Response to Review #1

Thank you for the helpful comments and suggestions. We appreciate your time for reviewing our paper. We have addressed all of your comments as detailed below:

Major comment:

As the authors indicate on multiple occasions, it is imperative to model atmospheric ozone better for the right reasons. This is a high standard to achieve in atmospheric modeling because numerous processes (both chemical and physical) may affect the concentration of a singular important species in the atmosphere. The first justification that the updated chemistry in TS2 improved the simulations of ozone for the right reasons was that its output in box modeling simulations closely matched that of more explicit mechanisms like the MCM as shown in Figures 3-6. This was summarized in the second paragraph of the Conclusions. However, in that same paragraph the authors highlighted important differences between TS2 and MCM seemingly contradicting their previous statement. Inter-model comparisons are not extremely useful in justifying updates to a model because both models may contain quite a few simplifications and/or uncertainties.

We revise the text in the conclusions to explain in more detail why in general MCM does compare well with MOZART-TS2, but due to some inaccurate assumptions in MCM there are differences between the two mechanisms that impact ozone formation. Although we agree that field campaign comparisons are very useful for evaluating new chemical mechanisms, we also believe inter-comparisons between different chemical mechanisms are valuable. Without such comparisons, it would be difficult for future studies to accurately pick the best chemical mechanism to use to answer their specific science question. Also we want to highlight the inaccurate assumption in MCM here, so that future studies that use MCM for terpene oxidation update this chemistry.

"The box modeling results (Section 4.1 and 4.2) demonstrate that TS2 simulates 1st- and later-generation isoprene and terpene oxidation products better than TS1 in comparison to more explicit schemes like the Caltech mechanism and MCM. Verification that the isoprene and terpene oxidation chemistry is correctly represented in TS2 enhances confidence that ozone is accurately simulated for the right reasons. The box-modeling results also uncovered a simplification in MCM where terpene unsaturated hydroxy nitrate oxidation is not accurately represented, leading to large impacts on NO_x recycling and ozone formation (Section 4.2). Future studies using MCM v3.3.1 to simulate the oxidation of terpenes, especially those that contain more than one double bond, should update this simplification."

A better justification was made when comparing the model outputs with experimental data. While Figure 7 illustrates that TS2 does reduce the bias of modeled surface ozone concentrations across the US when compared with US EPA CASTNET data, Figure 9 (1st panel) shows that the model vertical profile is still inaccurate with overpredictions below the planetary boundary layer and underpredictions above it when compared with SEAC4Rs flight tracks. While the changes involving predominantly the organic nitrate chemistry have reduced surface level biases in ozone predictions, challenges remain

including: "PBL height, mixing schemes, clouds, vertical resolution, or ozone dry deposition schemes" (bottom of pg. 25). This should be echoed in the abstract and conclusions with further discussion in the section from which the quote was extracted (Section 4.4 after pg. 25). While the discussion of Figure 9 is extensive, model biases for different observables should be tied back to the ozone profile since this is the focus of the paper. For example, can corrections to jNO2 or the concentrations of biogenic VOCs be enough to predict the correct shape of the ozone vertical profile?

Good points. We revise the text to further highlight how biases in various products like jNO2 and biogenic VOCs will influence ozone:

"The vertical profile shape for ozone is quite different between the model and observations. There are also clear differences between the model and observations for NO_2 photolysis and ozone precursors like NO_x and VOCs. Possible explanations for the remaining biases are further described below and will be explored more completely in future work."

"A cloud-induced reduction in j_{NO2} below 1 km and an increase between 2-4 km would improve the ozone and j_{NO2} profile shapes."

"Future work will evaluate whether using finer horizontal resolution (14 km) removes these biases in biogenic VOCs in CAM-chem. If isoprene and monoterpenes are still under-predicted, increasing these biogenic emissions will enhance the overall bias in ozone."

We also add the following to the conclusions to highlight what the next steps will be in improving the ozone bias in CAM-chem in the future:
"This bias could be caused by remaining uncertainties in the chemistry (Section 5.2) or by processes other than chemistry, which will be evaluated in future work. Considering the analysis against the SEAC^{4}RS field campaign results, the first step toward reducing the remaining ozone bias will be to evaluate how finer horizontal resolution (14 km) impacts the results. Because biogenic and anthropogenic emissions in the southeast U.S. are spatially segregated, improvements in simulated ozone and biogenic VOCs are expected with finer horizontal resolution. Future work will also include evaluating different anthropogenic emission inventories and a more thorough investigation into whether biogenic emissions are accurately represented by MEGAN in CAM-chem. Additionally, cloud biases in CAM-chem will be investigated more in the future given their likelihood for improving the vertical profile shape of ozone, ozone precursors, and j_{NO2}. Considering that biases in the ozone profile shape are enhanced with stronger nudging to meteorological data (Figure S6), a more thorough analysis on the impact of nudging on CAM-chem dynamics and cloud parameterizations should be conducted. Future work will also evaluate whether enhanced vertical resolution is needed to improve PBL height and mixing schemes. Further evaluation of different chemical solvers (Sun et al., 2017) is also needed. Additionally, ozone dry deposition has a large impact on simulated surface ozone (val Martin et al., 2014; Clifton et al., 2019) and a thorough evaluation and update to the ozone dry deposition scheme used in CAM-chem should be performed. Ozone is a complicated pollutant to accurately simulate in models. This work demonstrates that updating isoprene and terpene gas-phase chemistry clearly improves simulated surface ozone in CAM-chem and that additional studies evaluating and updating other processes are needed to further reduce the ozone bias."

