Responses to Referee #2

This paper demonstrates the incorporation of phase-separation and phase state within CMAQ and shows this incorporation leads to a decrease in overall simulated IEPOX-SOA formation. Three models were used to predict phase state, which each used a different combination of parameters, which led to large discrepancies in Tg predictions between models for some compounds contributing to differences in phase state predictions between models. The addition of phase separation and phase state predictions leads to better predictions of 2-MT, but an underprediction of MTS and overall IEPOX-SOA formation. Overall, I believe this will be suitable for publication in *ACP* after the authors address the following comments.

General comments:

Please ensure that all of your figures are consistent and easy to follow (i.e., be consistent with latitude and longitude lines, label model used, be clear when observational data is from LRK or CTR on the figure, increase font size when possible). Also, ensure to resolve the problem with readability that is on several figures.

We thank the Referee for pointing this out. Clarity and resolution have been addressed for all figures and tables. Model simulation labels were put in Figures 3, 4 and 6. Lines of Latitude were added where missing (Figures 2 and 6). Markers were also placed on spatial plots (Figures 2, 3, and 6) to show where the CTR and LRK SOAS sites were.

I would recommend either using different species abbreviations for the most common IEPOX-SOA compounds (2-MT for 2-methyltetrols, OS for organosulfates, MTS for methyltetrolsulfates, etc.) or being explicit that these are the species names given in CMAQ as this could be confusing for readers who do not use CMAQ.

We thank the Reviewer for their recommendation. Although species properties for 2-methyltetrols and methyltetrol sulfates (O:C, saturation concentrations, and MW) are used for AIETET and AIEOS respectively, dimers formed from these two products are based on lumped properties and therefore to be consistent across all IEPOX-SOA species we prefer to label them in the manuscript as AIETET and AIEOS. It is now, however, explicitly stated that these are the CMAQ (and specific to the SAPRC mechanism) species in the manuscript.

> match isoprene measured at the Centreville, AL SOAS site (CTR) as detailed in (Pye et al., 2017). The State Air Pollution Research Center version 07tic with extended isoprene chemistry and aero7i treatment of SOA (SAPRC07tic_ae7i) was used as the chemical mechanism (Xie et al., 2013) as it explicitly tracks 2-methyltetrols (corresponding to AIETET in the SAPRC07tic_ae7i mechanism) and methyltetrol sulfates (corresponding to AIEOS in the SAPRC07tic_ae7i mechanism, also known as IEPOX organosulfate) (Pye et al., 2013). These are the predominant IEPOX-derived SOA species permitting the tracking of the influence of sulfate aerosols on the acid-driven multiphase chemistry (reactive uptake) of IEPOX (Budisulistiorini et al., 2015a, 2015b; Budisulistiorini et al., 2017; Pye et al., 2013).

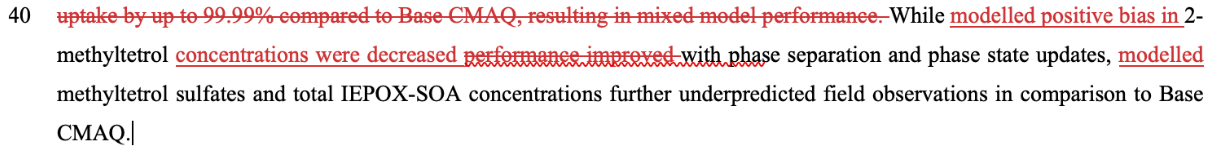
Make sure you are consistent with units used.

We thank the reviewer for pointing this out and have edited our manuscript accordingly.

Specific comments:

Line 40: “2-methyltetrol performance improved” Please be more specific.

In this line we refer to the decrease in modelled positive bias for 2-methyltetrols with phase state and phase separation algorithms included. The following change has been made to reflect this specification:

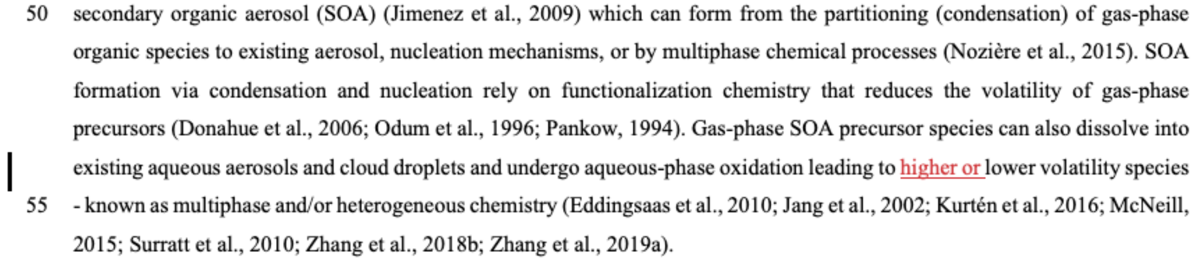


40 ~~uptake by up to 99.99% compared to Base CMAQ, resulting in mixed model performance.~~ While modelled positive bias in 2-methyltetrol concentrations were decreased ~~performance improved~~ with phase separation and phase state updates, modelled methyltetrol sulfates and total IEPOX-SOA concentrations further underpredicted field observations in comparison to Base CMAQ.

Line 52: “Gas-phase SOA precursor species can also dissolve into existing aqueous aerosols and cloud droplets and undergo aqueous-phase oxidation leading to lower volatility species - known as multiphase and/or heterogeneous chemistry” While heterogeneous chemistry can lead to lower volatility species, there are also heterogeneous reactions that can lead to more volatile products.

We thank the reviewer for raising this valid point. In this paragraph we aim to describe different mechanisms by which fine particulate matter exists in the atmosphere, and therefore omit the mention of fragmentation products which can be the result of heterogeneous and/or multiphase chemistry in this paragraph.

