

## 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<sup>-1</sup>. 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<sup>-1</sup> 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 ( $M > 450 \text{ g mol}^{-1}$ ) 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  $M > 450 \text{ g mol}^{-1}$ ."*

*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 ( $\kappa$ ), fragility and Gordon-Taylor constant ( $k_{GT}$ ). Especially  $T_{g,dry}$  and  $\kappa$  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  $\alpha$ -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  $M > 450 \text{ g mol}^{-1}$  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  $M > 450 \text{ g mol}^{-1}$ .”*

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.