We thank the reviewers for careful consideration of our article. We have attached a revised version of the manuscript and supplementary document to address the comments made by the reviewer. The reviewer comments are in black text, the authors' responses are in red text and the revised text is in "double quotation marks" (with Line number(s) in updated manuscript).

Response to Reviewer Comment #1 (RC#1):

Specific comments:

- To estimate organic water, it is assumed that "10% of the aerosol water was present in the organic phase, within the range of organic water reported by Pye et al. (2017)." However, Fig 12 of the cited paper shows the fraction of organic water to vary significantly, and even exceed 60% in some areas. With this in mind," within the range" appears to be a massive simplification of expected conditions. How was this 10% number chosen? What could be the expected consequences of a more explicit organic water mechanism (or even simply a greater amount of organic water in the SE)? Another sensitivity case study may be appropriate here.

CMAQ model version 5.2.1 used in this study has a limitation in regards to lack of an explicit representation of aerosol water uptake by organic constituents. In CMAQ v5.2.1, total aerosol water in the model is just the water associated with inorganics calculated with ISORROPIAv2.2 (Fountoukis and Nenes, 2007) without accounting for hygroscopocity of organic constituents at all. We do highlight in Section 4 (Discussions and atmospheric implication- Lines 806-809):
"Organic water uptake, even if higher than the amount assumed here, will still follow the diurnal trend of RH since it is diverted from the aqueous core that is derived from ISORRORPIA-based aerosol water in CMAQ v5.2.1."

Guo et al. (2015) found strong diurnal trends in the fraction of organic water content with the percentage increasing to as much as 50% at night, and reducing much lower during the day (~ 10%). As isoprene chemistry primarily occurs during the day, we selected 10% organic associated water as a model simplification to better predict IEPOX chemistry during the day. Nighttime have higher organic water than the assumed 10% fraction of total aerosol water but it has negligible impact on IEPOX chemistry, which is the primary focus in this work. Furthermore, due to the strong effect of organic water on the viscosity of the organic rich shell in particles with a core-shell morphology, a lower value was selected because instances where diffusion limitations occur are likely to have lower water fractions.

The following text was added in section 2.2 (Lines 217-222) to clarify our assumption:

"Approximately 10% of total aerosol water is associated with the organic phase during daytime when IEPOX chemistry is more prevalent as indicated by the observations collected during the SOAS 2013 campaign (Guo et al., 2015). To best replicate daytime IEPOX chemistry, the 10% value was chosen under the assumption that the underprediction of nighttime organic water would negligibly impact overall IEPOX-derived SOA. Naturally, this is not applicable for rest of multiphase chemistry and should be addressed accordingly in future work."

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A. and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmospheric Chemistry and Physics, 15(9), 5211–5228, doi:10.5194/acp-15-5211-2015, 2015.

The most recent release of CMAQ version 5.3 has the explicit organic water mechanism based on κ-Köhler theory as described by Pye et al. (2017) accounting for the hygroscopocity (κ_{org}) of each organic constituent in the total aerosol budget. The proposed 'PhaseSep' algorithms in this study need to be implemented in the updated version of CMAQ (v5.3) to quantify the expected impact of a more dynamic representation of organic water uptake on phase state. This implementation is ongoing and a subject of a future study (subsequent paper), but is beyond the scope of this paper.

- As the authors note in their conclusions, organic hydrophobicity is not considered in this work, including impacts of aging. This seems to me to be a very significant (though understandable) omission, and worthy of more discussion than currently provided.

The following text was added and modified in the conclusions (section 4; Lines 809-819) to address the comment above and add caveats to be addressed in further model development:

"In this work, the O:C ratio of individual organic constituents as listed in Table 1 was used to calculate $T_{g,org}$ based on Shiraiwa et al. (2017). The O:C provides an indication of hygroscopocity of different organic species (Pye et al., 2017), but it is only a surrogate. Lack of explicitly representing hydrophobicity or hygroscopic growth of various organic constituents is a limitation in the CMAQ modeling framework that was used. More recently, degree of diffusivity or uptake of semivolatile organic compounds (SVOCs) such as isoprene oxidation products and ONs in to more viscous or semi-solid particle-phase are found to differ. These changes in η_{org} profoundly impacts both aerosol growth kinetics and their size distribution dynamics (Vander Wall et al., 2020; Zaveri et al., 2020). To assess the actual impacts of aging and hygroscopic growth under varying conditions updates in the CMAQ model are required by adding explicit reactive uptake mechanisms for a wider range of non-IEPOX SOAs."

Following references were added accordingly:

Vander Wall, A. C., Perraud, V., Wingen, L. M., and Finlayson-Pitts, B. J.: Evidence for a kinetically controlled burying mechanism for growth of high viscosity secondary organic aerosol, Environmental Science: Processes & Impacts, 22, 66-83, 10.1039/C9EM00379G, 2020.

Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Zawadowicz, M. A., Suski, K., China, S., Bell, D. M., Veghte, D., and Laskin, A.: Particle-Phase Diffusion Modulates Partitioning of Semivolatile Organic

Compounds to Aged Secondary Organic Aerosol, Environmental Science & Technology, 10.1021/acs.est.9b05514, 2020.

- Page 19: Which species specifically contribute to the modeled change in O:C with elevation?

We added a detailed explanation to address the above comment in Section 3 (Lines 444-454):

"Species with high O:C (> 1.6) parametrized in CMAQ as anthropogenic OA collectively can be used as a surrogate for Highly Oxygenated Organic Aerosol (OOA); specifically low-volatility-LVOOA and semi-volatile-SVOOA oxygenated OA. Table 1 shows the species which are attributed to this specific modeled change in O:C with elevation. The mean mass fraction of anthropogenic OA increased from ~ 40% at surface to ~ 65% at the upper troposphere and eventually ~ 80% at layer 35. Whereas, biogenic OA comprising of isoprene-derived OA drops from ~ 30% at surface to 24% at the upper troposphere and eventually ~ 20% at layer 35. This is in agreement with the findings from airborne measurements in the southeastern United States as part of the Southeast Nexus (SENEX) field campaign that show a sharp drop in isoprene-derived OA and drastic increase in OOA with rising altitude (Xu et al., 2016)."

The following reference was also added:

Xu, L., Middlebrook, A. M., Liao, J., de Gouw, J. A., Guo, H., Weber, R. J., Nenes, A., Lopez-Hilfiker, F. D., Lee, B. H., Thornton, J. A., Brock, C. A., Neuman, J. A., Nowak, J. B., Pollack, I. B., Welti, A., Graus, M., Warneke, C., and Ng, N. L.: Enhanced formation of isoprene-derived organic aerosol in sulfur-rich power plant plumes during Southeast Nexus, *Journal of Geophysical Research: Atmospheres*, 121, 11,137-111,153, 10.1002/2016jd025156, 2016.

- Section 2.7: For the specific locations examined, how well did the modeled O:C values match observations?

In the updated manuscript we added the brief description of recently reported field observations of O:C values at Centreville, AL during Southern Oxidant and Aerosol Study (SOAS) 2013. In section 2.7 (Lines 382-386) the following text has been added:

"We also use observed O:C ratios of various HOMs as reported by Massoli et al. (2018) recorded at Centreville forest site, Alabama during the SOAS 2013 study to compare with the simulations. Massoli et al. (2018) used a high-resolution time-of-flight chemical ionization mass spectrometer with nitrate reagent ion (NO_3^- CIMS) for these observations. More details are provided in the Results section."

More detailed discussion on the modeled O:C values vs O:C observations at Centreville, AL for SOAS 2013 has been added as follows in section 3 (Lines 539-556):

"Massoli et al. (2018) reported the observed O:C at Centreville, AL during SOAS 2013 that ranged between ~ 0.5 to 1.4 and averaging at 0.91. Massoli et al. (2018) presents the first instance of ambient measurements with a NO_3^- CIMS in an isoprene-dominated environment and identified Organic nitrates or Organonitrates (ONs) originating from both isoprene and monoterpene to be a significant component of the NO_3^- CIMS spectra and dominating the observed SOA at Centreville throughout the day, reflecting daytime and nighttime formation pathways. Both isoprene- and monoterpene-derived ONs have very high O:C > 1 and accounting for up to 10% of total oxygen at Centreville site (Xu et al., 2015; Lee et al., 2016), explaining the high overall observed average O:C. Our modeled O:C at the Centerville, Alabama site during SOAS 2013 ranged between ~ 0.5 to 1 and averaging ~ 0.68. CMAQv5.2.1 with carbon bond chemistry (used in this study) uses *aero6* aerosol mechanism, without any explicit representation of formation pathways of isoprene and monoterpene-derived ONs. Specifically CMAQ with *aero6* significantly underestimates monoterpene oxidation that accounts for ~ 50% of organic aerosol in the southeastern United States in summer (Zhang et al. 2018). Consideration of explicit monoterpene organic nitrates and updated monoterpene photoxidation yields in aero7 eliminates the CMAQ model-measurement bias (Xu et al. 2018). The lack of explicit organic nitrates here can explain the lack of high O:C (> 1) predictions in this work for the Centreville, Alabama Forest site during SOAS 2013 possibly leading to the low correlation of model estimated $T_{g,org}:T$ with observations."