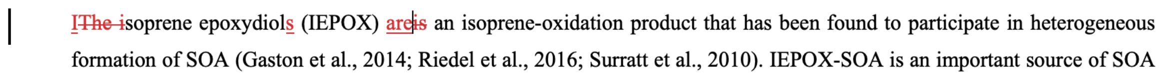
Given that this paper is specifically focused on the heterogeneous formation of two explicit IEPOX-SOA species (which are the product of functionalization reactions) and one lumped category of IEPOX-SOA (dimers; and also the product of functionalization reactions) and not heterogeneous chemistry in general, we are hesitant to include noting this in our paper for risk of confusing the audience. Heterogeneous oxidation of IEPOX-SOA (by hydroxyl radical) has been shown to lead to some fragmentation of dimers that result in monomers that can off-gas (namely 2-methyltetrols and C5-alkene triols), however, these reactions either require higher oxidant concentrations in the atmosphere or have a k(OH) rates that are very slow (Armstrong et al., 2022; Hu et al., 2016; Yan et al., 2025; Yan et al., 2023). Nonetheless we have made the following changes:



50 secondary organic aerosol (SOA) (Jimenez et al., 2009) which can form from the partitioning (condensation) of gas-phase organic species to existing aerosol, nucleation mechanisms, or by multiphase chemical processes (Nozière et al., 2015). SOA formation via condensation and nucleation rely on functionalization chemistry that reduces the volatility of gas-phase precursors (Donahue et al., 2006; Odum et al., 1996; Pankow, 1994). Gas-phase SOA precursor species can also dissolve into existing aqueous aerosols and cloud droplets and undergo aqueous-phase oxidation leading to higher or lower volatility species
55 - known as multiphase and/or heterogeneous chemistry (Eddingsaas et al., 2010; Jang et al., 2002; Kurtén et al., 2016; McNeill, 2015; Surratt et al., 2010; Zhang et al., 2018b; Zhang et al., 2019a).

Line 56: “The isoprene epoxydiol (IEPOX) is…” Referring to IEPOX in the singular and as a definite subject here is slightly confusing since IEPOX has multiple isomers, I would recommend removing “the” from the beginning of the sentence.

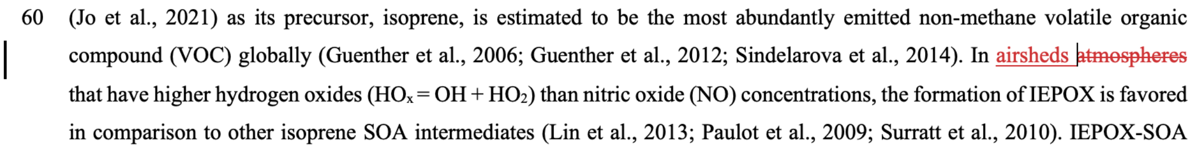
We have made the following changes:



I~~The i~~soprene epoxydiols (IEPOX) are~~is~~ an isoprene-oxidation product that has been found to participate in heterogeneous formation of SOA (Gaston et al., 2014; Riedel et al., 2016; Surratt et al., 2010). IEPOX-SOA is an important source of SOA

Line 59: “In atmospheres that have higher hydrogen oxides (HOx = OH + HO2) than nitric oxide (NO) concentrations,” Implies that you are discussing at a planetary level, alter wording to clarify.

We thank the Reviewer for raising this point and have made the following changes:



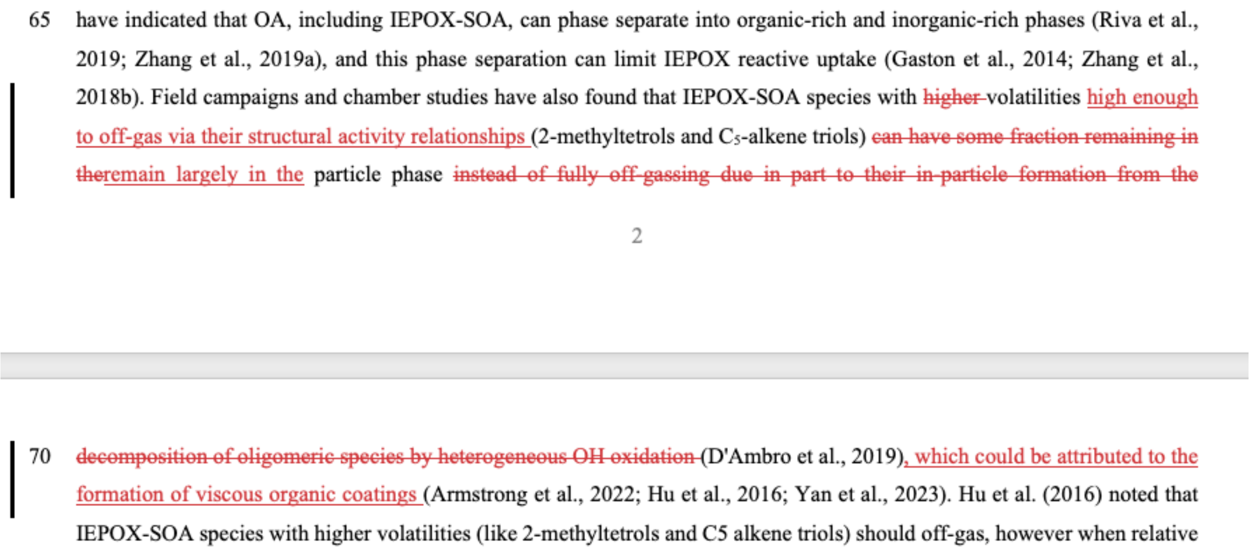
(Jo et al., 2021) as its precursor, isoprene, is estimated to be the most abundantly emitted non-methane volatile organic compound (VOC) globally (Guenther et al., 2006; Guenther et al., 2012; Sindelarova et al., 2014). In airsheds ~~atmospheres~~ that have higher hydrogen oxides ($HO_x = OH + HO_2$) than nitric oxide (NO) concentrations, the formation of IEPOX is favored in comparison to other isoprene SOA intermediates (Lin et al., 2013; Paulot et al., 2009; Surratt et al., 2010). IEPOX-SOA

Line 65: “Field campaigns and chamber studies have also found that IEPOX-SOA species with higher volatilities (2- methyltetrols and C5-alkene triols) can have some fraction remaining in the particle phase…” Wording is confusing here, what is higher volatility in reference to in this case, these species should be much lower in volatility than IEPOX. According to your source for the following sentence, based on the C*s alone the alkane triols should be mostly in the gas phase but 2-MT should only be 43% in the gas phase.

