements (Fig. 6a). When $T_{g,org}$ reaches 316 K, isoprene SOA can
370 occur as a solid for RH lower than ~40%. Compared to α-pinene SOA, a variation in D has a
371 larger effect on the calculated viscosity (Fig. 6b). For a range of 5 - 30 for D, calculations with
372 the D value of 10 agreed well with the measurements, while other D values resulted in calculated
373 viscosity outside of the measured ranges. Figures 6c and 6d show that decreasing κ and k_{GT}
374 below the reference values, the predictions overestimate the measured η by one or two orders of
375 magnitude. The latter is most evident at RH > 60%, where the calculated values were higher than
376 the upper limit of measurements. Modeling results with κ and k_{GT} increasing to 0.15 and 4.0,
377 respectively, were within the lower limit of measurements.

The above comparison between the measured and predicted viscosity demonstrates that the method described in this study can reproduce reasonably well the measured RH-dependent viscosity of SOA formed from α-pinene and isoprene. The sensitivity calculations showed that $T_{g,org}$ contributed the most to the uncertainty in the viscosity estimates. Previous studies have shown that the experimental conditions such as particle mass concentrations (Grayson et al., 2016) and RH upon SOA formation (Kidd et al., 2014; Hinks et al., 2018) can impact chemical composition of SOA and hence the phase state and viscosity. Further efforts to constrain the uncertainties are needed both in experiments and parameterizations.

3.2. SOA formed from toluene

In this and the following sections, we examine the feasibility of calculating the value of $T_{g,org}$ from mass spectrometry data on SOA. Hinks et al. (2017) measured the elemental composition of toluene SOA using nanospray desorption electrospray ionization high-resolution mass spectrometry (nano-DESI-HRMS) (Roach et al., 2010a, b). Toluene SOA were formed by OH photooxidation in an aerosol smog chamber at <2% RH (mass loading = 23 μg m^{-3}) and 75% RH (mass loading = 8 μg m^{-3}) to investigate the effect of RH on the chemical composition of toluene SOA formed under low-NO_x conditions. Measurements revealed a significant reduction in the fraction of oligomers present in toluene SOA generated under high RH conditions compared to SOA generated under low RH conditions (Hinks et al., 2017). The detected molar mass of individual oxidation products spanned a range of 102 - 570 g mol^{-1} at high RH, which increased up to 726 g mol^{-1} at low RH.

Figure 7(a) shows the interdependence of glass transition temperature, volatility, and molar mass of the detected toluene SOA compounds. Glass transition temperatures were

calculated using Eq. (2). Saturation mass concentrations or volatilities of detected compounds were estimated from the elemental composition by using the parameterization of Li et al. (2016). The analysis is based on the molecular corridor approach—a two-dimensional framework of volatility and molar mass of SOA components constrained by boundary lines of low and high atomic O:C ratio, corresponding to *n*-alkanes (C_nH_{2n+2}, O:C = 0) and sugar alcohols ($C_nH_{2n+2}O_n$, O:C = 1), respectively (Shiraiwa et al., 2014; Li et al., 2016). The toluene SOA constituents are well constrained by the molecular corridor and T_g are higher for compounds with higher molar mass and lower volatility.

Eq. (1) was used to calculate T_g for individual compounds with $M < 450$ g mol^{-1}, while excluding compounds with molar mass higher than 450 g mol^{-1}. This approach was deemed reasonable as such high molar mass compounds account for < 10% of all toluene SOA products formed at low RH, and for < 2% formed at high RH. Eq. (2) was used to calculate T_g for all the detected compounds. T_g of dry toluene SOA ($T_{g,org}$) was then computed using the Gordon-Taylor approach with $k_{GT} = 1$ (Sect. 2.1). The relative mass concentrations of individual components were assumed to be proportional to their relative abundance in the nano-DESI-HRMS spectrum. This assumption has a number of caveats (Bateman et al., 2012; Nguyen et al., 2013), and as we will see below, it results in deviations between the predicted and measured viscosity. Table 2 summarizes the results of such calculations, showing that the $T_{g,org}$ by Eq. (1) – excluding high molar mass compounds – is about 10 K lower as compared to $T_{g,org}$ by Eq. (2). $T_{g,org}$ at low RH is predicted to be higher than $T_{g,org}$ at high RH, which results from a lower abundance of high molar mass compounds observed at high RH. This trend is consistent with Kidd et al. (2014), who showed that SOA material formed under dry conditions is more viscous than that formed under wet conditions.

Figure 7(b) shows the predicted viscosity of toluene SOA as a function of RH, as compared to the measured viscosity of toluene SOA formed in an oxidation flow reactor at 13% RH (Song et al., 2016a). Indirect viscosity measurements are also included in shaded boxes (Bateman et al., 2015; Li et al., 2015). Lines with shaded areas are calculated viscosities using $T_{g,org}$ as described above. κ was assumed to be 0.25 based on laboratory measurements (Lambe et al., 2011a; Hildebrandt Ruiz et al., 2015). To achieve good fit, D was set to 13 and k_{GT} was assumed to be 3.0 (Dette et al., 2014). Estimations with Eq. (1) match the measured viscosity values very well over the entire RH range. Predictions with Eq. (2) overestimated the measurements by one or two orders of magnitude at moderate RH between 30% and 50%, while they agreed with the measurements derived at RH $\geq$ 60% and at the dry conditions.

There are several possible reasons for the difference between the measurements and predictions. First, the relative abundance of high molar mass compounds observed in HRMS measurements may be overestimated, as high molar mass compounds tend to have higher (yet generally unknown) ionization efficiencies compared to lower molar mass compounds. Second, the nano-DESI-HRMS analysis of toluene SOA was limited to m/z range of 100 -1000 (Hinks et al., 2017). It is possible that some SOA products with lower molar mass were present in particles but not detected, which would lead to an overestimation of T_g. Third, the chemical composition of toluene SOA are likely different between Hinks et al. (2017) and Song et al. (2016) because of the differences in the experimental conditions. Specifically, toluene SOA was formed in a Teflon chamber in Hinks et al., while Song et al. used an oxidation flow reactor to generate toluene SOA. The O:C ratios are 0.71 at low RH and 0.63 at high RH based on nano-DESI-HRMS measurements in Hinks et al. (2017), while it was 1.06 based on the aerosol mass spectrometry (AMS) measurements in Song et al. (2016).

