Response to Review #2

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:

Overall

The mechanism is expected to be included in future versions of the CESM model and is offered to any interested party if they'd like to access the updates prior to the new release. If for whatever reason the TS2 mechanism does not make it into a future CESM release the authors should guarantee an alternative location for the code to be made available.

We have updated the code data availability section to include more details. The TS2 chemistry will very likely be released as a new compset in CESM 2.2. We include reference to the CAM-chem wiki, which will always have the updated status of the new and old chemical mechanisms available in CAM-chem. If for some very unlikely reason, TS2 is not implemented into CESM 2.2, we will provide directions for how to implement the changes on this referenced wiki-page. We do not want to upload the code now as the updates include both a new chemical mechanism and source code modifications, and we do not want users to inaccurately implement the code. We also upload ozone hourly and SEAC^{4}Rs flight track data used in this work to a repository and describe this here:

"The code updates described in this work will be made available as a new compset in a future release of CESM likely CESM 2.2. Chemical mechanisms used in CAM-chem are listed on the CAM-chem wiki page at https://wiki.ucar.edu/display/camchem/Gas-Phase+Chemistry, which includes a brief description, a citation reference, and information on their current status. Please contact Rebecca Schwantes (rschwant@ucar.edu) if you would like the TS2 updates prior to their future release in CESM. CESM/CAM-chem output for 2013 August hourly ozone, 2013 August monthly average default output, and SEAC^{4}RS flight tracks used in this work are provided on NCAR's Digital Asset Services Hub (DASH) here: https://dashrepo.ucar.edu/dataset/68_rschwant.html (Schwantes and Emmons 2020)."

Comments

Figures 1 and 2 should point to Table S2.

The following has been added to the caption for Figure 1 and 2:
"All species names used in TS2 are described in Table S2."

Figures 1 and 2 are schematics of OH oxidation and Figures S1 and S2 are schematics of NO3 oxidation. Why were no schematics of O3 oxidation included (and only described in Sections 2.2.2 and 2.3.2). For completeness, I feel that O3 oxidation schematics could be included in the supplement.

For clarity we have added a schematic for O_3 oxidation of isoprene and terpenes to the Supplement in Figure S3. We add reference to Figure S3 in Section 2, 2.2.2, 2.3.2.

"and for O_3-initiated oxidation in Figures S3."
"O_3-initiated oxidation of isoprene is simply described in Figure S3"
"O_3-initiated oxidation of the terpene surrogate compounds in TS2 is described in a simplified schematic in Figure S3."

Page 7, Line 1: The authors mention that "multiple isomers were only incorporated into TS2 if grouping them together would bias HOx or NOx budgets." How was this determined? Were there sensitivity or testing runs conducted and that are not described? Please describe.

We have reworded this and added more detail. We did not run sensitivity tests for this. Instead this was determined based on the chemistry.
"To save computational cost, multiple isomers were only incorporated into TS2 if grouping them together would bias the HO_x or NO_x budgets. For example, the two dominant isomers of ISOPOOH react with OH to produce similar yields of OH and a similar distribution of IEPOX isomers (Wennberg et al. 2018), so grouping isomers of ISOPOOH and IEPOX together to reduce computational cost is warranted. In contrast, TS2 includes multiple isomers of HPALDs and hydroxy nitrates because different isomers react with OH to produce varying levels of OH and NO_2, so combining these isomers together would inaccurately influence the HO_x and NO_x budgets."

Page 7, Line 9: The authors mention that the "number of organic nitrates in TS2 was optimized to accurately represent" varying reaction rates. What sort of optimization was done? What were the optimization criteria? This needs more detail.

Good point, we updated this sentence below. Specifically, we changed "optimized" to "selected" here because there was not an optimization program run. The selection was instead based on reaction rates, products, and atmospheric fate of each isomer.
"The organic nitrates in TS2 were carefully selected to account for these varying fates, but also when possible to combine isomers with similar reaction rates, oxidation products, and overall atmospheric fate together to reduce computational cost."

The supplemental Figures S1 and S2 should be referenced more thoroughly in the manuscript, esp. within the captions of Figures 1 and 2 and in the accompanying sections (Section 2.2.3 and 2.3.3).

We add additional references to Figures S1 and S2 in Section 2.2.3 and 2.3.3.
"Isoprene NO_3-initiated oxidation in TS2 is described in a simplified schematic in Figure S1 and …"
"Where structurally similar, organic nitrates from OH and NO_3 oxidation are shared to reduce computational cost (Figure 1 and S1).
"as summarized in a simplified schematic in Figure S2."
"… and TERPNPS1 (unsaturated primary/secondary) (Figure S2)"
"… the corresponding saturated nitrooxy hydroperoxide (Figure S2)"

As suggested, we also now reference the NO_3 and O_3 supplemental figures in the caption of Figure 1 and 2 to make certain the reader knows these figures are available.
"Similar schematics for NO_3- and O_3-initiated oxidation of isoprene are provided in Figure S1 and S3 in the supplement."
"Similar schematics for NO_3- and O_3-initiated oxidation of terpenes are provided in Figure S2 and S3 in the supplement."

Page 10, Line 10: Were there any alternative approaches that could be made to represent terpene products here? Were these approaches tested or considered? A description of why this particular choice was made (and what the likely impact on computational cost and resulting chemistry would be) should be included.

