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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding isoprene photo-oxidation using observations and modelling over a subtropical forest in the Southeast US" *by* L. Su et al.

Anonymous Referee #1

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This manuscript combines aircraft observations made at two sites in the Southeast US with a mixed layer chemistry model to investigate the influences of chemistry and dynamics on the budget of isoprene (and to a lesser extent, monoterpenes and ozone). The model is also used to evaluate changes in chemistry as a function of the NO:HO2 ratio.

The combination of a fairly novel measurement (from the WASP system) with the mixed layer model is an interesting approach that allows the authors to account for both chemical and dynamical boundary layer processes. The analysis generally seems appropriate, and this work is certainly within the scope for ACP. In some cases (details below),

details are missing that make it difficult or impossible to work out exactly what has been done and where the analysis is based on model vs. observations. This is associated with an occasional lack of clarity in the writing (although the writing is otherwise clear).

General comments

1. Throughout, PTR-MS (and PTR-ToF-MS) measurements of MVK and methacrolein (MACR) are used. There is a known interference in the MVK+MACR detection caused by ISOPOOH (Rivera-Rios et al., 2014). This could especially impact the observed diurnal cycle in Fig. 5h, given the timing of ISOPOOH growth shown in Fig. 8. Has this interference been accounted for (I don't see any mention in the text). If not, it should at least be discussed, but better yet would be to present a range for the measurements, with different assumptions about how strong the interference is.

2. There is some focus in the text and the analysis on O3, but this comes as a bit of a shock because it is not mentioned in the title, abstract, introduction, or conclusions. Why not? If the ozone budget analysis stays in the paper, it should at least be mentioned in the abstract, introduction and conclusions. Ideally, it would be nice if its inclusion were more closely tied to the isoprene work. As it stands now, the relevant text/figure just seem unrelated to the rest of the paper but nonetheless interesting).

3. NOx flux and ISOPN yields. The different values used (NOx flux 5-30, yield 6-12%) represent a very large range, and there needs to be more discussion of this in the text. In particular, I think Fig. S8 should be brought into the main text, and also made easier to read/interpret (i.e., how about solid/dashed/dotted to represent one parameter and colours to represent the other). The figure neatly shows that for most species (exception ISOPN), the choice of parameter has a smaller impact on the simulation than the existing measurement uncertainty.

For ISOPN, a more nuanced discussion is also needed. The ISOPN yield used here is on the extreme low end of the range found by Xiong et al. (2015), and much lower than used in the GEOS-Chem simulation that theoretically provides the basis for this model

(Mao et al., 2013). Both Xiong et al. (2015) and Wolfe et al. (2015) found an extra ISOPN sink was needed (although disagree on what that might be). A higher yield (and possible extra sink) here would make this work more consistent with the recent literature. I also think it would make this work more self consistent – if the simulation is overestimating peak NO at 7am, surely ISOPN should also be overestimated at the same time – as seen in the simulations run with 9-12% yield.

Specific comments

31625, final paragraph: These details about terminology don't seem relevant to the introduction. To some extent, NO:HO2 is just another metric with arbitrary "low" and "high" values (beyond the "balanced situation at 1). Where do you draw the line? I understand why this is a more useful metric, but I don't think it's clear or relevant yet at this stage in the paper, and I suggest moving this discussion to the section where it is actually used (6.4). Also, I don't understand what is meant by the sentence "Second, HO2, RO2, . . . are not explicitly represented. . ." You mean, just in the nomenclature? They are still influencing what happens in different regimes.

31629, 23-25: As written this is somewhat misleading because Fig. S1 only shows profiles for 1 day. If this day is representative of other days this should be mentioned at least in the figure caption.

31630, 18-19: Derived from where? From observations or from an external model?

31630, 19: What is meant by "species segregation" here?

31631, 1-5: This is one place where more information is needed to understand what was done. Looking at Fig. S2, it's clear why the 7th wasn't included, but less clear what is wrong with the 9th. What does "consistency of O3-NOx-VOC diurnal profiles" mean, and how was that determined? How much tolerance was allowed?

31632, 2: "depending on different conditions" is too vague – what were the most important factors influencing this?

31632, 7-22: NOx flux is assumed to be entirely from soil. Is there no influence from nearby anthropogenic areas? Could anthropogenic sources help explain why you need a larger NOx flux later on when you included more detailed chemistry?

31632, 24 – 31633, 7: This paragraph starts by saying *both* chemical schemes are a subset from MOZART, but then goes on to say the second one is actually from GEOS-Chem (which is a separate model) – that first statement needs to be removed.

31633, 10-16: Is this meant to be a list of things that characterise the complex scheme in GEOS-Chem v9-02, or things that are different between this implementation and the version in GEOS-Chem? If the former, 3 isn't right, because Mao et al. (2013) do include isoprene + NO3 reaction. If the latter, this should be rewritten to clarify what is meant here.

31633, 25-26: Rather than R09, etc. it would be much clearer to list the actual species (especially since this table is in the SI, not in the main text!).

31633, 26: I don't understand the reference to Fig. S6 here – S6 only shows O3, which is not one of the species outside the 20% range.