In addition, different mass loadings may have affected viscosity. Song et al. (2016) measured viscosity at two different mass loadings (60-100 and 600-1000 μg m^{-3}) and compared their results to Bateman et al. (2015) (30-50 μg m^{-3}) and Li et al. (2015) (44-125 μg m^{-3}), observing little impact of mass loadings on viscosity. We carried out a sensitivity study of mass loadings on viscosity using a set of compounds detected by HRMS. The saturation mass concentration was predicted for each component using the molecular corridor approach (Li et al., 2016). Assuming that the mass signal intensity is proportional to the total mass concentration of the compound in the mixture, and applying the absorptive partitioning theory (Pankow, 1994), particle-phase concentrations of each compound were predicted to estimate T_g at different organic aerosol mass loading values (1-1000 μg m^{-3}). The glass transition temperature of the SOA mixture decreases as mass loading increases. Viscosity decreases up to two orders of magnitude at low RH, while at high RH they have little difference as shown in Fig. A3. Simultaneous measurements of viscosity and chemical composition with different mass loadings should be performed in future studies.

3.3 Biomass Burning Particles

To further explore the applicability of our viscosity prediction method using elemental composition as measured by HRMS, we performed similar calculations for biomass burning organic particles emitted from test facility burns of subalpine fir and lodgepole pine trees, conducted as a part of the FIREX 2016 campaign (Selimovic et al., 2017). These samples were analyzed by HRMS using two different ionization sources: electrospray ionization (ESI) and atmospheric pressure photoionization (APPI). Mass spectra shown in Fig. 8(a) and (b) indicate that a substantial number of compounds were detected by both methods (109 and 170

compounds for subalpine fur and lodgepole pine, respectively). However, pronounced differences are also observed between the ESI and APPI spectra both in terms of the identity and signal intensities of the detected compounds.

Glass transition temperatures for the assigned CH and CHO compounds were computed using Eq. (2). Nitrogen and sulfur containing compounds (CHON and CHOS) are not yet covered by Eq. (2) and were therefore excluded from the analysis. CHON and CHOS compounds comprised less than 10% of the detected ion intensity and <15% of the assigned compounds. Please note that we do not intend to provide accurate estimates of ambient biomass burning particles (as inorganic components are also not included in this analysis), but we investigate how the use of different ionization methods would lead to variations in our viscosity predictions. T_g of organic mixtures ($T_{g,org}$) were then calculated using the Gordon-Taylor approach with k_{GT} = 1, assuming that the relative concentration of each compound is proportional to its MS signal intensity. The calculated $T_{g,org}$ values for the mixtures are specified in the legend of Figure 9. For both types of mixtures, the calculated $T_{g,org}$ for the APPI MS data is lower than the value calculated based on the ESI MS data with a difference of 32 K for subalpine fir and 11 K for the lodgepole pine. Figure 9 shows the predicted viscosity as a function of RH, assuming D = 10, κ = 0.10 and k_{GT} = 2.5. The difference in $T_{g,org}$ derived from ESI and APPI results in a variation of predicted viscosity at low RH by up to five and two orders of magnitude for subalpine fir and lodgepole pine, respectively.

The difference in the calculated $T_{g,org}$ values is attributed to the chemical profile of the species detected using different ionization techniques as shown in mass spectra in Fig. 8(a) and (b). Van Krevelen diagrams in Fig. 8(c) and (d) illustrate these compositional differences between chemical species detected by ESI and APPI. ESI is more efficient at detection of polar

493 compounds (Kiontke et al., 2016), which typically have higher O:C ratios and therefore would
494 result in higher predicted values of viscosity (Koop et al., 2011; Saukko et al., 2012). APPI
495 enables the detection of nonpolar compounds with lower O:C ratios, in particular polycyclic
496 aromatic hydrocarbons (PAHs), that have low ionization efficiencies when analyzed by ESI MS
497 (Raffaelli and Saba, 2003; Itoh et al., 2006). Due to the complementary nature of these ionization
498 methods, it is most likely that the actual glass transition temperature and viscosity of each type of
499 SOA are somewhere in between the values inferred from ESI and APPI data sets: ESI MS may
500 be viewed as providing the upper limit of viscosity, while APPI MS gives the lower limit. Our
501 results indicate that the use of complementary ionization techniques may help evaluate the
502 associated uncertainty for the prediction of viscosity values based on the elemental composition
503 as measured by HRMS.
504
505 **4 Conclusions**
506 We have developed a parameterization for calculation of the glass transition temperature
507 of individual SOA compounds with molar mass up to ~1100 g mol^{-1} using the number of carbon,
508 oxygen, and hydrogen atoms. Viscosity of SOA was estimated using the T_g-scaled Arrhenius plot
509 of viscosity versus T_g/T and the Gordon-Taylor approach to account for mixtures of SOA and
510 water. The fragility parameter D was compiled for organic compounds and we found that D
511 approaches a lower limit of ~10 (+/- 1.7) as the molar mass increases. The resulting viscosity
512 estimations agree well with measured viscosity of α-pinene and isoprene SOA, validating our
513 method. Using HRMS data, glass transition temperatures of individual components and viscosity
514 of toluene SOA were predicted, also resulting in a good agreement with measurements.
515 However, we note that the predicted viscosities were slightly higher than the measured values

516 suggesting that additional considerations may need to be taken into account. For example, the
517 ionization efficiency of both low and high molar mass compounds may have a pronounced effect
518 on the relative abundance of different classes of compounds in HRMS data. The viscosity
519 prediction method was also applied to biomass burning particles, whose elemental composition
520 was measured using HRMS with two different ionization techniques. Substantial differences in
521 viscosity estimations were obtained using ESI and APPI mass spectra.

