Response to the comments of Anonymous Referee #2

Referee General Comment: The manuscript by Li et al. extends the previous parameterizations of the glass transition temperature (T_g) based on the vapor pressure of a large number of pure organic compounds. The authors explore several parameterizations and use them to estimate ambient organic aerosol viscosity. The diversity of parameterizations is useful but can be distracting form the take-home message of the manuscript. After revisions of the modeling description and discussion section, this manuscript should be published. On the content of the manuscript, the main points I take away are the new parameterizations and their modeling of ambient data. Some of the details presented deviate from this main narrative (i.e., multiple FIGAERO-CIMS analysis), so even though the details may be necessary for the calculations, they distract from the narrative. I would suggest putting details that are not key to manuscript narrative into the supplemental information, which will help improve the message of the manuscript.

Response: We thank Referee #2 for the review and the positive evaluation of our manuscript. To improve the presentation quality, we divide the Method section into three subsections and keep the main parameterization predicting the glass transition temperature as a function of volatility in the main text. We move other parameterizations and related comparisons to the Appendix to focus the narrative of the manuscript.

Referee Major Specific Comment:

1. Parameterizations section: This section needs subsections to delineate the different models. Also tell the reader which of these parameterizations is most important to focus on for the rest of the paper. Or you could add an introduction paragraph to this section, where you discuss the merits of each model parameterizations. A revision along those lines would help focus the narrative of the manuscript.

Response: In the revised manuscript we move the parameterizations predicting T_g as a function of elemental compositions to Appendix A; the comparison of T_g predictions with Zhang et al. (2019) to Appendix B. We divide the Method section into three subsections as below:

"2.1 Dataset of glass transition temperature"

Section 2.1 describes the training dataset used to develop parameterizations and the test dataset used to validate the parameterizations predicting T_g of SOA components. This section also addresses the uncertainty in the input data. Please refer to our responses to the comment 3 from the Referee 1.

"2.2 Parameterizations of T_g as a function of volatility"

"2.3 Predictions of T_g and viscosity of organic aerosols"

2. Figure 1-3: These Figures do not stand apart very well, and conceptually blur. If you delineate the parameterizations more, that will help in understanding the importance of each Figure. To me, Figures 1b and 1c convey similar information (i.e., good predictive behavior), so show one and put the other in the SI. The O:C ratio coloring could be removed (since the lack of correlation could just be stated in the text) and instead color

by functional group. Figure 3 could be replaced in a table that summarizes the AAVRE and R-squared values.

Response: The resolution of the figures has been improved. We keep both Fig. 1b and 1c in the main text as the dataset in Fig. 1b is same as the points in Fig. 1a, which were used to develop the parameterizations (training dataset). The points in Fig. 1c were used as the test dataset to validate the performance of the parameterizations predicting T_g of SOA components. In the revised manuscript we add a new subsection 2.1 describing the training dataset and the test dataset. Please also refer to our response to the comment 3 of Referee 1. We keep the markers in Fig.1 color-coded by the O:C ratio. We add the following sentences in the revised main text to state the reason:

Line 160-162: "Note that a tight correlation between T_g and the O:C ratio has been observed for oxidation products formed from specific precursors including *α*-pinene (Dette et al., 2014), *n*-heptadecane and naphthalene (Saukko et al., 2012)".

Following your suggestion, we added Fig. S2a showing the dependence of T_g on C^0 with markers color-coded by chemical composition:

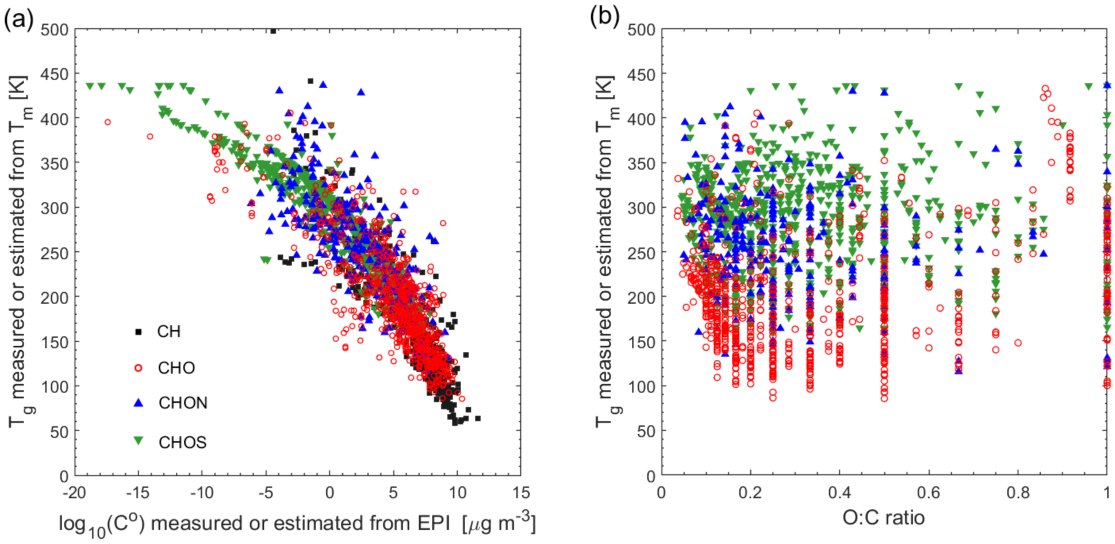

Figure S2. T_g of organic compounds in the training dataset plotted against (a) pure compound saturation mass concentration (C^0) and (b) the atomic O:C ratio.

