

Geosci. Model Dev. Discuss., referee comment RC1
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Comment on gmd-2022-240

Anonymous Referee #1

Referee comment on "AMORE-Isoprene v1.0: A new reduced mechanism for gas-phase isoprene oxidation" by Forwood Wiser et al., Geosci. Model Dev. Discuss.,
<https://doi.org/10.5194/gmd-2022-240-RC1>, 2022

This study presents the development of a new reduced isoprene oxidation scheme for application in a large-scale atmospheric model, using a benchmark state-of-the-science full description of the isoprene chemistry as a starting point, utilising a novel graph-theory based approach. The mechanism is then optimised and evaluated against its benchmark and other reduced schemes specifically designed for use in US regulatory models as well as limited chamber data, in box models as well as being incorporated into the US EPA Community Multiscale Air Quality modelling system (CMAQ v5.3.3) and evaluated against NE US air quality data.

This interesting study highlights the process of transparently developing a hierarchy of chemical schemes traceable to a benchmark mechanism that reflects the state-of-the-science in chemical understanding (Kaduelia et al., 2015, doi:10.1016/j.atmosenv.2015.10.031).

The authors demonstrate a directed graph path-based automated model reduction approach, going through the necessary steps needed to reduce complex atmospheric chemical mechanisms, such as that for isoprene degradation, including optimisation and evaluation. This approach is certainly one of the main ways forward that atmospheric chemists should be using for dynamically constructing chemical mechanisms for a range of applications.

The motivation and application of this study are well founded and reasonably well executed. However, I am not clear on what the main focus of this work is. Is it to demonstrate the first steps in using graph theory in the development of reduced chemical mechanisms from benchmark descriptions of (atmospheric) chemistry, or is it the development of a new reduced isoprene scheme, optimised and evaluated for specific conditions for use in US regulatory models? It could be both, but the paper should then be split into two clear sections, focused on these two motivations.

For example, the graph theory method sections are really interesting and initially set the paper off as a description of a new method for reducing complex chemical mechanisms. This is great and it's clear that a lot of effort has gone into the approach. However, this is largely undone by the requirement for the manual steps outlined in sections 2.3.5 and 2.4. The changes made here are quite substantial (adding a handful of reactions to a mechanism with 22 reactions soon represents a high proportion of the total mechanism) and so this paper does not demonstrate a method for automated mechanism reduction but rather is aiming to show off a new isoprene mechanism, optimised for a certain specific range of conditions.

With this in mind, it feels like the validation/evaluation of the mechanism in section 3 focuses quite heavily on comparison to other mechanisms rather than comparison to measured data (whether from limited chamber experiments or ambient measurements). Again, if this were a paper displaying a mechanism reduction technique then it would be reasonable to make comparisons only to the mechanism you have reduced, but since there have been extensive manual changes to form the mechanism, this seems like more of an exercise to produce a good isoprene mechanism, in which case comparison to real-world data is required.

I also do not think that it has been demonstrated how well this mechanism performs under different atmospheric conditions for applications in other regional models. The input parameters used in the pathway importance algorithm and the model scenarios outlined in Table 2 and Table 3 do not demonstrate an ability to work in high-NO_x environments. The High-NO_x case included is 5 ppbv. How would this mechanism work, for example, in urban conditions in China (where ozone titration of NO effects the NO/NO₂ ratio as the day progresses) or even modelling atmospheric chemistry over the Bornean rain forest?

Having said this, this work is certainly of great interest to the atmospheric science community and does indeed show a potentially interesting way forward for the future development of reduced chemical mechanisms. The work is therefore ideally suited for publication in GMD. I would recommended publication after the above and following comments have been considered by the authors.

Specific Comments

- **Table 1.** The authors have chosen to compare the new scheme against those included in mechanisms primarily designed and optimised for use in US Regulatory models (except for the benchmark MCM and CalTech mechanisms). Why have you not also included comparisons to the Common Representative Intermediate (CRI) mechanism (CRIv2.2; <https://doi.org/10.1016/j.atmosenv.2019.05.055>)? This is a reduced scheme developed from the MCM (using a different lumping approach) for use in the EMEP MSC-W chemistry-transport model.
- **L40:** CRI should also be mentioned (and referenced) as a further example of a "lumped" approach.