522 Figure 10 summarizes the predicted range of viscosity of α-pinene SOA, isoprene SOA,
523 toluene SOA, and biomass burning particles. Isoprene SOA has lower viscosity, reflecting lower
524 glass transition temperature due to relatively low molar mass of isoprene oxidation products. α-
525 pinene and toluene SOA have much higher viscosity with a different shape of the RH
526 dependence due to differences in glass transition temperatures and hygroscopicity. Biomass
527 burning particles have moderate viscosity between the two extreme cases. Currently, both
528 predictions and measurements are subject to large uncertainties and variations. Complementary
529 measurements of viscosity and chemical composition employing different ionization techniques
530 are desired to further constrain RH-dependent viscosity in future studies. Current T_g
531 parameterizations do not consider functionality or molecular structure explicitly and further
532 measurements of T_g and viscosity of SOA would allow us to refine the method presented in this
533 study. Nevertheless, current results offer a promising starting point and such simple
534 parameterizations are practical for predicting viscosity of particles as measured by HRMS. The
535 developed viscosity prediction method should also be useful in recent efforts of simulating the
536 distribution of SOA phase state and related properties in regional or global air quality models
537 (e.g., Maclean et al., 2017; Shiraiwa et al., 2017).
538

Appendix A: Conversion of fragility steepness index (*m*) to fragility (*D*)

Fragility steepness index (m) is defined as:

$$m = \lim_{T \to Tg} \frac{d\, log\eta}{d(T_g/T)} \tag{A1}$$

Combining Eq. (A1) with Eq. (4) gives:

$$m = \lim_{T \to Tg} \frac{d}{d(T_g/T)} \left(-5 + 0.434 \frac{T_0 D}{T - T_0} \right) \tag{A2}$$

Considering that $\eta = 10^{12}$ Pa s at $T = T_g$ (Angell, 1991), and by defining Δx = 1- T_g/T, and a combination with Eq. (5) leads to:

$$m = \lim_{\Delta x \to 0} \frac{1}{\Delta x} \left(12 - \left(-5 + 0.434 \frac{\frac{39.17\, T_g}{D + 39.17} D}{\frac{T_g}{1 - \Delta x} - \frac{39.17\, T_g}{D + 39.17}} \right) \right)$$

$$= \lim_{\Delta x \to 0} \frac{1}{\Delta x} \left(17 - 0.434 \frac{39.17 T_g D (1 - \Delta x)}{D T_g + 39.17 T_g \Delta x} \right)$$

$$= \lim_{\Delta x \to 0} \frac{(665.89 + 17D)}{(D + 39.17\Delta x)}$$

$$= \frac{665.89 + 17D}{D} \tag{A3}$$

Note that Eq. (A3) is derived assuming the high temperature limit of viscosity η_∞ is equal to 10^{-5} Pa s (Angell, 1991) in the VTF equation (Eq. 3). Similar equations for the relation between *m* and *D* were given by previous studies using different η_∞ and units (Angell et al., 1994; Angell, 2002; Bones et al., 2012) and applying those gave very similar results in our study.

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Table 1. Composition classes and the n_C^0 and b values (K) for glass transition temperature parameterizations obtained by least-squares optimization using the measurements compiled in Koop et al., (2011), Dette et al., (2014) and Rothfuss and Petters (2017).

Classes	n_C^0	b_C	b_H	b_{CH}	b_O	b_{CO}
CH	1.96 (±1.81)	61.99 (±53.65)	–113.33 (±44.47)	28.74 (±20.86)		
CHO	12.13 (±2.66)	10.95 (±13.60)	–41.82 (±14.78)	21.61 (±5.30)	118.96 (±9.72)	–24.38 (±4.21)

Table 2. Glass transition temperatures calculated using Eq. (1) and (2) for toluene SOA mixtures at low relative humidity (low RH < 2%) and high relative humidity (high RH = 75%) conditions.

$T_{g,org}$ (K)	low RH	high RH
Equation (1)*	299	295
Equation (2)	313	303

* Compounds with M > 450 g mol^{-1} were excluded from the analysis.

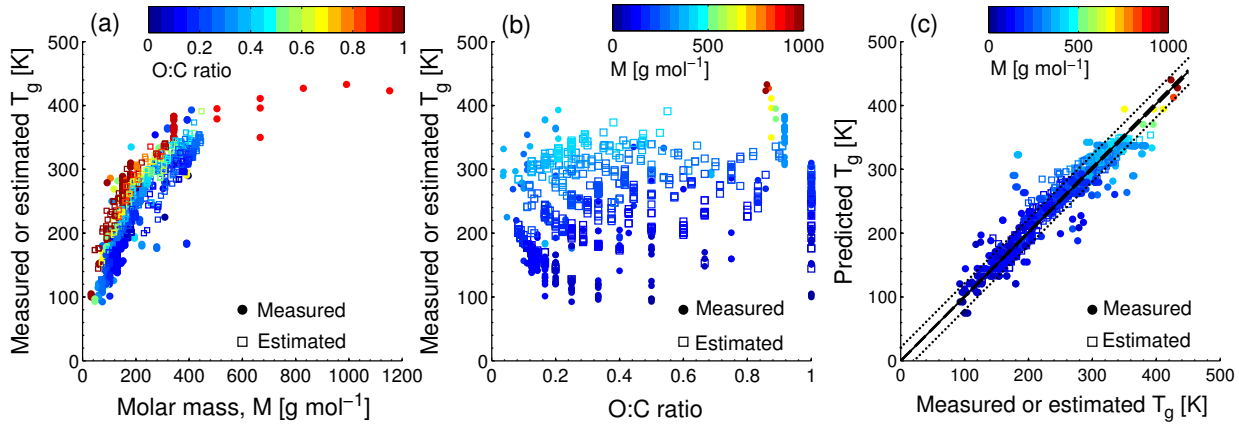


Figure 1. Characteristic relationships between molecular properties and the glass transition temperature (T_g) of organic compounds. (a) T_g of organic compounds as measured (circles) and estimated with the Boyer-Kauzmann rule (squares) plotted against molar mass. The markers are color-coded by atomic O:C ratio. (b) Measured (circles) and estimated (squares) T_g of organic compounds plotted against O:C ratio. The markers are color-coded by molar mass. (c) Predicted T_g for CHO compounds using a parameterization (Eq. 2) developed in this study compared to measured (circles) and estimated T_g by the Boyer-Kauzmann rule (squares). The solid line shows 1:1 line and the dashed and dotted lines show 68% confidence and prediction bands, respectively.