We thank the reviewer for raising this point of confusion. We aim to convey that these species are found to be in the particle phase with a higher frequency than the volatility (via their structural activity relationships) would imply (D'Ambro et al., 2019). The rationale behind this thought was to set up organic coatings as being a mechanism by which these higher volatility species remain locked in the particle phase.

In Armstrong et al., 2022 IEPOX-SOA were exposed to OH, in anticipation that higher volatility fragments would be generated and off-gas, however, instead found dimers and oligomers fragmented from exposure, regenerating monomer species (2-methyltetrols and methyltetrol sulfates) and that these species were not lost to gas phase partitioning (Armstrong et al., 2022). In section 3.3 of Armstrong et al., 2023 it was noted that in a previous study by Hu et al., that the formation of an organic coating and the increase in its viscosity from OH exposure cold explain why these seemingly higher volatility species where not off-gassing (Armstrong et al., 2022; Hu et al., 2016). Although Yan et al., 2023 looked at the impact of acidity on heterogeneous decay of IEPOX-SOA, they also concluded that the limited gas-phase partitioning of monomer species could be attributed to the role organic coatings play (Yan et al., 2023).

We have made the following changes to clarify:



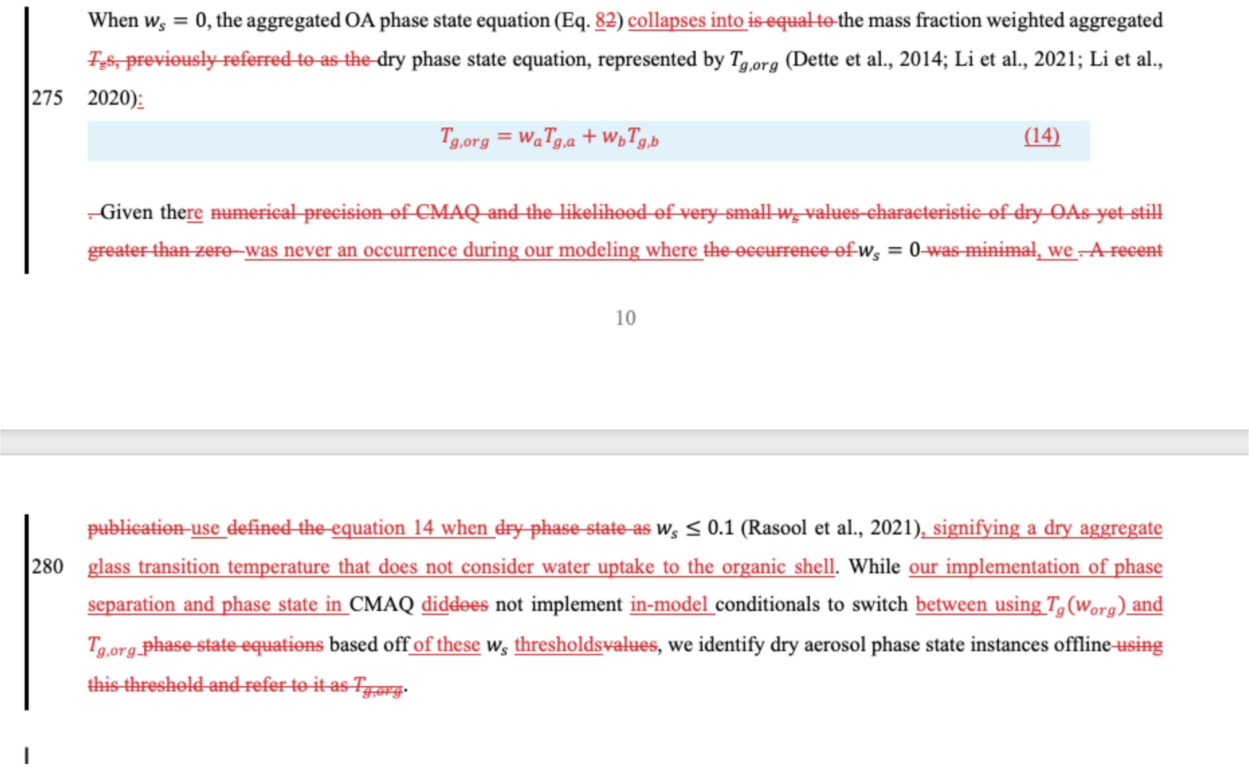
have indicated that OA, including IEPOX-SOA, can phase separate into organic-rich and inorganic-rich phases (Riva et al., 2019; Zhang et al., 2019a), and this phase separation can limit IEPOX reactive uptake (Gaston et al., 2014; Zhang et al., 2018b). Field campaigns and chamber studies have also found that IEPOX-SOA species with ~~higher~~ volatilities high enough to off-gas via their structural activity relationships (2-methyltetrols and C_5-alkene triols) ~~can have some fraction remaining in the~~remain largely in the particle phase ~~instead of fully off-gassing due in part to their in-particle formation from the decomposition of oligomeric species by heterogeneous OH oxidation~~ (D'Ambro et al., 2019), which could be attributed to the formation of viscous organic coatings (Armstrong et al., 2022; Hu et al., 2016; Yan et al., 2023). Hu et al. (2016) noted that IEPOX-SOA species with higher volatilities (like 2-methyltetrols and C5 alkene triols) should off-gas, however when relative

Figure 1 is very hard to read, please increase the font and line size where possible and ensure that there are no compression issues during export.

We thank the reviewer for raising this point and have regenerated Fig. 1 to be more legible.