We move the Fig. 3 in the ACPD to the Appendix B. We keep this figure as it is necessary to show the comparison of our parameterizations with the parameterization in Zhang et al. who also related T_g to volatility (they used the vapor pressure instead of the saturation mass concentration).

3. Field Observations: Line 259: I suggest adding a sentence motivating why Figure 4 is shown and what the reader will gain from it. I take away that viscosity can be estimated from C^* measurements and ambient OA spans solid to liquid states depending on the method used, was that the main message?

Response: Yes, correct. We have added the following sentence:

Line 253-255: "In this section we predict glass transition temperatures and phase state of ambient OA during the SOAS campaign which took place in the southeastern

United States (Centreville, Alabama) in summer 2013 (Carlton et al., 2018)".

4. Line 286: The discussion of the FIGAERO-CIMS analysis can be shortened, as the main point starts at Line 312.

Responses: We re-arrange this paragraph by stating the main point at the beginning, moving the less credible $T_{g,org}$ values calculated from the "Formulas" and "Partitioning" methods to another paragraph:

Lines 260-263: "Figure 2 shows that $T_{g,org}$ of total OA (TOA) range from 232 K to 334 K, depending on volatility distributions measured by different methods, while the most credible predicted $T_{g,org}$ values span in the range of 313 – 330 K. The reasons are stated below by comparing the different methods deriving the C^* distributions".

Lines 283-285: "The lower $T_{g,org}$ values (< 280 K) calculated from the C^* distributions estimated from the "Formulas" and "Partitioning" methods (Stark et al., 2017) are less atmospherically relevant".

Lines 303-308: "These analyses indicate that the volatility distributions derived from different methods, even when based on the same measurements, significantly affect the predicted $T_{g,org}$, and the most atmospherically relevant volatility distributions should be carefully chosen to reasonably predict the glass transition temperature of ambient OA. In summary, the $T_{g,org}$ values during the SOAS campaign should be in the range of 313 – 330 K".

5. The added value of Figure 8 seems to be limited. If the goal is to show how well the CTM model output and your T_g models agree, this is not the ideal way to show that. It would be clearer to pull the viscosity values for each of the 11 sites from the CTM output and make a scatter plot vs. the measurement derived viscosities. The actual global distributions are irrelevant for this comparison, and instead, point the reader to the Shiraiwa et al. (2017) paper.

Response: Following your suggestion, we have added the scatter plot (Fig. 6b in the revised manuscript). We keep the global distributions as Fig. 6a, as global distributions of viscosity are new and were not included in Shiraiwa et al. (2017). We edited the main text as follows:

Line 449-452: "the amorphous solid or semi-solid phase occurs over relatively dry areas, including the sites in western US, Mexico City, Beijing and coastal sites in Greece; the lower viscosity occurs in southeastern US and Paris".

Line 464-467: "Similar cases are observed in Athens and the two sites in the western US, that our predictions based on volatility distributions indicate the glassy phase state while the global model predicts the occurrence of a semi-solid phase".