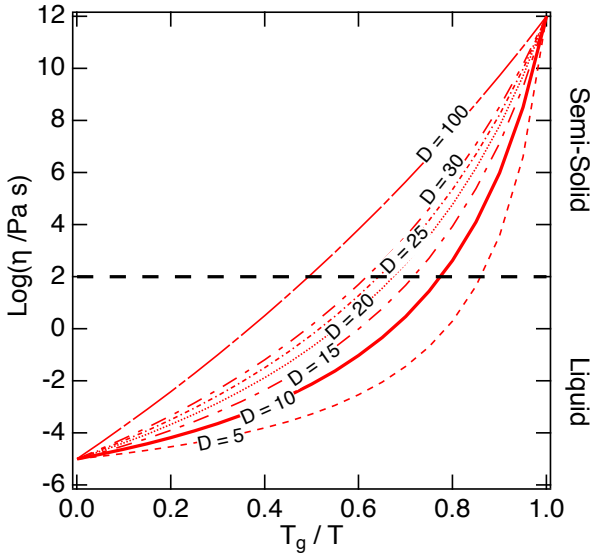


Figure 2. The Angell plot of viscosity (η) vs. T_g/T. The lines represent different fragility parameter (D) values in the range of 5 - 100, with D = 10 (the solid line) used as a base case for this study. A large fragility parameter value is associated with a strong glass former, while fragile materials are associated with lower values. The black dashed line at viscosity of 10^2 Pa s indicates the approximate threshold between liquid and semi-solid states.

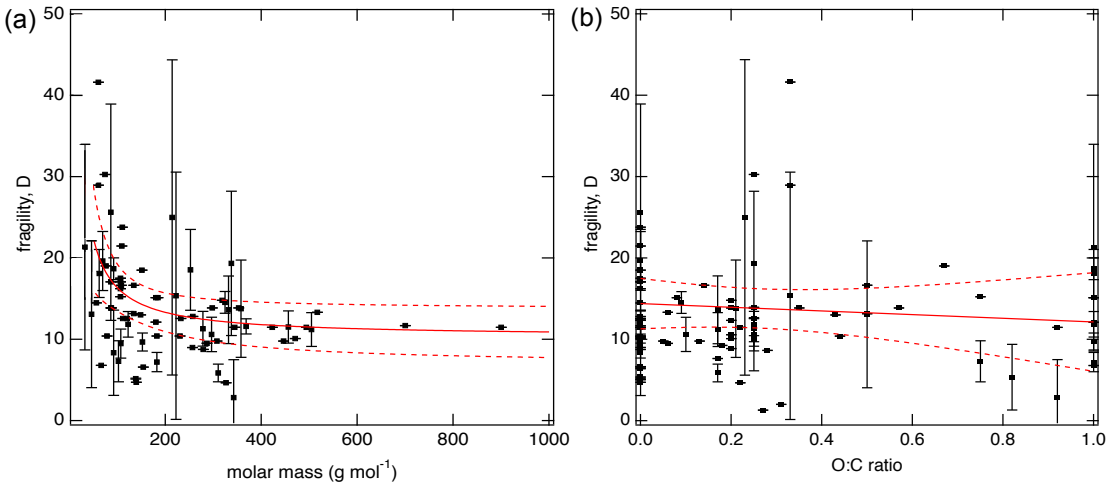


Figure 3. Fragility parameter of organic compounds (D) plotted against (a) molar mass and (b) atomic O:C ratio. Error bars are standard deviations. The solid red lines represent the fitted curves with fitted equations for (a) $D = 602.6/M + 10.3$ and (b) $D = 14.4 - 2.3(\mathrm{O{:}C})$ respectively. Dashed red lines indicate the 95% confidence band.