Line 168: “Given the numerical precision of CMAQ and the likelihood of very small *ws* values-characteristic of dry OAs yet still greater than zero-the occurrence of *ws* = 0 was minimal.” Please rephrase, this sentence was very hard to parse.

We have made the following change:



When $w_s = 0$, the aggregated OA phase state equation (Eq. 8~~2~~) collapses into ~~is equal to~~ the mass fraction weighted aggregated ~~T_gs, previously referred to as the~~ dry phase state equation, represented by $T_{g,org}$ (Dette et al., 2014; Li et al., 2021; Li et al., 2020):

$$T_{g,org} = w_a T_{g,a} + w_b T_{g,b} \qquad (14)$$

~~.~~ Given there ~~numerical precision of CMAQ and the likelihood of very small w_s values characteristic of dry OAs yet still greater than zero~~ was never an occurrence during our modeling where ~~the occurrence of~~ $w_s = 0$ ~~was minimal~~, we ~~. A recent~~

~~publication~~ use ~~defined the~~ equation 14 when ~~dry phase state as~~ $w_s \leq 0.1$ (Rasool et al., 2021), signifying a dry aggregate glass transition temperature that does not consider water uptake to the organic shell. While our implementation of phase separation and phase state in CMAQ did~~does~~ not implement in-model conditionals to switch between using $T_g(w_{org})$ and $T_{g,org}$ ~~phase state equations~~ based off of these w_s thresholds~~values~~, we identify dry aerosol phase state instances offline ~~using this threshold and refer to it as $T_{g,org}$~~.

Line 255: It would be helpful to indicate the CTR SOAS site on the plots shown in Figure 2 since you reference it here.

We thank the reviewer and have made this change in Figure 2, 3, and 6 to identify both the CTR and LRK SOAS sites:

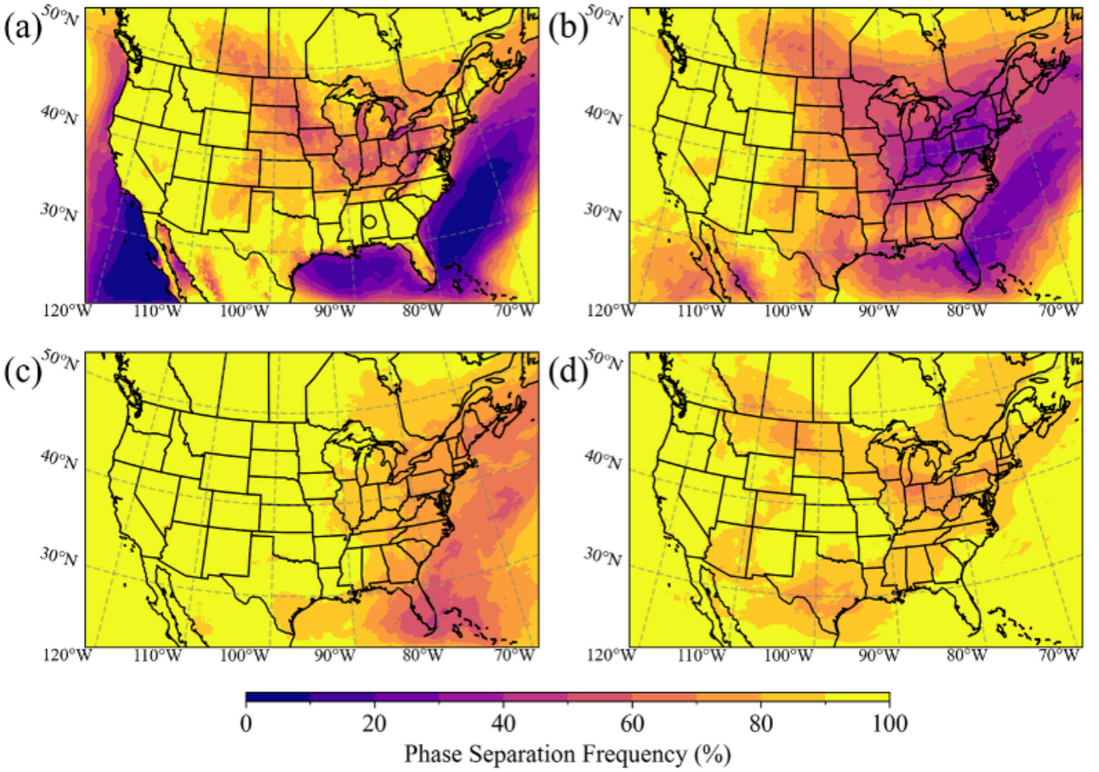


Figure 2. Frequency of modelled aerosol phase separation for the SOAS 2013 Field Campaign episode (June 1st – July 15, 2013) at layer 1 (surface layer; 1-0.9975 atm (a)), layer 18 (corresponding to ~1.8km; 0.82-0.8 atm (b)), layer 28 (corresponding to ~8km; 0.4-0.35 atm (c)), and layer 35 (corresponding to ~17km; 0.05-0 atm (d)) across hourly model estimations. Black open circles in panel (a) correspond to Look Rock, Tennessee (LRK) and Centreville, Alabama (CTR) SOAS observation sites.

Line 261: "The frequency of time that the organic coating of an aerosol is in a liquid phase in layer 1 (i.e., ground level, GL) across the whole modeling episode when an appreciable amount of ALW is present in the organic coating (when $ws > 0.1$) and when $ws \leq 0.1$, corresponding to $Tg(worg)$: T and Tg,org: T, is shown in Figure 3." Please clarify if this is the same modeling episode as Figure 2 (June 1 – July 15, 2013).

