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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 #3

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Review of "Comprehensive isoprene and terpene chemistry improves simulated surface ozone in the southeastern U.S." by R.H. Schwantes et al. (manuscript #acp-2019-902).

This manuscript describes the development of a detailed scheme for photooxidation of isoprene and terpenes in CESM/CAM-chem. The new scheme (MOZART-TS2) includes a significantly more complex representation of isoprene and terpene chemistry compared with the default mechanism (MOZART-TS1), with 21 additional transported species and over 100 additional reactions. The chemistry updates are informed by observationally based constraints from recent experimental data and explicit mechanisms

(MCMv3.3.1 and the Caltech isoprene mechanism). While still greatly reduced compared with explicit mechanisms, MOZART-TS2 includes significantly more detail than other mechanisms used in chemistry-climate models, particularly in the case of terpene chemistry. The new scheme is tested against these two explicit scheme in a box model context, and its broader impacts are assessed against SEAC4RS and USEPA CASTNET observations in the context of CESM/CAM-chem.

The study finds, in a box model context, that TS2 improves the simulation isoprene and terpene oxidation products over TS1, in comparison with explicit schemes. Several discrepancies between TS2 and MCM are attributed to faulty assumptions included in MCM. In the global model context, TS2 is found to reduce surface ozone biases and, in general, more accurately represent ozone, ozone precursors, and NOx reservoir species than TS1, in comparison with field observations. The new chemistry scheme, however, imposes a significant cost, increased in the computational time of CESM/CAM-Chem by $\sim$50%.

This manuscript is quite comprehensive and generally well written. The mechanisms, while complex, are presented clearly. Sufficient motivation and justification are provided for the decisions made. The evaluation, using both box models and global chemistry-climate models, give a very clear sense of the impacts of this mechanism on tropospheric chemistry, in particular on ozone. Some of the significant uncertainties remaining in the chemistry are explored and documented through carefully selected sensitivity simulations. While the manuscript is quite lengthy, this seems appropriate given the high level of detail being presented. Suitable use is made of supplementary material to convey somewhat lower-priority information. Overall, this is a very impressive piece of work. With relatively modest revisions, as described below, this paper would be suitable for publication in ACP, and would provide a valuable reference for chemical mechanisms of BVOC oxidation.

General comments

1) The box model simulations, comparing TS2 with TS1 and explicit mechanisms, currently only uses one set of chemical and meteorological conditions (August in Mississippi). It would have been helpful for box model simulations to have been conducted separately for high-NOx and low-NOx conditions. Given the very different oxidation pathways under these conditions, this would have provided a more stringent set of tests for the new mechanism. (I realize that new simulations would impose a significant analysis burden on the authors, so may not be practical.)

2) It might be helpful to split Results (4.1-4.4) and Discussions (4.5-4.6) into separate sections.

Specific comments

1. Introduction

page 3, lines 11-12 – Rephrase for clarity. For instance, "to determine the extent to which [improvements to] the chemical mechanism can explain ...."

2.1 Updates to Henry's Law Constants

p.5, l.15-16 – Clarify the definition of Henry's law temperature dependence (given here as 6014 K).

p.5, l. 16 – Add "used for dry deposition" after "reactivity factor (F0)."

3.1 Box modeling

p.13, l.24 – Planetary boundary layer *height*?

p.13, l.24 – Clarify here that only "general" photolysis rate constants are taken from CESM/CAM-chem-TS1 (as explained later).

p.13, l. 27-28 – Explain how deposition from CESM/CAM-chem is implemented in box model. For instance, dry deposition velocities? wet deposition loss frequencies? No ventilation/dilution of the box with background air is included, correct?

p.14, l.13-14 – "These are ideal scenarios designed" to "These idealized scenarios are designed ...."

3.2 Global modeling

p.14, l.18-21 – Which meteorological fields are nudged to reanalysis?

p.15, l.4-5 – Which years were used for spinup?

4. Results and Discussions

Figures 3-6 – Difficult to distinguish some of the individual lines in these plots. Try to modify colors, or make lines thicker.

p.17, l.8-9 – Explain the differences between the representations of PAN formation and loss (TS2 versus RCIM).

p.17, l.11 – Add "from RCIM" after "The PAN assumptions."

p.17, l.13 – Are the RCIM photolysis rates faster or slower? By how much?

4.2 Terpene Evaluation Against Explicit Species

p.19, l.5 – Clarify what is meant here by "total products produced."

p.20, l.3 – Add "oxidation of" before "the alpha-pinene."

4.4 Evaluation Against Field Campaign Data

Figure 7 – Add mean bias for Eastern US / Western US to figure panels.

p.28, l.1-3 – How do the dry deposition velocities of OVOCs compare in GEOS-Chem versus CESM/CAM-chem?

4.6.2 Uncertainties in Loss of Organic Nitrates

p.35, l.24 and l.26 – Clarify the meaning of "largely" here, e.g., do you mean "primary and secondary organic nitrates *largely* will not" and "... are *largely* lost ...."

Technical corrections

1. Introduction

p.3, l.3 – Hyphenate "terpene-derived" (and "isoprene-derived" throughout manuscript).

2. Development of MOZART-TS2

p.3, l.11 – Capitalize "Model."

3.1 Box modeling

p.14, l.6 – Include units for lat/lon (deg N, deg E).

3.2 Global modeling

p.14, l.22 – Run-on sentence. Break into two, starting with "Using a weak ...."

p.14, l.34 – Change to "(Table S3), using ...."

4. Results and Discussions

p.15, l.15 – "suggests" –> "suggest"

p.17, l.1 – Hyphenate "NO3-initiated."

4.2 Terpene Evaluation Against Explicit Species

p.20, l.1 – "Terpene-rich"

4.4 Evaluation Against Field Campaign Data

p.27, l.3 – Change to "above 2km; when clouds ...."

4.5 Organic Nitrate Formation and Fate

p.28, l.34 – "isoprene- and terpene-derived."

p.29, l.6 – Delete comma.

4.6.1 Uncertainties in Formation of Organic Nitrates

p.33, l.6 – Delete comma.

4.6.2 Uncertainties in Loss of Organic Nitrates

p.35, l.13 – Delete comma after "(Figure 1)."

p.35, l.16 – "under-constrained, leading to ...."

5. Conclusions

p.36, lines 15, 18, 31 – Missing commas.

p.37, line 9 – Missing comma.

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