And we added in the abstract:
“Although the updates to isoprene and terpene chemistry greatly reduce the ozone bias in CAM-chem, a large bias remains. Evaluation against SEAC^{4}RS field campaign results suggests future improvements to horizontal resolution and cloud parameterizations in CAM-chem may be particularly important for further reducing this bias.”

Minor comments:

1. Reference to CMAQ isoprene updates should be added to the Introduction on page 2 line 29 (see Pye et al. Environ. Sci. Technol. 2013, 47, 19, 11056-11064)

Yes, thanks for pointing this out. We have added this reference.

2. It was unusual not to see some of the organic nitrates in Figures 1 and 2 in blue when they are isomers of other species that undergo aerosol uptake. It isn’t until 2.2.1 (pg. 7 line 7) that the author’s mention tertiary nitrates are more likely to experience reactive aerosol uptake. This could also be specified in the captions to avoid confusion.

Yes, we have added:
“As shown, only certain isomers of organic nitrates undergo aerosol uptake as explained in Section 2.4.

3. Are there gray boxes that can be added to Figure 2 like in Figure 1 to denote new chemistry?

Yes, we have added gray boxes as done in Figure 1 for clarity.

4. dH/R should precede “6014 K” on line 16, page 5 of the manuscript for clarity of where the value comes from.

Yes, we update this sentence to:
“If the Henry's law temperature dependence **(dH/R)** was unavailable in the literature, 6014 K was assumed consistent with GECKO-A.”

5. The yield of IEPOX from ISOPOOH + OH should be stated in the text on page 6 in order to understand its contribution to recycling HOx and aerosol formation. Other products of ISOPOOH + OH include the formation of isoprene dihydroperoxides (ISOPOOHOOH) that consume HOx (and therefore may give rise to less ozone) as in Liu et al. Environ. Sci. Technol. 2016, 50, 9872-9880 and Piletic et al. J. Phys. Chem. A, 2019, 123, 4, 906-919. Why were such products that potentially affect HOx, ozone and aerosol yields not included in an updated isoprene mechanism?

The MOZART-TS2 mechanism does not treat ISOPOOHOOH as a separate species in order to reduce cost because it is a minor product. However, ISOPOOHOOH is included in the surrogate compound ISOPHFP, which represents all isoprene highly functionalized hydroperoxides and there is a yield of ISOPHFP from ISOPOOH + OH reaction. Considering the yield of ISOPOOHOOH and other low-volatility products formed from 1,5-H-shifts from ISOPOOH + OH reaction is uncertain including a lumped tracer ISOPHFP for these processes is reasonable. ISOPHFP and other low-volatility products do have a loss to aerosol in CAM-chem, so that HO_x and O_3 are more accurately represented, but they do not form SOA directly. In CAM-chem, SOA is formed via a VBS scheme, which was not updated in this work. Future work will link products like ISOPHFP to form SOA directly in CAM-chem, but such updates are beyond the scope of this work.

We update the title to "Comprehensive isoprene and terpene **gas-phase** chemistry improves simulated surface ozone in the southeastern U.S." to emphasize the scope of this work is to update the gas-phase mechanism.

We recognize that the description did not include enough detail for the isoprene low-NO_x chemistry and so have added the following to the MOZART-TS2 mechanism description in Section 2.2.1 and cited the papers above:

"OH addition to ISOPOOH forms a 0.85 yield of isoprene epoxydiol (IEPOX) & OH; a 0.07 yield of glycolaldehyde, hydroxyacetone, & OH; and a 0.08 yield of ISOPHFP, which is a surrogate compound for all isoprene highly functionalized hydroperoxides (Krechmer et al. 2015; Riva et al., 2016; St. Clair et al., 2016; Liu et al., 2016; Piletic et al., 2019). ISOPHFP undergoes aerosol uptake in TS2 to more accurately represent loss processes of HO_x, but like organic nitrates does not explicitly form SOA. SOA is formed by a volatility basis set (VBS) scheme in CAM-chem, which was not updated in this work. Directly forming SOA from low-volatility products like ISOPHFP in CAM-chem is a goal for future work."

6. Many papers regarding Criegee intermediates have the 'C' capitalized. Please correct this in the manuscript.

Thanks, we have updated this.

7. On page 17, line 8, it states that "TS2 was altered to use RCIM assumptions for formation and loss of PAN and: : :" What specifically was altered in this sensitivity test?

We remove "which are explicitly listed in Table S7" and add in a more complete sentence stating: "The revised reactions for each of these sensitivity tests are listed explicitly in Table S7." And added:
"Unlike TS2, RCIM does not include PAN photolysis or the CH_3CO_3 + CH_3CO_3 reaction and RCIM uses different reaction rate constants than TS2 for PAN formation, thermal decomposition, and reaction with OH (Table S7)."

8. On page 19, line 18, it states "Commonly, in MCM, unsaturated hydroxy nitrates will react with OH via H-abstraction : : :". Please add "derived from terpenes" after nitrates to specify that this does not involve hydroxy nitrates derived from isoprene.

Very good clarification, thanks this has been added in this location and a couple others for clarity.

9. Figure 9 should have same color scheme for TS1 and TS2 with its predecessors (Figs 3-6) for consistency.

This has been updated TS1 is red and TS2 is purple in all figures now.

10. The equation used to derive the organic nitrate yields using alpha and n in the Supporting Information (pgs. 49-51) should be stated with the reference included for clarity.

We updated the description in the Table S6 to “see notes [a]” with a link, so that it is clear that more information is in the table notes. Then we also update the note to include the formula used along with the reference.