Yes – for all figures the entire SOAS episode (June 1st – July15th, 2013) was used. The following changes have been made:

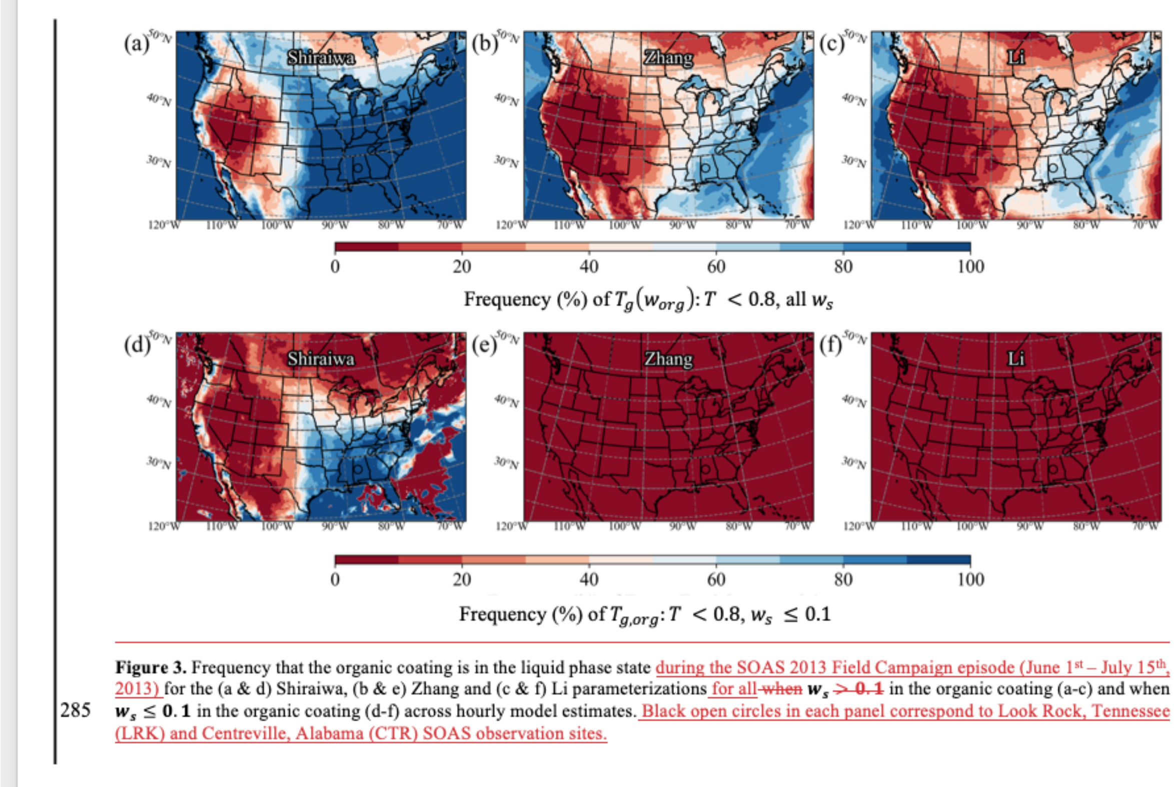


Figure 3. Frequency that the organic coating is in the liquid phase state during the SOAS 2013 Field Campaign episode (June 1st – July 15th, 2013) for the (a & d) Shiraiwa, (b & e) Zhang and (c & f) Li parameterizations for all ~~when~~ $\boldsymbol{w_s}$ ~~$\boldsymbol{> 0.1}$~~ in the organic coating (a-c) and when $\boldsymbol{w_s \leq 0.1}$ in the organic coating (d-f) across hourly model estimates. Black open circles in each panel correspond to Look Rock, Tennessee (LRK) and Centreville, Alabama (CTR) SOAS observation sites.

Figure 3: It would be helpful to add subheadings for the model used on the columns and water content condition for the rows, also please fix the legibility issues.

We thank the reviewer for the recommendation and have made the following changes:

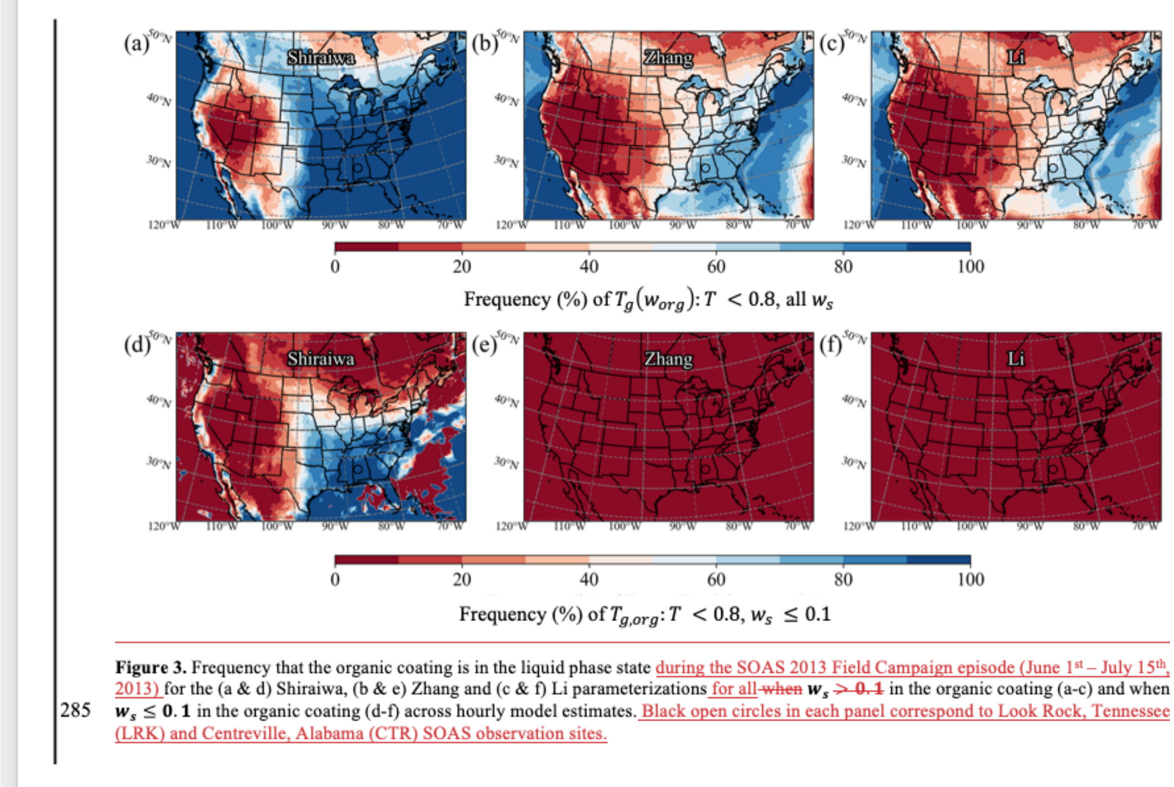
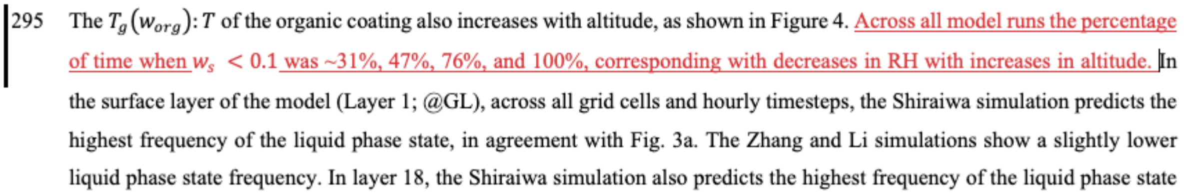


