Geoscientific
Model Development
Discussions

Interactive comment on "Chemistry and deposition in the Model of Atmospheric composition at Global and Regional scales using Inversion Techniques for Trace gas Emissions (MAGRITTEv1.0). Part A. Chemical mechanism" *by* Jean-François Müller et al.

Anonymous Referee #1

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This manuscript describes simplified gas-phase oxidative chemical mechanisms of isoprene and other biogenically emitted hydrocarbons, and their incorporation into a new chemical transport model for use at global and regional scales. The introduction provides a detailed and comprehensive summary of the importance of recent advances in our understanding of the isoprene mechanism and the need for up-to-date mechanisms for use in simulations. This is followed by a lengthy description of the isoprene mechanism employed here, which is largely derived from a recently published review

(Wennberg et al. 2018) but with a couple notable alterations derived from recent work not incorporated into the review. The description of the mechanism is divided between text sections, which contain broader overviews of mechanistic pathways and the major recent changes due to new advancements, and the extensive footnotes of the table containing the complete mechanism. A subsequent section is dedicated to the results of regional and global simulations using this newly developed mechanism, including the general effects of isoprene oxidation on tropospheric composition, comparison to measurements of isoprene oxidation products in the southeast US, and discussions of the global budgets of formic acid, acetic acid, and glyoxal.

The well-recognized importance of isoprene to tropospheric chemistry means that it's always beneficial to have an up-to-date assessment of the isoprene mechanism, which this study provides. While much of this manuscript simply pulls together results from previous work, it does provide an important benchmark of both isoprene chemistry in the global atmosphere and the sources of gas-phase organic acids, which continue to elude explanation. However, it leaves the reader with a number of concerns regarding some elements included in the model but only given a cursory treatment, along with a need for more concrete discussions of the uncertainties associated with the implementation of this mechanism in global and regional models. These concerns are detailed below in reference to the locations in the manuscript at which they appear, but briefly, they generally include the effects of specific (particularly the more poorly-understood) isoprene oxidation pathways on model outcomes along with the treatment of SOA and monoterpenes. The authors acknowledge that all of these aspects come with substantial uncertainty, but without any quantification of that uncertainty in the model, it is difficult for the reader to know how much proverbial stock to put into simulation results. It is perfectly reasonable that the model is not intended to provide detailed accounting of global biogenic SOA formation or the effects of terpene oxidation, but more discussion is needed regarding the limitations of these aspects of the model. For example, while some SOA formation pathways are included in the model (e.g. IEPOX reactive uptake), others are only mentioned as the likely sinks of isoprene oxidation

products, without any physical reaction parameterized in the model (e.g. dinitrates and the hydroperoxy-epoxides from D'Ambro et al. (2017)). A modeler could assume that these products form SOA immediately with a 100% yield, but because some of the low-volatility species that lead to SOA formation would likely also have high deposition velocities, this could overestimate the SOA yield. How do these (and other) sources of uncertainty in the important results from this mechanism (e.g. HOx budgets, organic acid budgets, SOA) manifest themselves in a global model, and what should the reader take away regarding the potential for bias and error in simulating the overall effects of isoprene's oxidation on the chemistry of the global troposphere?

Specific questions and comments:

p4 L17: 5% can still be a lot of carbon for isoprene! Other pathways that also account for less than 5% of the total carbon from isoprene are included in this mechanism. Are there other reasons the bimolecular reactions of the delta-hydroxyperoxy radicals are excluded? Do we have any knowledge of how much this simplification might bias the results of simulations using this model?

p4 L25 & the rest of this section: the discussion of remaining uncertainties in this mechanism pathway is welcome, but given the important effects of this pathway on simulation results (e.g. as a source of HOx radicals in the otherwise HOx-consuming mechanism), it would be useful to provide the reader with some discussion (perhaps in the model results section) of how these uncertainties manifest themselves in the model. What range of possible HOx recycling rates would be compatible with what is currently known about this part of the mechanism? Given the uncertainties, can the boundary layer OH change due to this mechanistic pathway (Figure 3) be considered a bound or a best guess, and is the uncertainty on that at all quantifiable?

p9 L15: Fig 1 doesn't show latitude dependence as claimed here. It also convolutes the pressure and temperature dependences in a way that might not be useful for readers who would like to extrapolate for conditions other than 40 degrees N in January and

July. I would suggest either clarifying some of the details of these conditions (e.g. add side plots of temp & pressure vs. altitude in January and July, or separate this into plots of yield vs. temp and yield vs. pressure).

p9 L19: "such" should be "this". Also, Wennberg et al. (2018) does not show that this procedure inherently overestimates most measured nitrate yields, though it does suggest that this equation provides yields that seem excessive for dinitrates. Instead it goes off the recommendation of Teng et al. (2017), which explicitly says that this provides a better estimate than just n=#C, and improves this with a structure-activity-relationship-style modification.

p11: why is PAN included in C1 compounds? Also, this table would benefit from more clarification on what some of these groups mean; is OOH hydroperoxide or acid? Is OOOH trioxide or peracid? I realize this can usually be inferred from the hydrogen balance but it'd still be useful.