The following relevant references are now added in the updated manuscript:

Xu, L.; Suresh, S.; Guo, H.; Weber, R. J.; Ng, N. L. Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates. *Atmos. Chem. Phys.*, *15*, 7307–7336, 2015. (already in manuscript)

Lee, B. H.; Mohr, C.; Lopez-Hilfiker, F. D.; Lutz, A.; Hallquist, M.; Lee, L.; Romer, P.; Cohen, R. C.; Iyer, S.; Kurtén, T.; Hu, W.; Day, D. A.; Campuzano-Jost, P.; Jimenez, J.-L.; Xu, L.; Ng, N. L.; Guo, H.; Weber, R. J.; Wild, R. J.; Brown, S. S.; Koss, A.; de Gouw, J.; Olson, K.; Goldstein, A. H.; Seco, R.; Kim, S.; McAvey, K.; Shepson, P. B.; Starn, T.; Baumann, K.; Edgerton, E. S.; Liu, J.; Shilling, J. E.; Miller, D. O.; Brune, W. H.; Schobesberger, S.; D'Ambro, E. L.; Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets. *Proc. Natl. Acad. Sci. U. S. A.*, *113* (6), 1516– 1521, 2016. (Lee et al., 2016b in manuscript)

Zhang, H, et al.: Monoterpenes are the largest source of summertime organic aerosol in the southeastern United States, Proceedings of the National Academy of Sciences, ***115****, 2038-2043,* *https://doi.org/10.1073/pnas.1717513115, 2018. (Zhang et al., 2018b, already in manuscript)*

Massoli, P., Stark, H., Canagaratna, M. R., Krechmer, J. E., Xu, L., Ng, N. L., Mauldin, R. L., Yan, C., Kimmel, J., Misztal, P. K., Jimenez, J. L., Jayne, J. T., and Worsnop, D. R.: Ambient Measurements of Highly Oxidized Gas-Phase Molecules during the Southern Oxidant and Aerosol Study (SOAS) 2013, ACS Earth and Space Chemistry, 2, 653-672, 10.1021/acsearthspacechem.8b00028, 2018.

- Page 27: The authors argue that the worsened NMB of hourly PM2.5 organic car-bon mass vs. observations is likely explained by poorly constrained Henry's law coefficients (and perhaps other parameters). This may be true, but I do not find Figure S6 to be compelling evidence for the argument. Visual and statistical ex-amination of the differences found when using a modified Henry's law coefficient seems to indicate that its importance is actually very low in terms of impacts on overall OC mass. How can such modest "improvements" be considered evidence supporting this explanation for worsened model performance?

We rephrased and added (at end of section 3.3 on sensitivities, Lines 727-739) to explain and resolve the above comment:

"While modest improvement in model performance of $PM_{2.5}$ OC by aforementioned sensitivity simulations (*HighHorg* and *PhaseSep2*- see section 3.2.2.1) occurs, it does not addresses other major issues in the base CMAQ model performance. Firstly, these updates to phase state and phase separation considerations only translate to IEPOX SOA, the only explicit parametrization of multiphase reactive uptake in CMAQ. IEPOX SOA also just makes up approximately 12% of the total $PM_{2.5}$ OC mass simulated by CMAQ on an average for SOAS 2013 period. There are other more important factors introducing major source of uncertainty in models across spatial scales including CMAQ. A very prominent uncertainty being missing representation of species like ONs reported as dominant in SOAS 2013 by new instrumentation providing higher molecular detail (Lee et al., 2016b; Massoli et al., 2018). Furthermore, field or laboratory studies on a wider suit of SOA are needed to explicitly parametrize their multiphase chemistry and are still missing in CMAQ. It is a challenge to implement these mechanistic representations of different SOA holistically, without increased computational cost in CMAQ."

- The authors note that previous work in which phase-separation was included in a box model showed a drastic improvement in NMB (-66.2% to -36.3%). Why would this work not show such improvements? Are there any major differences in the handling of Henry's law coefficients or other parameters that could explain the differences in the performance of the CTM implementation?

Schmeddding et al. (2019), *Atmospheric Environment* uses a 0-D box model that calculated NMB using data from filter samples taken at the Look Rock site in a pristine environment in rural Tennessee (Budisulistiorini et al, 2015). These filter samples only focused on speciated IEPOX-SOA data i.e. reported % NMB was only on IEPOX-SOA. In CTM implementation during this work, % NMB was calculated for the rural Centreville, Alabama, and urban Jefferson Street, Atlanta, Georgia sites, both of which have SEARCH total $PM_{2.5}$ organic carbon measurements. Because these sites use total organic carbon measurements rather than IEPOX-specific measurements, larger changes in IEPOX-SOA due to changes in the Henry's Law constant would still register as smaller changes in total organic carbon once all of the other species are taken into account.

Moreover, the drastic improvement in Box-model study can be attributed to the fact that it assumes core-shell morphology/Phase separation all the time (resulting in drastic reduction in % NMB compared to reactive uptake ignoring impact of organic coating). While in CTM implementation in this work, we clearly have a more refined conditional parametrization on when phase separation does or does not occur. Hence, it is not advisable to compare the model performance of the two approaches.