Figure 3. Frequency that the organic coating is in the liquid phase state during the SOAS 2013 Field Campaign episode (June 1st – July 15th, 2013) for the (a & d) Shiraiwa, (b & e) Zhang and (c & f) Li parameterizations for all ~~when~~ $\boldsymbol{w_s}$ ~~$\boldsymbol{> 0.1}$~~ in the organic coating (a-c) and when $\boldsymbol{w_s \leq 0.1}$ in the organic coating (d-f) across hourly model estimates. Black open circles in each panel correspond to Look Rock, Tennessee (LRK) and Centreville, Alabama (CTR) SOAS observation sites.

Figure 4: What was the normalization process? Additionally, what fraction of the time was $w_s > 0.1$?

Distributions were normalized in the sense that the area under each curve was equal to 1 and are representative of densities as opposed to counts. Across each run the fraction of time ws > 0.1 was ~31%, 47%, 76%, and 100% corresponding to layers 1, 18, 28, and 35. The following changes have been made:



The $T_g(w_{org})$: T of the organic coating also increases with altitude, as shown in Figure 4. Across all model runs the percentage of time when w_s < 0.1 was ~31%, 47%, 76%, and 100%, corresponding with decreases in RH with increases in altitude. In the surface layer of the model (Layer 1; @GL), across all grid cells and hourly timesteps, the Shiraiwa simulation predicts the highest frequency of the liquid phase state, in agreement with Fig. 3a. The Zhang and Li simulations show a slightly lower liquid phase state frequency. In layer 18, the Shiraiwa simulation also predicts the highest frequency of the liquid phase state

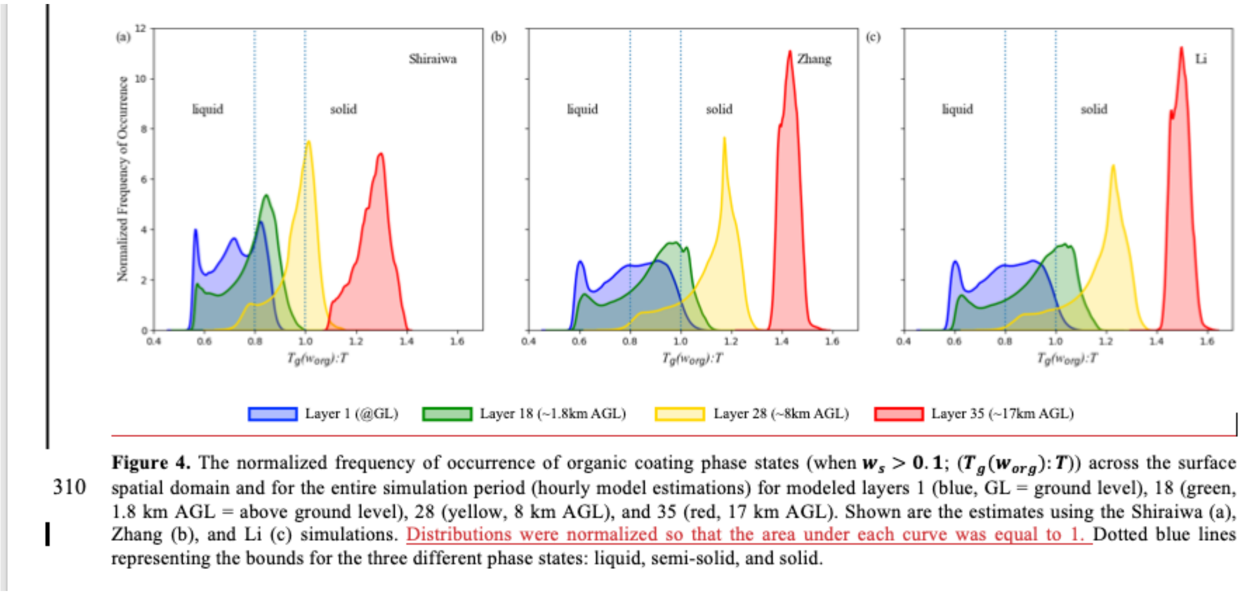


Figure 4. The normalized frequency of occurrence of organic coating phase states (when $\boldsymbol{w_s > 0.1}$; $(\boldsymbol{T_g(w_{org}):T})$) across the surface spatial domain and for the entire simulation period (hourly model estimations) for modeled layers 1 (blue, GL = ground level), 18 (green, 1.8 km AGL = above ground level), 28 (yellow, 8 km AGL), and 35 (red, 17 km AGL). Shown are the estimates using the Shiraiwa (a), Zhang (b), and Li (c) simulations. Distributions were normalized so that the area under each curve was equal to 1. Dotted blue lines representing the bounds for the three different phase states: liquid, semi-solid, and solid.