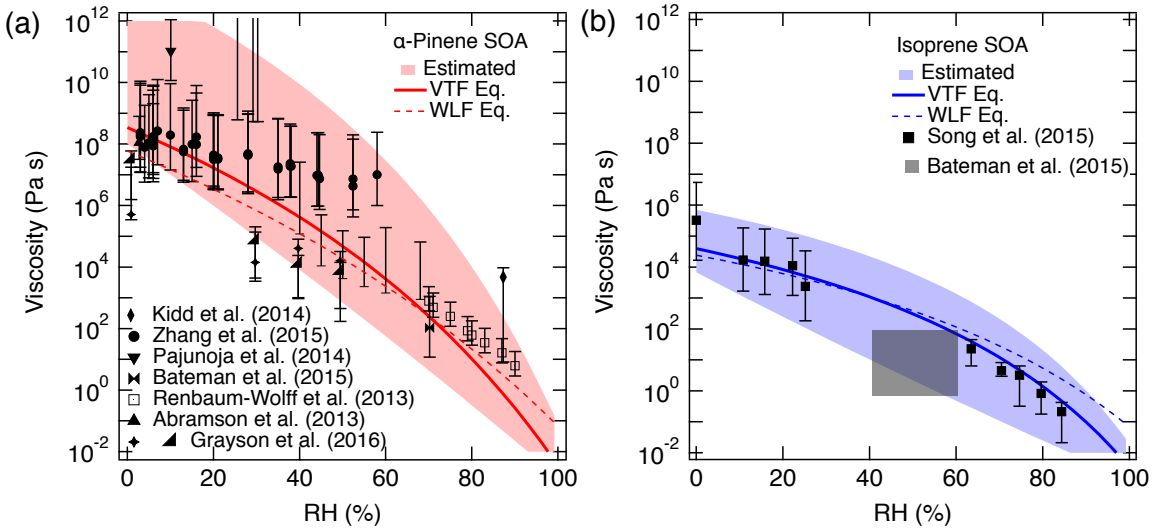


Figure 4. Comparison of measured and predicted viscosity of (a) α-pinene SOA and (b) isoprene SOA at 295 K as a function of RH. The solid lines represent base simulations with the VTF equation, while the dotted line represents viscosity predicted using the WLF equation [parameters: glass transition temperature of dry SOA ($T_{g,org}$), fragility (D), hygroscopicity (κ) and Gordon-Taylor constant (k_{GT})]: (a) 278.5 K, 0.1, 10 and 2.5; (b) 255 K, 0.1, 10 and 2.5. The shaded regions were determined by varying these parameters (a) upper (lower) limit: $T_{g,org}$ = 300 K (278.5 K), κ = 0.1 (0.1), D = 20 (10), k_{GT} = 2.5 (2.0); (b) upper (lower limit): $T_{g,org}$ = 255 K (255 K), κ = 0.10 (0.15), D = 15 (8), k_{GT} = 2.5 (4.0). Panel (a): Renbaum-Wolff et al. (2013) data represents viscosity for water-soluble portion of SOA; Grayson et al. (2016) data in the panel (a) represents two different mass loadings (121 μg m^{-3}; 520 μg m^{-3}). Panel (b): The gray box in panel (b) represents estimated viscosity based on bounce measurements of Bateman et al. (2015).

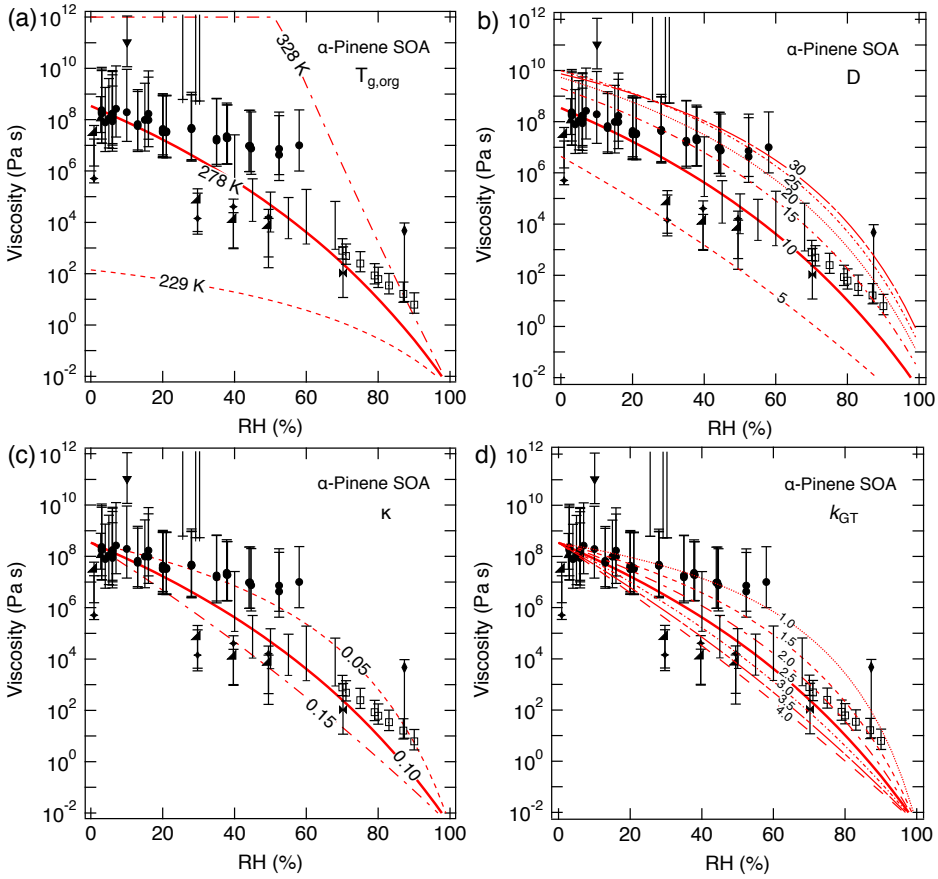
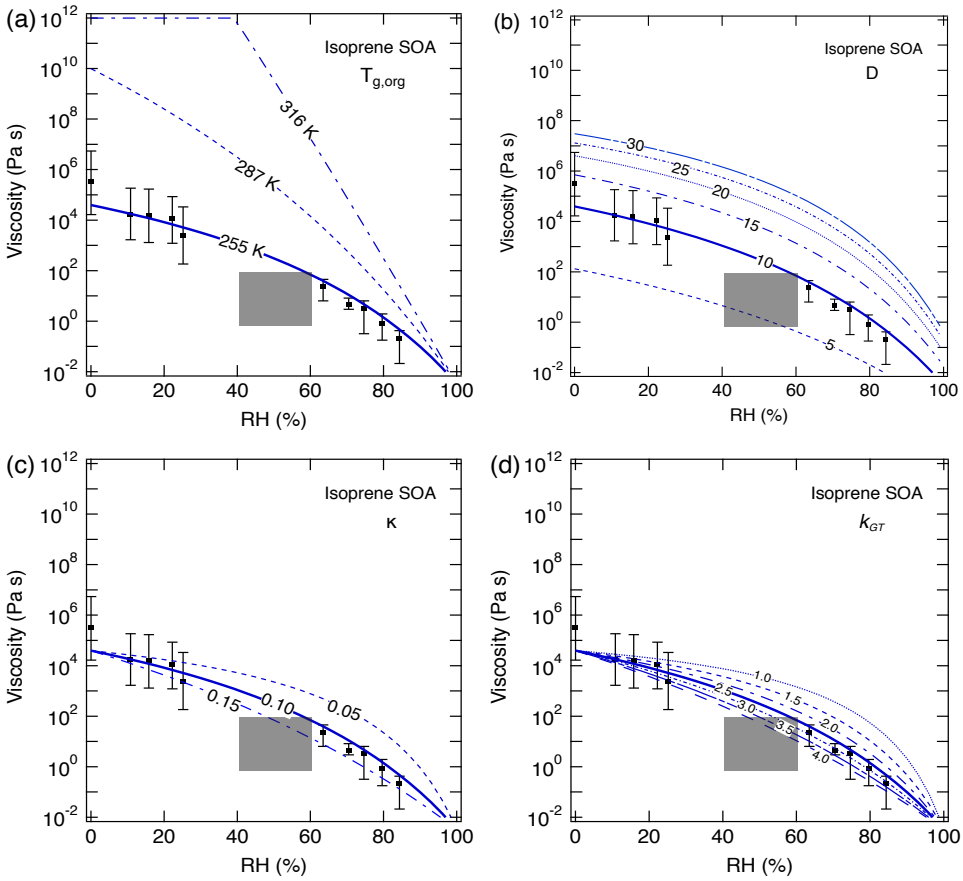


Figure 5. Sensitivity calculations for viscosity of α-pinene SOA at 295 K as a function of RH by varying: (a) glass transition temperature of dry SOA ($T_{g,org}$), (b) fragility (D), (c) hygroscopicity (κ), and (d) Gordon-Taylor constant (k_{GT}).