We also mentioned this point about the 0-D box model study in the manuscript text as (Lines 143-146):
"The aforementioned previous model study (Schmedding et al., 2019) highlighted the significant impact of an organic coating layer on IEPOX-derived SOA formation, but lacked any quantification of conditions that result in phase separation creating such organic coating and its phase state."

- Figures throughout the manuscript and supplementary materials are formatted poorly, overall. Text, colors, positioning, labels, and spacing should all be examined carefully. In particular:

–Fig 2: Panel and colorbar labels are missing completely.

Added Panel and colorbar labels in the updated manuscript.

–Fig 3: This figure is presented as a time series, but the text describes it ex-clusively in terms of the diurnal cycle. I see no benefit to including individual dates, and it's very hard to tell day from night as shown. I suggest a change to diurnal averages.

Figure 3 in the updated manuscript now is in form of diurnal cycle instead of individual dates and shows diurnal averages of $T_{g,org}$ and its dependence on organic aerosol constituents-anthropogenic, biogenic and organic water uptake (Also look at the response to second last major comment by Reviewer 2).

–Fig 7 B and C, and Fig 8: Panel labels for maps needed.

Panel labels added now to Figure 7 (A, B and C) and Figure 8 (Also see response to last Minor Comment by Reviewer 2) in the updated manuscript.

–Fig 9: Statistical information insets are very hard to read. A transpose of the table may help.

Figure 9 updated with statistical information in bigger fonts and other enhancements. Refer to comment on Figure S6 for update on more statistics moved to Table S1 in updated supplementary document now.

–Fig 10: Panel labels are missing. In addition, the colorbar chosen for this map is particularly difficult to interpret. A two-tone version in which zero is white or grey would help.

Panel labels are added and a two-tone color bar with zero represented by white is included to Figure 10 in updated manuscript.

–Figure S6: y-axis is missing label and units.

We have removed older Figure S6 and transposed statistics on model performance with sensitivity simulations in it to Table S1 in supplement to address Reviewer #2's comment.

Response to Reviewer 2:

Major Comments

The authors should clarify the very central assumption in their manuscript that all semisolid particles > 100 Pa s phase separate. What is this assumption based on? A reference is given (Shiraiwa et al. 2017), but I do not see this manuscript making a statement about phase separation dependent on viscosity. All phase-separation percentages given in the text and figures are dominated by this assumption, but how realistic is it and what does it add to our understanding of SOA? The uncertainty of the SSPS assumption strongly diminishes the validity of total fractions of phase-separated particles in the atmosphere that are prominently discussed in this manuscript (l. 659 – 666). Please add sufficient caveats and error estimates in the appropriate places.

The SSPS assumption was chosen as a model simplification to better understand the effects of morphology on the formation of IEPOX-SOA. Schmedding et al (2019) showed that particles with a core-shell morphology and an outer shell that had a liquid like viscosity did not exhibit any diffusive limitations when calculating the reactive uptake of IEPOX. Furthermore, there is little information on the criteria necessary for a particle that is specifically in a semi-solid or glassy state to undergo phase separation. Prior work (Song et al., 2018; Zuend and Seinfeld, 2012) has focused on particles that have a liquid-like viscosity and have highlighted the aerosol and ambient properties that dictate transition from a homogenous mixture of organic and inorganic compounds to a liquid-liquid phase separated particle. The threshold of viscosity > 100 Pa.s, only indicates the transition in phase state of the 'organic coating' from liquid (< 100 Pa.s) to semi-solid or solid (> 100 Pa.s) and should not be confused with dictating phase separation itself.

We edited text in section 2.1 (Lines 178-185) to addresses this comment on the SSPS assumption:

"This simplification is based on recent observations showing higher than anticipated rebound fractions in phase-separated OA that has been attributed to organic aerosol constituents with viscosities > $10^2\ Pa.s$ (Reid et al., 2018). These aerosols were phase-separated with an amorphous solid coating, which, unlike liquid particles, can only dissipate energy by rebounding.

(Bateman et al., 2015a, 2015b, 2017; Reid et al., 2018; Virtanen et al., 2010). A higher bounce factor implies that a particle is more viscous and therefore more likely to exhibit diffusive limitations in reactive uptake."

Whether, this particle viscosity is due to a viscous solid organic coating or a viscous homogenous morphology is a matter of further experimental investigation and the focus of future work. (See response to 'minor comment on 169' as well)

Therefore the 100 Pa.s cut off was chosen as an extreme upper bound scenario for particle morphology to better understand the effects of a core-shell morphology on the heterogeneous chemistry of IEPOX.