p26 L3: what is "isoprene-OH segregation"? What was the logic behind the 7% minor addition channel, and behind including those but not the E/Z-delta bimolecular products?

p26 L10: if you include the description of Y(Arey) in the table heading, you don't need it in the footnote; I think the table heading should be shorter and this could be a footnote. Also, don't all the scaling factors >1 suggest that N=#heavy atoms would've been better than N=#C?

p26 L11: define "room conditions" (this also comes up on p27 L4 & 13, p31 L15, 18 & 25, p32 L20, and p41 L34.

p26 L14: Does this inherently assume that all DHHEPOX is lost to aerosols? Are there any estimates of the OH reaction coefficient or uptake coefficient of DHHEPOX that might put this assumption in context, or provide the reader with some idea as to the uncertainty on this assumption? What fraction of carbon is lost to this pathway under

atmospheric conditions (and to other dead-end pathways assumed to either deposit or partition to aerosols, e.g. the dinitrates discussed in N9), and what is the resulting contribution to aerosol compared to other pathways (e.g. IEPOX)?

p26 L22: despite this being "well known" I think it deserves a citation, and more support than that the "majority" of exothermicity is alternately directed, making it "appear unlikely". It is difficult from reading this footnote to tell what is conjecture and what has experimental evidence to support the pathways used. The language generally implies certainty, but the lack of citations suggests that it is conjecture.

p32 L1: Here you state that H-abstraction from the carbon dominates, but with a higher yield of HCHO than HCOOH, the former of which is derived from H-abstraction from the hydroperoxide, isn't that backwards? Also, within their reported uncertainty, Allen et al. (2018) did not conclusively state that one path dominates over the other.

p32 L3: "he" should be "the"

p32 L5: the discussion here seems more suited for a subsection of section 2 than for a note at the bottom of a table; the generic monoterpene oxidation scheme provided here needs more discussion of its uncertainties and how the specific numbers were arrived at. While the complexity of terpene oxidation and the relative lack of quantitative knowledge about its oxidation mechanism make drastic simplification a necessity, it is not clear to the reader why this particular set of simplifications is ideal, or what the reasonable uncertainty bounds are on any of these rates and product yields. If pinene (or generic terpene) oxidation is to be included in this model, it should be given more than a paragraph in a footnote. The same might be said for MBO, but the relative simplicity of its oxidation mechanism, the overlap with isoprene oxidation products, and the smaller magnitude of its emissions make it less prone to substantial uncertainty and bias from mechanistic simplifications and shortcuts. Maybe some sensitivity studies showing the range of results you could get in a global model given the uncertainties in this mechanism would be most useful? (e.g. assuming more of less of the products

are lost to SOA/deposition, or assuming a range of nitrate and/or HOx yields). Some specific questions include: on line 10, where does the 45% number come from? How do these simulated acetone and formaldehyde yields compare to previous work? What does this mechanism inherently assume for the SOA formation from pinene, and how does that compare to both measured yields and the magnitude of SOA formed from isoprene globally? What might be the implications in a global simulation of skipping oxidative steps (and therefore likely sinks of OH, HO2, NO) in the oxidation mechanism, as is presumably the case when only one generation of products are used?

p37 L14: How is the oxidative degradation of anthropogenic NMVOCs treated in the model? I am particularly concerned about the possible contribution of degradation of non-isoprene compounds to the gas-phase budgets of glyoxal and the organic acids. Along those same lines, could some discussion of the potential for additional sources of the gas-phase organic acids not included in this model (e.g. degradation of other compounds, revolatilization from SOA) be added to those sections?

p37 L18: Are there primary emissions of MBO in the model? What is the effect of the MBO oxidation mechanism (and the terpene mechanism) in the model?

p40 L5: In the comparisons to SEAC4RS data, it would be helpful to list the measurement uncertainties and spreads alongside the over/underestimations of the model. Also, what exactly is the model output being compared with the measurements in this section? Are the simulated average profiles just the average over the entire SE USA between 0900 and 1700 hours, or are they points subsampled from the model concurrent with the flight paths? If it's the former, which assumes that the SEAC4RS observations (masked for plumes and stratospheric intrusions) are representative of the averaged regions, how might this skew the comparison between the model and measurements?

p41 L5: Are these non-HPALD compounds also isoprene products? Do we have any indication as to what they are? If they have the same mass as the HPALDs, are there other species in your mechanism that also have this mass that may account for this

mass?

Citations:

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D'Ambro, E. L., Moller, K. H., Lopez-Hilfiker, F. D., Schobesberger, S., Liu, J., Shilling, J. E., Kjaergaard, H. G., and Thornton, J. A.: Isomerization of second-generation isoprene peroxy radicals: Epoxide formation and implications for Secondary Organic Aerosol yields, Environ. Sci. Technol., 51, 4978–7987, 2017.

Teng, A. P., Crounse, J. D., and Wennberg, P. O.: Isoprene peroxy radical dynamics, J. Am. Chem. Soc., 139, 5367-5377, 2017.

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-phase reactions of isoprene and its major oxidation products, Chem. Rev., 118, 3337–3390, DOI: 10.1021/acs.chemrev.7b00439, 2018.