Figure 7: From your caption, it seems like a and b are from CTR and c is from LRK. However, the text states that b and c are both from LRK. Please clarify this in both the text and figure caption. Also, please address why these are all not from the same site, I assume it is due to what data was collected at each site but please be explicit. Also, if you only have one site for each species comparison, how confident are you that the addition of phase separation into the model will be consistent with underpredicting IEPOX-SOA and organosulfates, and overpredicting 2-methyltetrols?

We thank the reviewer for pointing this out and have made the following changes to this figure:

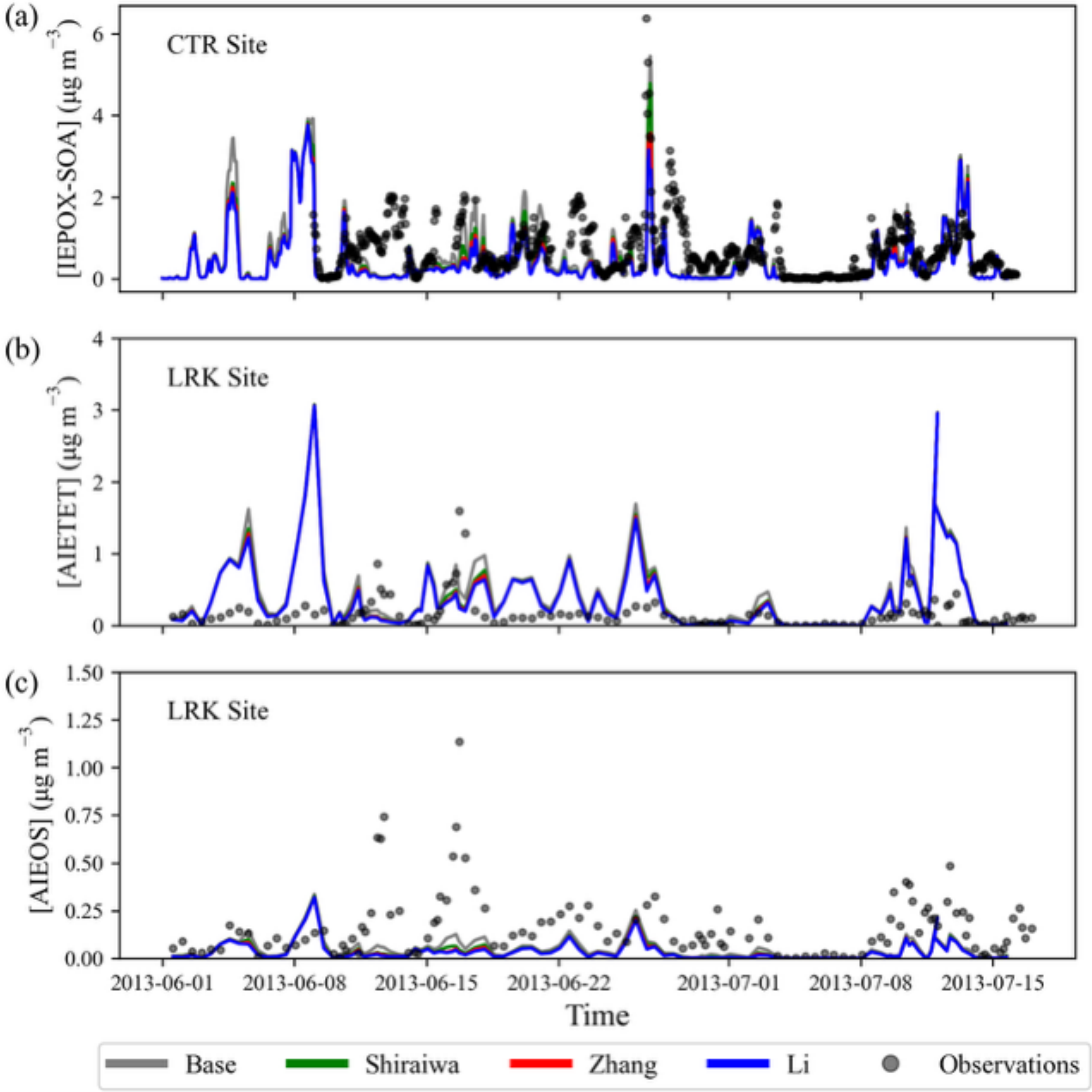
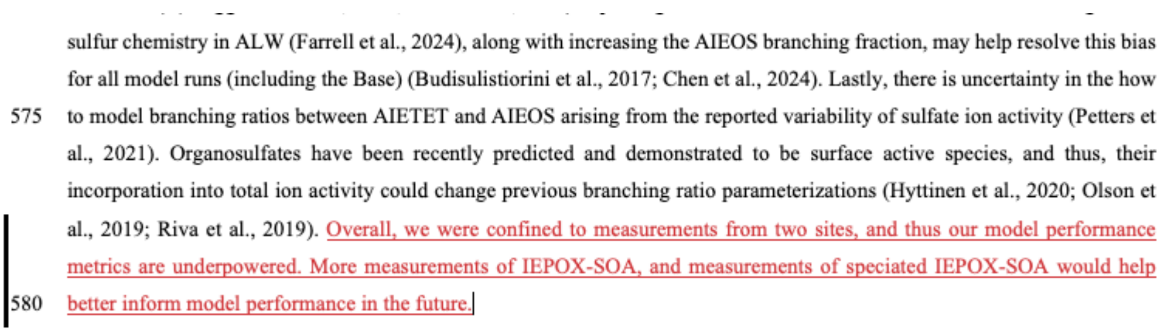


Figure 7. Observational and predicted concentrations of (a) total IEPOX-SOA at CTR and (b) AIETET and (c) AIEOS at the LRK SOAS site for June 1st – July 15th, 2013. Predicted concentrations are shown for base CMAQ (grey), Shiraiwa (green), Zhang (red), and Li (blue) model simulations.

