Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Comprehensive isoprene and terpene chemistry improves simulated surface ozone in the southeastern U.S." *by* Rebecca H. Schwantes et al.

Anonymous Referee #1

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In the manuscript, the authors have updated the isoprene and terpene chemistry in CESM/CAM-chem model to determine its impact on simulations of ozone. With the updates predominantly focused on organic nitrate production and fate, the bias in mean ozone concentrations was reduced by up to 7 ppb. The comprehensive study involved box model simulations and field study comparisons where the CESM/CAM-chem model was compared with more explicit atmospheric chemistry models such as MCM and the Caltech isoprene mechanism. While mean biases were reduced in the revised model, it still does not capture the vertical profile of ozone suggesting other chemical and/or physical processes are responsible which must be discussed further. The manuscript would have to be revised in order to be accepted for publication in ACP.

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. 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?

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)

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.

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

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

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?

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

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?

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.

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

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.