952
953
954 **Figure 6.** Sensitivity calculations for viscosity of isoprene SOA at 295 K as a function of RH by
955 varying: (a) glass transition temperature of dry SOA ($T_{g,org}$), (b) fragility (D), (c) hygroscopicity
956 (κ), and (d) Gordon-Taylor constant (k_{GT}). Data points are measured viscosity by Song et al.
957 (2015) and the gray box represents estimated viscosity based on bounce measurements of
958 Bateman et al. (2015).
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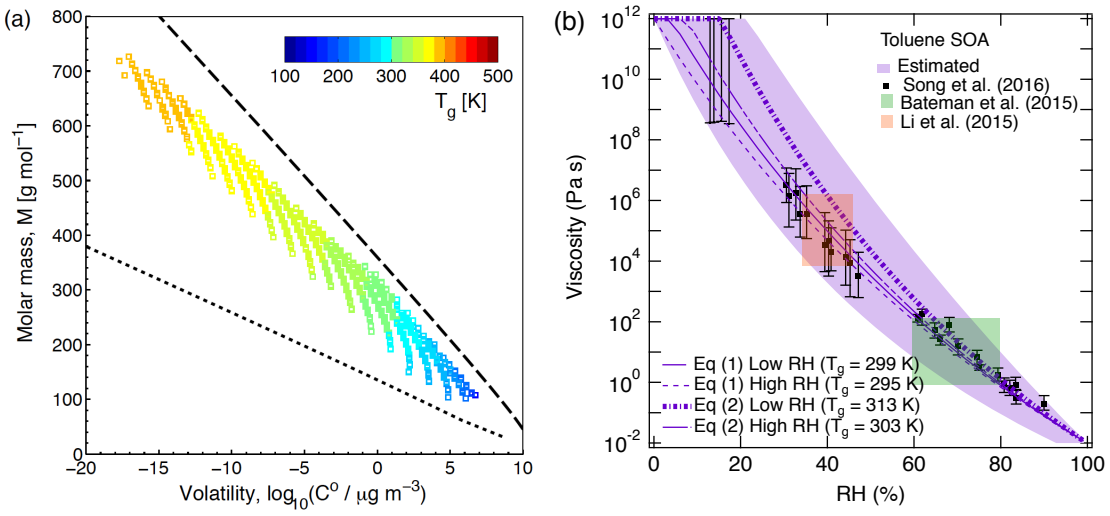

Figure 7. (a) Molecular corridor of molar mass plotted against volatility of toluene SOA formed under dry conditions (Hinks et al., 2017) color-coded by glass transition temperature (T_g) estimated using Eq. (2). The upper dashed line indicates the low O:C bound of the molecular corridor (linear alkanes C_nH_{2n+2} with O:C = 0), and the lower dotted line indicates the high O:C bound (sugar alcohols $C_nH_{2n+2}O_n$ with O:C = 1). (b) Comparison of measured (markers) and modeled (lines) viscosity of toluene SOA at 295 K as a function of RH. Viscosities were calculated using fragility (D) of 13, the hygroscopicity (κ) of 0.25 and the Gordon-Taylor constant (k_{GT}) of 3.0 with different glass transition temperatures of dry SOA ($T_{g,org}$) as estimated using Eq. (1) or (2) under low and high RH conditions. The shaded regions were calculated by varying those parameters: $T_{g,org}$ = 313 K (295 K), κ = 0.20 (0.25), D = 13 (10), k_{GT} = 2.5 (3.5) for the upper (lower) limit. Mass loadings were 23 μg m^{-3} for LRH and 8 μg m^{-3} for HRH (Hinks et al., 2017).