We did not test many different versions of the TS2 mechanisms, but agree that in the future creating reduced chemical mechanisms more systematically from explicit chemical mechanisms would be useful. We add the following to describe in more detail why the oxidation products selected here were used.

"The terpene products described above were selected, so that compounds that are chemically similar (i.e. contain the same functional groups and react with OH, O_3, and NO_3 at similar rates) are grouped together. The complexity of the chemistry is largely determined by the current knowledge of the system. There may be advantages to adding more complexity into TS2 in the future as more knowledge about terpene oxidation especially later-generation chemistry becomes available. Given terpene-later-generation chemistry is not well understood and that chemistry of many terpene products is largely estimated based on similar more well-studied compounds, adding separate products for each of the terpene surrogate compounds would increase cost without adding a lot of additional information into the system."

Section 2.4: I feel that a more thorough descriptions of the impacts of the TS2 mechanism on aerosol formation can be included. The existing section is sparse compared to the other sections, and although the authors make not of the large uncertainties that remain, I feel that more can be added. Perhaps the manuscript title can include the word "gas-phase" after the word "Comprehensive" in order to highlight that this manuscript is largely focused on the gas-phase chemistry of isoprene and terpene and that future development of the aerosol scheme is slated for future work.

Yes, good point we add "gas-phase" to the title. This work is more focused on the gas-phase chemistry. The Volatility Basis Set scheme that forms SOA in CAM-chem was not changed in this work. We update Section 2.4:

"In TS2, aerosol uptake of organic nitrates is only a gas-phase sink for organic nitrates and does not form SOA directly. SOA in TS2 only forms from a VBS scheme (Tilmes et al., 2020), which was not updated in this work. Better connecting gas-phase chemistry and SOA formation is a goal for future work as uptake of organic nitrates to form SOA is important for accurately representing gas-phase ozone as well as the overall magnitude of SOA. Aerosol uptake of organic nitrates is quite uncertain (Section 5.2) and further studies investigating the processes of organic nitrate uptake and hydrolysis as well as more complex implementation of these processes in models is warranted and a goal for future work."

The results and discussion section (Section 4) is very long (21 pages) and I feel can be split into separate sections. Perhaps the evaluation of the explicit schemes (Sections 4.1 and 4.2) and the global modeling evaluation against surface observations and field campaign data (Sections 4.3 and 4.4) can remain in Section 4, while the discussion of the organic nitrate fate (Section 4.5) and the overall discussion of uncertainties (Section 4.6) can be moved to a Discussion Section (Section 5). The existing Conclusion section (Section 5) can then me moved to Section 6.

We have split the results and discussion section and agree this adds clarity. Thanks for the suggestion.

In Figures 3, 4, 5, and 6, I find it somewhat difficult to differentiate between the blue colors used to label TS1 and TS2. Changing one of them to a more distinct color (green, perhaps?) would aid in clarity. [NOTE: This appears to be the case only when I print the manuscript out, and the colors are clearly distinguishable when I look at a digital copy]

The colors have been updated such that blue and cyan are no longer included together in any of the plots, so we have updated Figures 3, 4, 5, 6, S4, S5, 9, 10, S6, S7. We have also increased the width of the lines and all Test cases for the box-model analysis are in dashed lines to make it easier to differentiate the different lines on the plot.

The sensitivity tests in the Figures are labelled as "Test 1, Test 2", while in the captions are labelled "test 1, test 2" and in the manuscript as "first sensitivity test, second sensitivity test." I suggest sticking with the "Test 1, Test 2" format and making this consistent throughout the sections.

Yes, we have adjusted this to refer to the sensitivity tests as a whole as "sensitivity tests" and individually as Test 1, Test 2, etc.

Page 19, Line 26: The authors state that "These unrealistically fast cycles are commonly used in MCM to reduce the number of species...". Is there a citation for this claim? How do the authors know this is the case?

We have seen this for other systems too (e.g., cresol oxidation pathway - Schwantes et al. 2017, ACP), but because we have not done a thorough examination and it is possible these are the only 2 instances, we remove:
"are commonly used in MCM to reduce the number of species and"

Page 31 Line 7-8: Could you expand (speculate) on some of the possible sources of uncertainties that are less-well known?

Yes, we have added an example:

“For example, our understanding of reaction rates and products from peroxy radical isomerization reactions that lead to auto-oxidation is rudimentary and under-constrained (Wennberg et al. 2018). Because much is unknown about peroxy radical isomerization reactions, there is not a clear understanding of how important these reactions are in the ambient atmosphere.”

Page 34, Line 2 – Page 35, Line 1: This point has also been made by Mao et al. (2018) (www.atmos-chem-phys.net/18/2615/2018/) (see page 2622), and should be referenced.

This reference has been added.

Page 37, Line 28: I suggest including the Sun et al. (2017) reference in which they were able to reduce Eastern US ozone bias via the utilization of a new solver scheme (https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2016MS000863). Additionally, I believe a slightly expanded discussion of the remaining sources of uncertainty would significantly enhance this final paragraph.

Great point. This reference has been added to the introduction and chemical solver is added as an additional uncertainty in the conclusions. Additional discussion of the remaining sources of uncertainty also has been added to the conclusion:

“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.”