To clarify, phase separation and viscosity are expected to follow similar underlying system properties. For example, O:C ratio that drive phase separation (e.g. low O:C ratio organics tend to phase separate from water-rich phases) likely also dictate viscosity. Since low O:C species in ambient aerosols will necessarily have higher molecular weights to have vapor pressures consistent with their presence in the particle phase, given all other factors being equal. In this work, this empirical relationship between viscosity, phase separation, and system properties (O:C, OM to inorganic SO_4^{2-}, RH) has been leveraged to predict viscosity and phase separation simultaneously.

The following text was added in section 2.1 (Lines 185-189) to underline the reasoning of the assumption in question:

"The specific conditions under which a particle will form a glassy rather than liquid-like organic shell are unclear, but thought to be driven by the same underlying physical properties that drive viscosity. This led to the assumption that particles that exhibit a semi-solid or glassy organic shell would inherently adopt a core-shell morphology. This assumption can be thought of as an upper bound on the frequency of particles separating into core-shell morphologies."

And in the discussion emphasis was also added that there is limited information on the internal conditions of a particle that would lead it to adopt a core-shell morphology when in a semi-solid or glassy state (Lines 777-783):

"The conditions under which highly viscous SOA will separate from inorganics in a particle or if the particle will remain homogenously mixed should be further explored as well, given the differences in the frequency of predicted particle-phase separation between the *PhaseSep* and *PhaseSep2* simulations and the implications that this has for the reactive uptake of IEPOX (Table S1). Constraining the viscosity of SOA in low RH (< 30%) conditions is also an area that should be further explored to improve model performance."

The authors show many figures analyzing their model data. However, the manuscript text is widely used to list these numbers, without much interpretation or discussion. Discussion is often superficial and obvious as indicated in the minor comments below. I would suggest condensing the message of this manuscript to fewer, central figures and discuss them thoroughly.

We have improved on the figures as suggested by both reviewers and we have consistently added more detailed inferences and discussion following the presentation of results in Section 3 of the updated manuscript (Also see the subsequent response to various comments by Reviewer 2 and RC#1).

To avoid confusion, please consider the use of Tg,org instead of Torg for the glass transition temperature of the organic phase throughout the manuscript. In Fig. 2, it would probably be useful if the liquid to glass transition were marked with a distinct change in color. Here, this important transition lies in the middle of the pink/purple color range.

The text was updated to clarify that T_{org} refers to $T_{g,org}$ both in texts and figures. We highlighted in Figure 2 in the updated manuscript, the liquid to glass (semi-solid as well as solid) transition marked with a distinct change in color (next to the color bar).

I do not understand the point of Fig. 3 since it is very hard to see what is going on and do not find it illustrative. It seems that water is the constituent with the highest variability; it is thus very unintuitive to plot it on the base of this plot, especially because a high concentration leads to a low overall value. It would hence be more helpful to not stack these three lines, but just report the diurnal cycle of Tg,org along with the particle composition in a separate panel. A graphical representation like the one shown in Fig. S1 seems better suited to present the data.

Erstwhile Figure 3 has been replaced by updating the previous Figure S1 as both reviewers suggested (also addresses Comment by RC#1).

633 – In the discussion of the PhaseSep2 scenario, it would be very helpful to see how PhaseSep2 compares to NonPhaseSep, i.e. the equivalent of Fig. S7. Please discuss thoroughly which scenario is more likely correct. What effect does the addition of LLPS have on the simulation results?

We added Fig. S6 to discuss more on the comparisons between *PhaseSep2* and *NonPhaseSep*, along with a Table S1 listing comparison among all the simulation cases.

The following text was also added (Lines 717-725):

"Table S1 shows a modest 4% improvement in model performance for total $PM_{2.5}$ OC mass, in the isoprene-abundant southeastern United States with *PhaseSep2*. The range of phase separation frequency in semi-solid particles is still wide when compared to other cases i.e. 29-55.8% SSPS. Increased frequency of bulk phase in semi-solid conditions in *PhaseSep2* relative to *PhaseSep* causes much less resistance to reactive uptake, closer to but still more than in

NonPhaseSep. This is reflected in the similarity of γ_{IEPOX} between *PhaseSep2* and *NonPhaseSep* (Fig. 7C and Fig. S6). Hence, a very marginal difference in IEPOX SOA and biogenic SOA in *PhaseSep2* relative to *NonPhaseSep* occurs (Fig. S6), unlike much higher differences observed in *PhaseSep* (Fig. 8)."

Also, refer to text added for subsequent discussion on model performance and different simulations as part of response to comments by RC#1 on Page 27 (Lines 727-739). Which clarifies more on the fact that more work on including explicit representation of non-IEPOX SOAs consistent with reactive uptake mechanism of IEPOX SOA currently in CMAQ is needed to assess accurate impact of updates to phase state and morphology presented in this work on overall SOA mass.

Minor comments

114-116 – What's the point of this reference in this context? "Low" and "high" are obviously relative. Also, please specify what is meant with "remaining bulk".