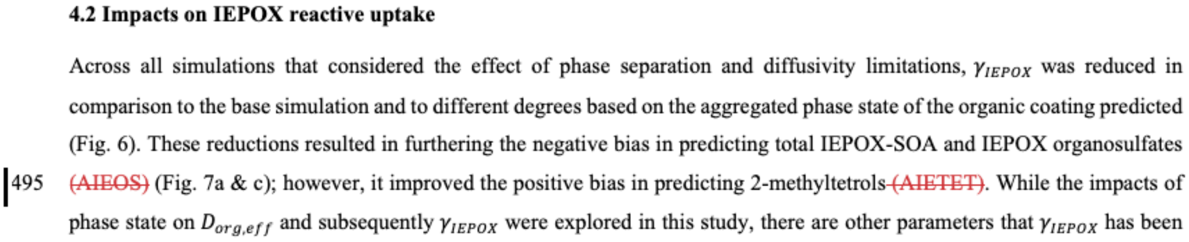
The measurements used from these sites were chosen because for this modeling episode, where the two sites where IEPOX-SOA specifically was measured and the LRK site was the only site to differentiate between different IEPOX-SOA species (i.e. 2-methyltetrols and methyltetrol sulfates). We agree that in terms of model evaluation metrics, the biases calculated are under-powered, and have made the following change to our results section:



sulfur chemistry in ALW (Farrell et al., 2024), along with increasing the AIEOS branching fraction, may help resolve this bias for all model runs (including the Base) (Budisulistiorini et al., 2017; Chen et al., 2024). Lastly, there is uncertainty in the how to model branching ratios between AIETET and AIEOS arising from the reported variability of sulfate ion activity (Petters et al., 2021). Organosulfates have been recently predicted and demonstrated to be surface active species, and thus, their incorporation into total ion activity could change previous branching ratio parameterizations (Hyttinen et al., 2020; Olson et al., 2019; Riva et al., 2019). Overall, we were confined to measurements from two sites, and thus our model performance metrics are underpowered. More measurements of IEPOX-SOA, and measurements of speciated IEPOX-SOA would help better inform model performance in the future.

Line 474: You have already introduced AIEOS and AIETET as acronyms previously.

Thank you for catching this, we've made the following correction:



4.2 Impacts on IEPOX reactive uptake

Across all simulations that considered the effect of phase separation and diffusivity limitations, γ_{IEPOX} was reduced in comparison to the base simulation and to different degrees based on the aggregated phase state of the organic coating predicted (Fig. 6). These reductions resulted in furthering the negative bias in predicting total IEPOX-SOA and IEPOX organosulfates ~~(AIEOS)~~ (Fig. 7a & c); however, it improved the positive bias in predicting 2-methyltetrols ~~(AIETET)~~. While the impacts of phase state on $D_{org,eff}$ and subsequently γ_{IEPOX} were explored in this study, there are other parameters that γ_{IEPOX} has been

Armstrong, N. C., Chen, Y., Cui, T., Zhang, Y., Christensen, C., Zhang, Z., Turpin, B. J., Chan, M. N., Gold, A., Ault, A. P., & Surratt, J. D. Isoprene Epoxydiol-Derived Sulfated and Nonsulfated Oligomers Suppress Particulate Mass Loss during Oxidative Aging of Secondary Organic Aerosol. *Environmental Science & Technology, 56*(23), 16611-16620. doi:10.1021/acs.est.2c03200 (2022).

D'Ambro, E. L., Schobesberger, S., Gaston, C. J., Lopez-Hilfiker, F. D., Lee, B. H., Liu, J., Zelenyuk, A., Bell, D., Cappa, C. D., Helgestad, T., Li, Z., Guenther, A., Wang, J., Wise, M., Caylor, R., Surratt, J. D., Riedel, T., Hyttinen, N., Salo, V. T., Hasan, G., Kurtén, T., Shilling, J. E., & Thornton, J. A. Chamber-based insights into the factors controlling epoxydiol (IEPOX) secondary organic aerosol (SOA) yield, composition, and volatility. *Atmos. Chem. Phys., 19*(17), 11253-11265. doi:10.5194/acp-19-11253-2019 (2019).

Hu, W., Palm, B. B., Day, D. A., Campuzano-Jost, P., Krechmer, J. E., Peng, Z., de Sá, S. S., Martin, S. T., Alexander, M. L., Baumann, K., Hacker, L., Kiendler-Scharr, A., Koss, A. R., de Gouw, J. A., Goldstein, A. H., Seco, R., Sjostedt, S. J., Park, J. H., Guenther, A. B., Kim, S., Canonaco, F., Prévôt, A. S. H., Brune, W. H., & Jimenez, J. L. Volatility and lifetime against OH heterogeneous reaction of ambient isoprene-epoxydiols-derived secondary organic aerosol (IEPOX-SOA). *Atmos. Chem. Phys., 16*(18), 11563-11580. doi:10.5194/acp-16-11563-2016 (2016).

Yan, J., Armstrong, N. C., Kolozsvari, K. R., Waters, C. M., Xiao, Y., Fankhauser, A. M., Cooke, M. E., Frauenheim, M., Buchenau, N. A., Parham, R. L., Zhang, Z., Turpin, B. J., Lambe, A. T., Gold, A., Ault, A. P., & Surratt, J. D. Effect of Initial Seed Aerosol Acidity on the Kinetics and Products of Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-

Derived Secondary Organic Aerosol. *The Journal of Physical Chemistry A, 129*(18), 4132-4147. doi:10.1021/acs.jpca.4c08082 (2025).

Yan, J., Zhang, Y., Chen, Y., Armstrong, N. C., Buchenau, N. A., Lei, Z., Xiao, Y., Zhang, Z., Lambe, A. T., Chan, M. N., Turpin, B. J., Gold, A., Ault, A. P., & Surratt, J. D. Kinetics and Products of Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-Derived Secondary Organic Aerosol. *ACS Earth and Space Chemistry, 7*(10), 1916-1928. doi:10.1021/acsearthspacechem.3c00073 (2023).