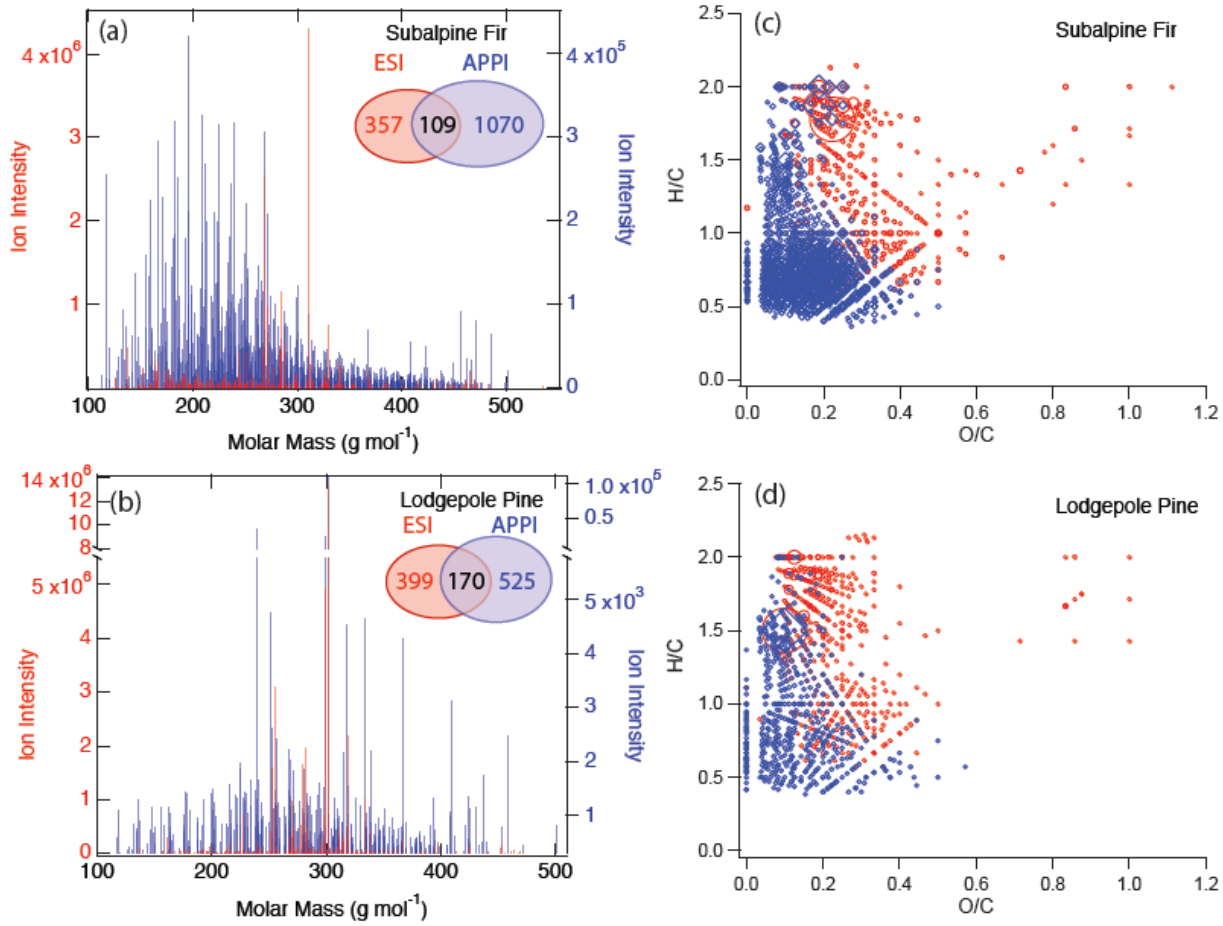

Figure 8. Mass spectra of biomass burning organic particles collected from test burns of (a) subalpine fir and (b) lodgepole pine as measured by high resolution mass spectrometry with two ionization techniques: electron spray ionization (ESI, red) and atmospheric pressure photoionization (APPI; blue). Numbers of elemental formulas identified by ESI (red), APPI (blue) and both modes (black) are also specified. Van Krevelen plots of the compounds identified by ESI (red) and APPI (blue) mode in BBOA from burning of (c) subalpine fir and (d) lodgepole pine.

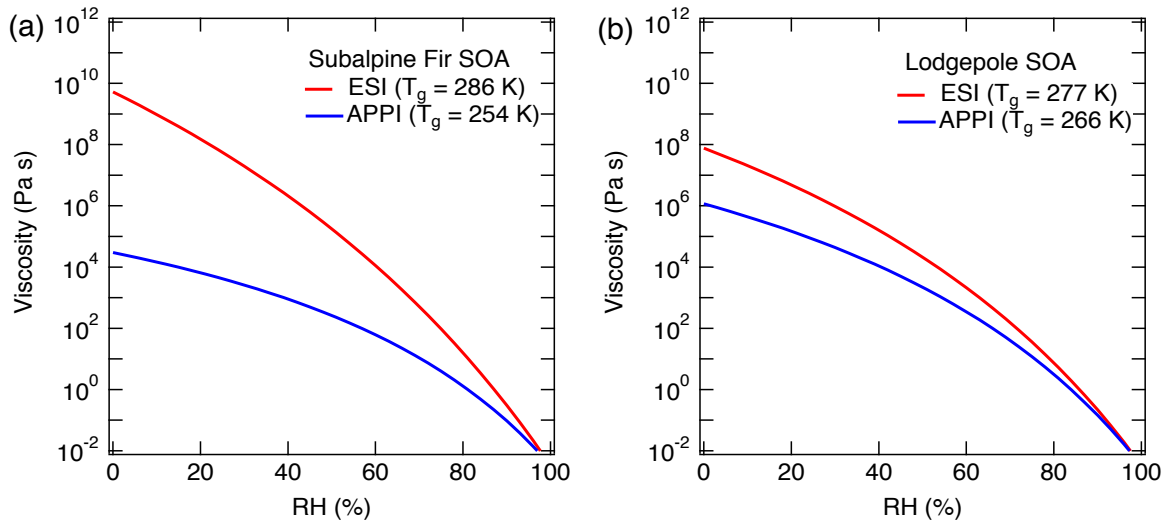

Figure 9. Predicted viscosity for biomass burning particles of (a) subalpine fir and (b) lodgepole pine trees as measured by high resolution mass spectrometry with two ionization techniques: electrospray ionization (ESI, red) and atmospheric pressure photoionization (APPI; blue). $T_{g,org}$ are specified in the figure legend and other used parameters are fixed to $\kappa = 0.1$, $D = 10$, $k_{GT} = 2.5$.

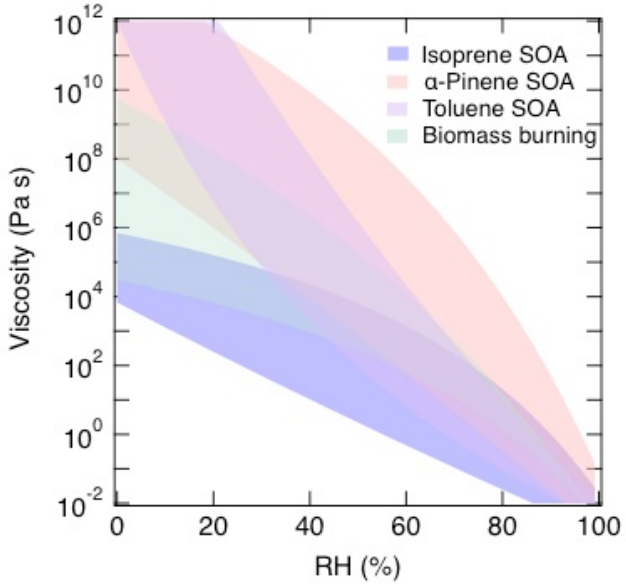

Figure 10. Summary of predicted range of viscosity of α-pinene SOA (red), isoprene SOA (blue), toluene SOA (purple), and biomass burning particles (green).