The text of the sentence was updated to clarify that remaining bulk refers to the non-IEPOX derived SOA and that there is 2 to 8 order of magnitude difference in volatility between the IEPOX-derived SOA and remaining OA. The low volatility of IEPOX-derived SOA was also clarified by including that the evaporation time of IEPOX-Derived SOA is greater than 100 hours under atmospherically relevant conditions.

See Lines 117-121 for updated text:

"IEPOX-derived SOA in the southeastern United States are found to exhibit higher volatility than the remaining bulk OA with saturation vapor pressures for IEPOX-derived SOA being 2 to 8 orders of magnitude larger than the remaining bulk OA, however IEPOX-derived SOA has a low overall volatility with evaporation time scales >100 hours under atmospherically relevant conditions (Lopez-Hilfiker et al., 2016)."

126 – Where is the amplification? Amplified compared to what?

The text was updated to (Lines 129-133):

"The reduced transport of semi- or low- volatile gas species such as IEPOX on to particles also highlight the effects of phase separation on aerosol formation by decreasing reactive uptake of IEPOX (Gaston et al., 2014). This is due to increased resistance to diffusion of IEPOX through the SOA coating (Zhang et al., 2018a)."

169 – What do you mean with “particles [. . .] can only dissipate energy by rebounding”. Are you talking about particle bounce measurements? How is this connected to the cited “almost full resistance to reactive uptake”? Please fill in the connections between these concepts.

The text was updated to eliminate the parenthesis referring to resistance to reactive uptake. The following clarifying sentence was also added to connect particle bounce measurements to reactive uptake (Lines 183-185):

“A higher bounce factor implies that a particle is more viscous most possibly due to a glassy organic coating and therefore more likely to exhibit diffusive limitations in reactive uptake.”

In equation (3), 205, the sum of wa, wb and ws is not 1. Is this intended?

The text was updated to correct equation (3) so that the 3 terms (w_a, w_b and w_s) sum to 1. The original equation was a typo.

367 – “This indicates that anthropogenic species have a higher range of glass transition temperatures than biogenic species” – The “range” is larger for biogenics, you probably want to point out the overall higher values. Same in 402.

The sentence was changed to (Lines 399-402):

“This indicates that anthropogenic species have a narrower range of glass transition temperatures but overall higher values than biogenic species; however, the maximum values of $T_{g,b}$ and $T_{g,a}$ are more similar than their minimum values.”

399 – How is a bimodal distribution relevant for Fig. 2?

The text was updated to mention that the low peak in Figure 1 occurs over the oceans as shown in Figure 2, and that the cluster of peaks between 0.8 and 0.9 in Figure 1 are caused by the Western US as shown in Figure 2 (Lines 429-437):

“Semi-solid particles with a higher range of T_g values (Fig 2A) were concentrated over areas associated with higher anthropogenic SOA (including anthropogenic POA listed in Table 1) and a low RH, aerosol liquid water content, and biogenic SOA, such as the American southwest and Rocky Mountains. These higher T_g values pulled the net $T_{g,org}$ value up closer to the ambient temperature, and thus, brought the $T_{g,org}$:T ratio closer to 1, which is shown in the cluster of peaks between $T_{g,org}$:T = 0.8 and $T_{g,org}$:T = 0.9. The particles with the lowest $T_{g,org}$:T ratios were located over the Atlantic and Pacific oceans, due to the substantially higher aerosol water content and low levels of anthropogenic and biogenic organics in these environments.”

419 – How is reduction of water connected to disappearance of bimodal Tg,org?

The following sentence was added for clarification (Lines 426-428):

"Particles dominated by w_s had $T_{g,org}$ similar to $T_{g,w}$, with reduced influence from w_a and w_b, which decreased their $T_{g,org}$:T ratio as $T_{g,w}$ is substantially lower than the predicted T_g values for organic species"

Fig. 4A – What is the black line at the bottom of the plot representing? Panels of Fig. 4 do not appear in the order they are presented in the manuscript.

We removed the black line at bottom of curve plot in Fig. 4A to satisfy the reviewer's comment. The text discussing Figure 4 presented Fig. 4F at start, as it is the most dominant factor that affects η_{org}. Figs. 4D and 4E are discussed in subsequent line to put things in perspective to compare the influence of biogenic, anthropogenic and organic water (4F) constituents of organic shell on its viscosity (η_{org}). The rest of Fig. 4 is discussed in order.

474 – "This suggests that anthropogenic aerosol components are likely more water soluble than biogenic components." - Do you have more than statistical evidence for that? Shouldn't that be easy to derive from model input rather than from model output.