- **L85 "Full Mechanism Input":** There are no files included in the supplementary giving the "full" mechanism, as described. It would be useful to give some examples of the extended/"missing" chemistry needed in the supplementary material. "We have done some preliminary testing of this mechanism in comparison to experimental data, but it was difficult to attain meaningful results. Thus, further assessment of this updated mechanism is required" This is a worrying statement. What are the issues in obtaining "meaningful results? The integrity of the reduced mechanism depends on the benchmark "full" description of the chemistry, and so testing and evaluation of this scheme is a key step in the process and needs to be evaluated/shown.
- **L109:** "NO_x" is not an oxidant. Do you mean "NO₃"? However, NO_x (i.e. NO and NO₂) are key species in the radical propagation cycles (NO to NO₂ conversion efficiencies are an important metric) and so should probably be included.
- **L125:** Include important representative references of the "many prior works"
- **Figure 2 (and within the text):** In what respect is NO an "oxidant" here? NO is often stated as an oxidant in the text, which I don't think it is (RO₂ is the oxidising species). If you want/need to describe NO as an oxidant you need to define why.
- **L156:** Which "oxidants" are held constant?
- **L189:** A visualization of the yield estimation algorithm is not shown in Figure S.4.
- **L196:** Again, not comfortable with NO and NO₂ being described as "oxidants".
- **Table 2** shows that the elevated NO and NO₂ conditions are very low. While I appreciate that the role of these elevated conditions is not to represent ambient conditions, setting these elevated values too low could result in pathways being deemed "not important" as the yields of species produced under really high NO_x conditions (10s of ppbv) would not be given a chance to change from the baseline conditions. How is "solar intensity" defined?
- **L220:** "Care was taken in the selection of inputs to balance breadth of input conditions with relevance to the atmosphere" Do the conditions outlined in Table 2 really cover the optimal range of atmospheric conditions?
- **Table 3** shows that all of the models start with 0 initial O₃ except for the High O₃ model. Given the effect of O₃ on NO_x partitioning, it seems that this could have quite an impact on NO concentrations in all of the models. It could be good to run at least a model with (properly) High NO_x and high O₃. Also in Table 3, I don't think it is specified what photolysis conditions the models are run under (or what low hv actually means, is it 0 photolysis?).
- **L371 and onwards** describe the addition of IHN as a priority species, but outlines that this addition was done manually. Why was IHN not included as a priority species from the beginning? It seems like this could lead to some changes in the mechanism since IHN has formation routes from OH and NO₃ but the current mechanism only includes formation from OH.
- **L382:** "Table 4"
- **L392-3** states that "the {NO₃, HO₂, hv} pathway was determined to be unnecessary...". If this is the case, why wasn't it excluded by the pathway importance algorithm? What was the rationale behind removing this pathway and replacing it with those listed?
- **Figure 3:** "ppb" to "ppb". Give reaction numbers which are adjusted. How do the comparisons highlighted in Figure 3 look for other conditions (NO)?
- **Section 2.4.4** outlines the Total Error Metric. This metric seems quite arbitrary, particularly with regards to the weightings applied to each group (Table 5). To avoid issues with the decisions made around weightings for each species in the total error calculation, I would suggest that the error for each species should be presented in Table 6 (particularly since the specific error values are listed below for many of the species anyway). The total error could still be kept in Table 6, though I don't know how much use it is since different use cases would prioritise better predictions of different species/groups.
- **L446:** Why not 5% for GLY?
- **L472:** Why only show comparisons for HCHO and HO₂? What about for other important

AQ species? (O₃, HO_x, NO_x, GLY/MGLY?)

- **L474** says "Figure 3.1" where it should say "Figure 4"
- **L507** says "shwon" instead of "shown"
- **Figures 4 and 5:** Why was the box model not "spun-up" first to radical steady state conditions (then show comparisons for non-radical important AQ species)? Comparisons seem to show new mechanism doing a better job than RACM but not CB6...

- **L515** should reference the table in the SI with a number. However, I can't actually find the full error tables for each mechanism in the supplementary.
- **Section 3.2 (box model comparisons)** is very short considering this is the first comparison of the mechanism to real data. The authors state that the "Caltech Full mechanism matched the concentrations of all measured species from the chamber study" but provide no evidence of this. It would be good to see some plots of major species of interest with the modelled and measured data included. This is especially necessary since their "Caltech full mechanism" is an adaptation of the published Caltech mechanism, so has the potential to show important differences. Including this data would also allow for a comparison of the new mechanism to measured data for species other than IEPOX (e.g. how does it do for the species groups listed in Table 5?). This is a very limited comparison to one specific chamber experiment under specific conditions. Why have the authors not compared to other isoprene chamber data? There must be significant amounts of isoprene chamber experiments available in the ICARUS (<https://icarus.ucdavis.edu>) and ACTRIS/EUROCHAMP (<https://data.eurochamp.org>) chamber databases.

- Similarly, in **Section 3.3**, the authors only show comparisons for formaldehyde and O₃. Although they state that there were no changes for NO_y, OC, and HNO₃, it would be good to see plots of this (probably in the SI).

- One final comment... The authors demonstrate the use of graph theory for the (significant) reduction of complex chemical mechanisms. What would be the outcome if you started from using the reduced form of the CalTech mechanism?