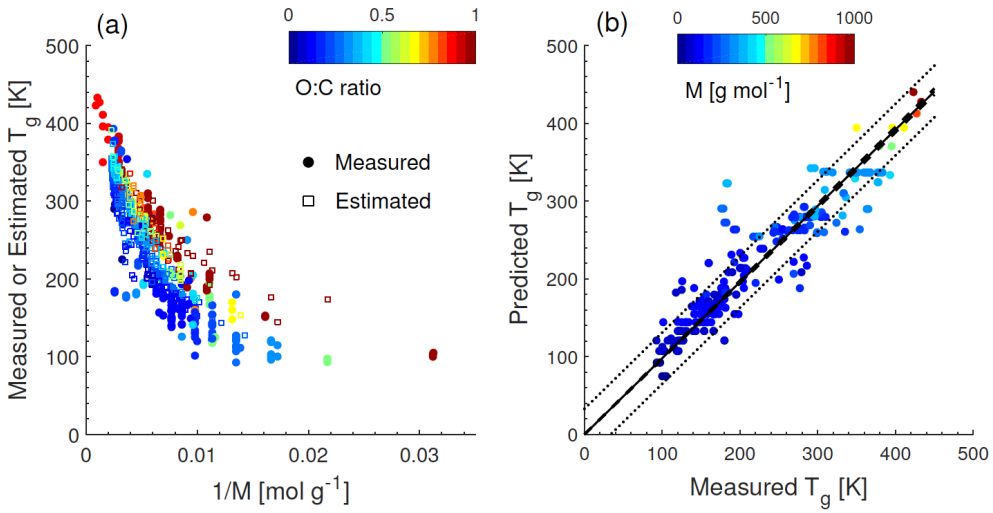

Figure A1. (a) T_g of organic compounds as measured (circles) and estimated with the Boyer-Kauzmann rule (squares) plotted against the inverse molar mass. The markers are color-coded by atomic O:C ratio. (b) Predicted T_g for CHO compounds using a parameterization (Eq. 2) developed in this study compared to measured T_g (circles). The solid line shows 1:1 line and the dashed and dotted lines show 68% confidence and prediction bands, respectively.

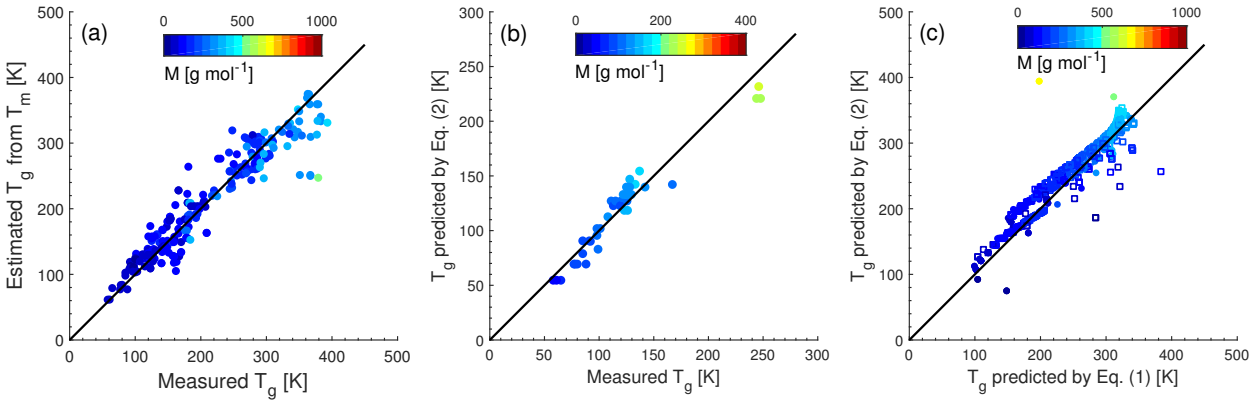

Figure A2. (a) Comparison of measured and estimated T_g by the Boyer-Kauzmann rule for 251 organic compounds (Koop et al., 2011; Dette et al., 2014; Rothfuss and Petters 2017) with their measured T_m available. The markers are color-coded by molar mass. (b, c) Predicted T_g using Eq. (2) compared with (b) measured T_g for CH compounds and (c) predicted T_g using Eq. (1) for CHO compounds. The solid line shows 1:1 line. Solid circle markers represent organic compounds as compiled in Koop et al. (2011) and open square marker represent SOA oxidation products in Shiraiwa et al. (2014) in panel (c).

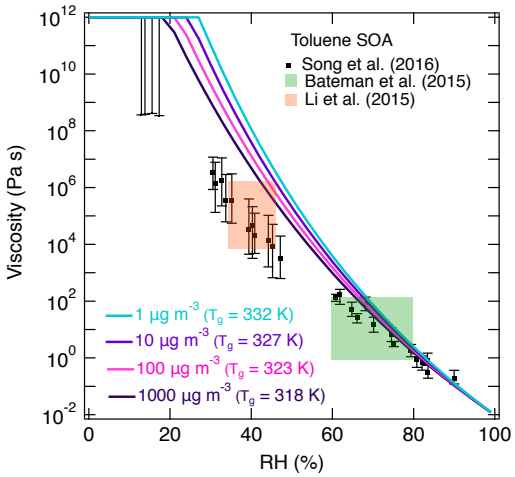

Figure A3. Effect of mass loading on predicted viscosity for toluene SOA. Solid lines represent the predicted viscosity with Eq. (2) using chemical composition of toluene SOA formed at low RH. Viscosity was predicted with different mass loadings ranging from 1-1000 μg m^{-3}. Markers and shaded boxes represent experimentally measured viscosity values. Song et al. (2016) mass loadings were 60-100 and 600-1000 μg m^{-3}. Bateman et al., (2015) and Li et al., (2015) mass loadings were 30-50 μg m^{-3} and 44-125 μg m^{-3}, respectively.