Yes, we can easily infer from model inputs as the reviewer suggests. Since, water solubility or hygroscopocity (κ_{org}) has been presented as being linearly proportional to O:C of aerosol components i.e. highly oxygenated species are more water soluble (Pye et al., 2017)- Also refer to response to Specific comment #2 by RC#1.

Average O:C for 26 anthropogenic components is 0.59 as compared to 0.72 for 9 biogenic components used in CMAQv5.2's *aero6* aerosol mechanism as listed in Table 1. Also, w_a and w_b does not indicate the water solubility but just the fraction occupied by anthropogenic and biogenic constituents respectively in total OA.

Hence, we also modified the text in the updated manuscript as (Lines 512-515):

"This suggests that anthropogenic aerosol components are more dominant than the biogenic components. Where biogenic components are likely more water soluble with their average O:C being 0.72 compared to 0.59 for anthropogenic constituents (Table 1)."

486 – "Some mismatch can be attributed to the lack of an explicit mechanism to compute organic aerosol water uptake and some unaccounted SOA formation mechanisms." - Please expand on

this, how would you attribute these to mismatch? Does the data make you recognize this or are these just general shortcomings of the model?

Like the reviewer points out in this comment, both the ‘lack of explicit mechanism on organic aerosol water uptake and some unaccounted SOA formation mechanisms’ actually refers to a ‘general shortcoming of CMAQ model algorithm’. Authors would like to clarify that these are not inherent shortcomings of CMAQ, but rather a limitation of CMAQv5.2 (used in this work). Recently released CMAQv5.3 includes uptake of water onto organic species, updated monoterpene SOA, and explicit SOA from organic nitrates (intended for use in subsequent future work).

We have hence expanded the discussion by presenting the further investigation of modeled O:C ratio with observed O:C ratio data (based on findings from newer instrumentation with higher molecular details) at Centreville, AL forest site to recognize the shortcomings of model in form of unaccounted SOA species (i.e. Organic Nitrates missing in CMAQ v5.2), actually dominant on field.

Updated text as part of this discussion is added in the Section 3.1.2: Lines 539-556 (Refer to response to RC#1 on Section 2.7 for the updated text).

492 – “The difference in observed and model estimated Torg:T range was statistically significant with a P-Value = 0.001” - What does this entail? You are testing the hypothesis that both data sets (model/field) are different. Why?

We agree with the reviewer’s comment and remove the ANOVA statistical test, as P-value can be unintuitive and confusing as a form of model validation often, and there is fair evidence based on correlation and mean values that model outputs compared fairly well (although not too high in terms of correlation) to the field data. The text was updated to include the following sentence (Lines 533-535):

“The model estimated $T_{g,org}$:T range compared to $T_{g,org}$:T range based on field observations at Centreville, AL for SOAS 2013 give a correlation coefficient of ~ 0.66 between them.”

Hence we added the comparison of field observation of O:C ratio at Centreville, AL with modeled estimated O:C ratio, to further explain the cause of not too high of a correlation (or some mismatch) between modeled and observation-derived $T_{g,org}$:T range for Centreville, AL (as presented in Figure 5). Refer to our response to RC#1 on Section 2.7 for the updated text (Lines 539-556).

500 – “Wider ηorg ranges at higher RH can be explained by increased diffusivity with higher aerosol liquid water in SOA causing quick mixing times often accompanied with drastic differences in composition” – Can you expand on this claim (i.e. drastic differences in

composition) and back it up with data? I would think high variance in ηorg at 80 % RH is simply due to a very steep η(RH) curve in that humidity range.

The text was updated to (Lines 560-565):

"Wider η_{org} ranges in the higher RH bins can be explained by increased diffusivity with higher aerosol liquid water in SOA causing faster mixing times leading to quick changes in composition. Furthermore, these contain the most atmospherically relevant RH ranges for the model simulation period. Therefore, a wide range of particle compositions is expected which also contributes to the wide range of predicted η_{org} values."

508 – "This can be attributed to shattering of highly viscous SOA (ηorg ≥ 10^6 Pa•s) for RH ≤ 30% that inhibits their flow in laboratory measurements of ηorg." - Explain how the shattering of SOA in these studies causes a general overestimation of viscosity. To my knowledge, the authors of these papers tried to account for shattering in their viscosity prediction. Is this really the only source of deviation? This would be a good place to talk about idealized laboratory SOA and field samples

The following text was added to further explore differences between our modeled results and experimentally measured viscosities (Lines 573-581):

"Huang et al. (2018) speculates that differences in physicochemical properties of α-pinene SOA, including viscosity, can exhibit a "memory effect" of the conditions under which the particle formed. This is regardless of the subsequent conditions to which the particle is exposed. This could lead to differences between model-predicted and experimentally measured viscosities, as these memory effects are not well characterized. Grayson et al. (2016) reports that the viscosity of α-pinene SOA may vary as a function of the mass loading conditions with higher mass loading leading to lower viscosity measurements. Unfortunately, there is also a lack of experimental data on viscosity measurements at RH < 60%."