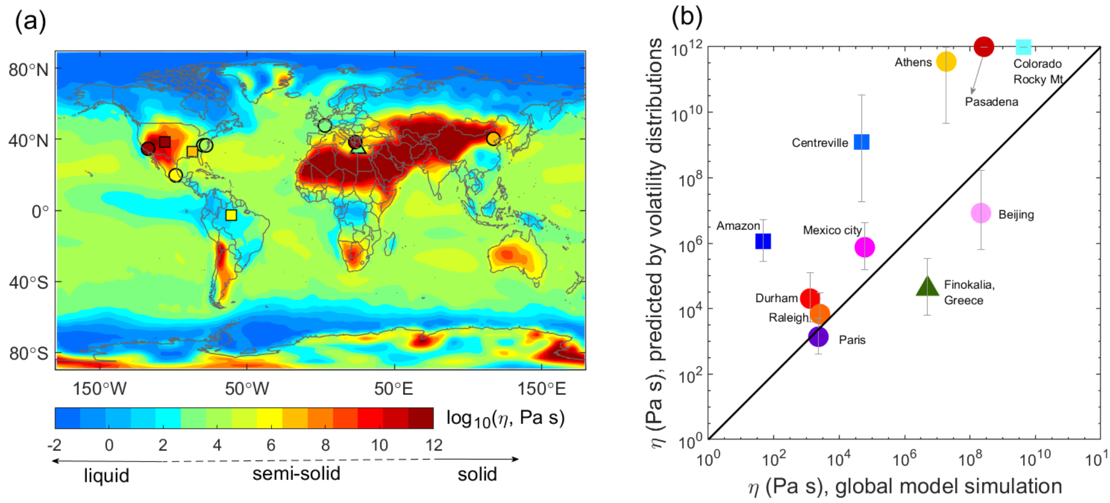

Figure 6. (a) Global distributions of SOA annually averaged viscosity at the surface simulated by a global chemical transport model (Shiraiwa et al., 2017) with the viscosity predicted by measured volatility distributions at 11 global sites (triangle, square and circle represent remote, forested and urban sites, respectively, Table S3). The color code indicates viscosity in a log scale. (b) Predicted viscosity based on measured volatility distributions compared against the viscosity in global simulations. The error bars correspond to uncertainties in viscosities calculated from uncertainties in predicted $T_{g,org}$ shown in Fig. 4.

6. Conclusion/discussion: I think a short conclusion or discussion would help tie the previous treatise of field observations and put them in a broader context. This is already started at Line 477 and should be expanded on.

Responses: We have put conclusions and implications in the new Section 5:

“5. Conclusions and implications

We have developed parameterizations to estimate the glass transition temperature of organic compounds using saturation mass concentration (C^0) and atomic O:C ratio. They can be applied to ambient observations of volatility distributions to estimate viscosity of ambient organic aerosols. The T_g and viscosity prediction method can be applied in the volatility basis set or the molecular corridor-based approach to improve OA simulations in chemical transport models by consideration of effects of particle viscosity on OA formation and evolution (Shiraiwa et al., 2017; Pye et al., 2017; Schmedding et al., 2019). Most of the current chemical transport models treat particles as homogeneously well-mixed liquid without considering particle-phase diffusion limitations, which can lead to bias in simulations of SOA mass concentrations and evolution of size distributions (Shiraiwa and Seinfeld, 2012; Zaveri et al., 2018). The SOA simulations applying the VBS framework have not yet included the effects of viscosity on SOA formation and evolution. When the gas-particle partitioning is limited by bulk diffusion, kinetic treatments of SOA partitioning may need to be applied (Perraud et al., 2012; Liu et al., 2016; Yli-Juuti et al., 2017; Li and Shiraiwa, 2019). Some chamber experiments probing the mixing timescales of SOA particles formed from isoprene, α-pinene, and limonene did not observe significant kinetic limitations at moderate and high RH under room temperature (Loza et al., 2013; Ye et al., 2016), while kinetic limitations of bulk diffusion of organic molecules in β-caryophyllene SOA have been observed at 75 % RH (Ye et al., 2018), warranting further investigations on the degree of kinetic limitations in ambient tropospheric conditions. In addition, the interplay of diffusion limitations and phase separation impacts heterogeneous and multiphase chemistry (Vander Wall et al., 2018; DeRieux et al., 2019; Zhou et al., 2019) and gas-particle partitioning (Zuend and Seinfeld, 2012; Shiraiwa et al., 2013; Freedman, 2017; Pye et al., 2017; Gorkowski et al., 2019a). The particle morphology and the degree of non-ideal mixing and liquid-liquid phase separation can evolve upon atmospheric aging (Gorkowski et al., 2019b). These aspects may also need to be considered for better representation of organic aerosols in future studies".

Line Comments:

1. Line 259: I would stray away from starting a sentence with a variable, as doing so reduces readability (and this paragraph does it repeatedly). So it would change to, "The T_g of ambient..." and line 262, "These T_g values are then placed..."

Response: Thanks for the suggestion. We revised all the sentences which had started with a variable all through the manuscript.

2. Figure 6a: I suggest filling in the dots, with the edge color (TOA, OOA, ...). The T_g fill color is already represented by the contour lines.

Response: We would like to keep the edge color denoting OA factors as the T_g values represented by the contour lines were calculated from the C^* (x-axis) and O:C (y-axis) values in the 2-D VBS framework, which are different from the $T_{g,org}$ values filling the dots calculated from the measured ambient volatility distributions. We clarified this in the caption of Fig. 4a in the revised manuscript:

"The isopleths in (a) correspond to the T_g calculated using Eq. (1) with C^* and O:C defined in the 2D-VBS".

3. Figure 6b: You have already shown the correlation between T_g and C^* (Figure 1a), so the added value to the manuscript is small. I suggest moving Figure 6b to the SI.

Responses: Figure 1a is for individual organic compounds. The correlation between predicted $T_{g,org}$ and the average volatility of ambient OA shown in Figure 6b agrees with the trend shown in Fig. 1a, which indicates that our newly developed parameterization works for ambient OA mixtures.

4. Figure 7 caption: Define BBOA, LO-OOA, and MO-OOA. I didn't find the definitions in the main text.

Responses: These OA factors are now defined in Line 374-378:

"The marker edge color represents OA components identified via source apportionment techniques on AMS mass spectra (Lanz et al., 2007), including biomass burning OA (BBOA), hydrocarbon-like OA (HOA), cooking OA (COA) and oxygenated OA (OOA) which is sometimes further separated into more oxygenated (MO-OOA) and less oxygenated OA (LO-OOA) factors".