Section 4: Seems like this belongs right after the Experimental section (so it would be 2. Experimental, 3. Data Processing, 4. Mixed Layer Chemistry Model)

31636, 18-19: Need to clarify that these profiles are from a different date and location! There are various things that could influence the changes seen in these profiles besides just the time difference. While the time difference is a compelling factor, it is highly misleading to imply (as is done in the text) that this is only showing diurnal variation. I think this point should also be made in the caption to Fig. 5.

31636, 24-26: Presumably this is the combination of the mixing (mentioned) and OH oxidation (not mentioned)?

31637, 19-21: Another place where it is not clear what was actually done. How were these variables adjusted? Was it ad hoc to get the best fix to BLH growth rate? Given

Table 2 shows an observed value for the BL potential temperature, can I assume it's actually just the FT potential temperature that was adjusted?

31639, 9: "faster photolysis rates" than what? How much faster? How small was the impact?

31641, 16-20: Another place where more detail is needed. Are these using observed or modeled values? How are Sprod and Sloss calculated? What is S's versus S'h? This is an important result so needs more basis.

31642, 1: How is the 6% loss to ozone calculated? Is this from the model?

31642, 28: If the chemistry term is mainly controlled by O3 photolysis, why is it net positive? What is the role of isoprene chemistry in this (nominally the topic of the paper)?

31643, 2-3: Does the inverse relationship between deposition & chemistry simply reflect the fact that if more is produced near the surface, more will be deposited?

31643, 10-14: For this discussion it would be really useful to refer to the diurnal cycle in Fig. 8. It would also be useful if the NO:HO2 line in Fig. 8 was on a log scale.

31643, 22-23 & Fig. 7: Another place where more detail is needed. How is Fig. 7 calculated? Is this based on the diurnal cycle plots, pulling out values at appropriate ratios (and if so, with what temporal resolution?)? Or is this several runs of the model, at different fixed NO:HO2 ratios? Or something else? On the figure, the x-axis should be clearly marked as starting at 1 (it looks like 0 which begs the question as to why there is any NO contribution at all). It would be nice to see a zoomed in version from e.g. 0-10, since this is where the behavior is actually changing.

31644, 1: Why is CH3(O)OO the dominant candidate? Is that just an output from the model, or something expected from literature?

31644, 6-7: Biggest difference is in the role of isomerisation. Are they both using the

same isomerisation rate from Crounse? Should be specified.

31644, 10-24: What is the dependence in this paragraph of the results on the choice of yield? Would a higher yield (see earlier comments) change the results?

31645, 22-24: This is true for isoprene, but not for monoterpenes (which are included in this sentence) – at least not consistent with the monoterpenes profile in Fig. 3.

Acknowledgements: Seems like a lot of the modeling relies on mechanisms made publicly available by the GEOS-Chem and MOZART groups – worth an acknowledgement perhaps?

Fig. 5: Need to make it clear that the "diurnal" variation measured from the WASP system represents different days / flights. I know this is stated elsewhere, but it needs to be made explicit here for those who don't do a careful reading. I don't think it's a problem, but there are other things besides diurnal variation going on for those species and readers need to be aware of that.

Technical corrections

31626, 3: "includes schematic" -> "includes a schematic"

31630, 19: "reates" -> "rates"

31630, 20: "In what follows. . ." should be a new paragraph, not part of point 5.

31631, 13: "South-East" -> "southeast"

31634, 19: "summed up" -> "summed"

31636, 23: "lifetime scale" -> "lifetime"

31637, 8: "details" -> "detail"

31639, 13: "at" -> "in"

31640, 15: "its" -> "their"

31645, 7: delete “Unfortunately”

Table 1: units?

Fig. S8 caption: clarify that this is using the complex scheme

References

Mao, J., F. Paulot, D. J. Jacob, R. C. Cohen, J. D. Crounse, P. O. Wennberg, C. A. Keller, R. C. Hudman, M. P. Barkley, and L. W. Horowitz (2013), Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res. Atmos., 118, 11,256–11,268, doi:10.1002/jgrd.50817.

Rivera-Rios, J. C., et al. (2014), Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: Observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry, Geophys. Res. Lett., 41, 8645–8651, doi:10.1002/ 2014GL061919.

Wolfe, G. M., et al. (2015), Quantifying sources and sinks of reactive gases in the lower atmosphere using airborne flux observations, Geophys. Res. Lett., 42, 8231–8240, doi:10.1002/2015GL065839.

Xiong, F., McAvey, K. M., Pratt, K. A., Groff, C. J., Hostetler, M. A., Lipton, M. A., Starn, T. K., Seeley, J. V., Bertman, S. B., Teng, A. P., Crounse, J. D., Nguyen, T. B., Wennberg, P. O., Misztal, P. K., Goldstein, A. H., Guenther, A. B., Koss, A. R., Olson, K. F., de Gouw, J. A., Baumann, K., Edgerton, E. S., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., and Shepson, P. B.: Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NOx, Atmos. Chem. Phys., 15, 11257-11272, doi:10.5194/acp-15-11257-2015, 2015.

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