Fig. 8 – Different color scheme for panels a and b is misleading. Caption text denotes that biogenic SOA mass is primarily driven by IEPOX SOA, which according to panel is clearly not the case.

Color scheme for Fig. 8 parts A and B are consistent now in the updated manuscript, in addition to adding panel labels to accommodate comments from both the reviewers.

We removed the 'primarily driven by IEPOX SOA' part from the caption text of Figure 8 to avoid any confusion. Since, we already discuss spatial variability in the proportion of IEPOX SOA making up the total biogenic SOA on average for SOAS 2013 separately through Figure S3 in both *PhaseSep* and *NonPhaseSep* cases.

Technical notes

Plase standardize the use of “O:C”. O:C is sometimes in parenthesis, sometimes not. O:Cavg can be misunderstood in way that only the carbon part is averaged.

The text was updated to change any instance referring to the average O:C ratio to $(O:C)_{avg}$.

Math equations in this manuscript appear overall messy, especially due to long italicized words.

Equations are now edited and long words have been removed wherever possible within the scope of manuscript.

Multiple inaccurate multiplication symbols are used: *, •. Please use ·.

All multiplication symbols were changed to “·” throughout the manuscript.

Check use of italic vs. non-italic symbols for variables is not consistent throughout the manuscript (kb and T should be italicized in 1 82, equation numbers are sometimes in italics sometimes not etc.).

The text of equations was updated to ensure accurate *italics* use.

“Tg can determine when aerosols are in a highly viscous glassy state” is a colloquialism.

This was changed to (Lines 174-177):

“Thus T_g can be used to determine when aerosols are in a highly viscous glassy state ($\eta_{org} \geq 10^{12}\ Pa \cdot s$), a semisolid state ($100 \leq \eta_{org} < 10^{12}\ Pa \cdot s$), or in a liquid state ($\eta_{org} < 100\ Pa \cdot s$) (Marcolli et al., 2004; Martin, 2000).”

l. 78-82 – Please revise too long sentence.

The text was updated to (Lines 80-85):

“Pye et al. (2017) used the ratio of organic matter to organic carbon (OM:OC) and the ambient relative humidity (RH) to predict phase separation frequencies. They found that phase separation was common at lower RH in urban areas with low OM:OC, but lower phase separation frequencies in rural areas were attributed to increasing OM:OC except for late mornings when phase separation frequency increased due to low RH.”

117 – What does “pathways that typically happen in the ambient conditions” mean? Are there other pathways that happen under other conditions? Please be specific.

For the sake of specificity and clarity, the text in updated manuscript is now (Lines 121-123):

“Specifically, acid-driven multiphase chemistry of IEPOX with inorganic sulfate aerosol results in significant yield of organosulfates that have potentially higher viscosities (Riva et al., 2019).”

120 – Extra white space before comma. Reference missing?

The white space was removed and text was updated: See Lines 123-125.

l.124 – Check subscript of Dorg.

An extra period was removed from the subscript in this instance (See Line 129).

l. 158, 160 and elsewhere – Consider changing the shorthand "phase" to the more proper "phase state" in this manuscript about phase separation.

The text was updated to more accurately describe phase state, phase, and particle morphology.

l. 176 – "Criteria" is plural, so this should be either "criterion" or "were applied"

"was applied" was changed to "were applied"(See Line 191).

l. 202 – superfluous comma

The comma was removed (Lines 223-224).

l. 204 – "adds" should be "add"

The text was changed to replace "adds" with "add" (See Line 225).

l. 215 – There seem to be formatting issues in lines 212 and 215.

The text was updated to more clearly refer which OA species are referenced in the subsequent equations (Refer to Lines 229-235).

l. 295 – Eq. (14) should read Eq. (15).

The text was updated to reflect the correct equations mentioned in each line (See Line 313, Line 316).

l. 308 – I would refrain from using the casual "off of" in a scientific paper.

The text was changed to replace "off of" with "on" (See Line 329, Line 336).

l. 339 – I suppose "chromatogram" should read "chromatography" or "chromatograph" here.

The term "chromatogram" was replaced with "chromatography" (See Line 363).

l. 341f – The term OA (organic aerosol) is misused in this paragraph. It appears you talk about molecules, yet you refer to speciation of particles.

The text in updated manuscript is now modified to clarify the above confusion (Lines 364-367):

"The combined measurements provide comprehensive and quantitative characterization of particle-phase OA composition with over 800 OA components in this data identified as SOA produced predominantly through VOC oxidation, with a time resolution of 4 hours."

l. 359 – "of" missing?

The text was updated to "calculation of γ_{EPOX}." (See Line 391).

l. 522f – Do you really know these numbers to four significant digits?

Three significant digits with scientific notation is used now throughout the text.