Reviewer 1

This is an interesting and well written evaluation paper of the SIMCA reduced chemical complexity mechanism for the degradation of isoprene. Oomen et al. first detail the development of the reduced chemical mechanism from the MAGRITTE v1.2 mechanism including the box model experiments used to derive the key parameters. They then compare the performance of the SIMCA mechanism in a full CTM simulation to that of a corresponding simulation using the MAGRITTE v1.2 mechanism. Finally, they use inversion techniques and TROPOMI observations of formaldehyde columns to derive new spatial estimates for isoprene emissions.

We thank the anonymous referee for the positive evaluation of the paper and for their remarks that have resulted in a significant improvement in this work.

Based on the recommendations of the reviewers, we have made various changes to the chemical mechanism and to the manuscript. We first briefly summarize the most important changes to SICMA.

In SICMA, we have introduced an additional reaction: ISOP + O_3. This brings the total to six reactions. The ozonolysis reaction is introduced to improve the nighttime chemistry in the model. During the day, this reaction has a near-negligible impact, but it is dominant during the night and significantly affects the diurnal cycles of isoprene, HCHO, and the nighttime HOx concentrations. Additionally, we have made the following changes to the parameter optimization algorithm:

- We now optimize parameters for HOx recycling in the isomerization reaction (R4).
- We increased box-model simulation period to 5 days in order to improve sensitivity of parameter optimization for the IOX reaction rate (k_5).
- We changed the fixed diurnal isoprene concentration profile to a diurnal isoprene emission profile to better account for the feedback of OH on isoprene.

Based on this new reaction scheme and optimization setup, we derived a new set of parameters, which we implemented and tested in the MAGRITTE CTM. This updated version of SICMA leads to improved diurnal cycles in the CTM and a smaller bias in HCHO and isoprene compared to the reference chemistry. The updated results have been incorporated into the revised version of the paper.

Below, we address the different remarks of the referee (in black). Our response is formulated in blue font.

Major Comments

Parameter optimisation – a fixed temperature of 298 K is used in all box model simulations. While this is a sensible daily mean value for the tropics, the 1,6-H shift of the isoprene is highly temperature dependent (as you capture with your large exponent for R4). How did you derive this temperature dependence if you weren't changing the temperature in the box model?

The reaction rates for reactions R1 to R3 are not derived from the box models. They are obtained directly from the reaction rates for the analogous reactions in the full chemistry. For the isomerization reaction (R4), we have calculated the mean rate of the different isomerization reactions of MAGRITTE

for a temperature of 298 K, which gives 0.0089 s^{-1}. Next, we used a typical temperature dependence for the isomerization, based on the full MAGRITTE mechanism, i.e. exp(-9000/T), with T being the temperature in K.

Please explain how you forced the concentration of isoprene to follow a diurnal profile in the box modelling. Does this run this risk that, as there is a fixed source of isoprene, that any feedbacks between oxidants and isoprene, which could be different between the mechanisms, are suppressed?

The reviewer is correct that the potential feedback of isoprene on OH was suppressed in the box model runs described in the manuscript. At each time step, the isoprene concentration was forced to the same diurnal profile with a maximum noontime concentration of 1 ppb.

In the box model simulations of the revised manuscript, we have replaced the fixed diurnal isoprene concentration by an isoprene emission source, similarly following a diurnal emission profile. The emission source has a cosine shape with a maximum at noon, and emissions set to zero during the night (from 17.30 LT to 6.30 LT). This setup is of course more realistic and leads to different isoprene concentrations in the different runs. Additionally, we have included parameters for HOx recycling in the isomerization reaction (R4) and have increased the duration of the box model simulations to 5 days. By shifting from the fixed isoprene concentration to an emission source, the relevant feedback processes are now included in the box model simulations.

The role of monoterpene chemistry is an important feature of the SIMCA chemistry and needs greater explanation. As I interpret it, while the SIMCA mechanism has no explicit monoterpene chemistry, it implicitly includes a 10:1 ratio of isoprene to monoterpene emissions and this is captured in the fitted parameters. Therefore, its parameters (Table 3) are not describing an isoprene-only situation, but an isoprene + monoterpene situation where the monoterpene concentration is ~10% of the isoprene concentration. If this is correct, this needs to be made much clearer in the abstract and throughout the main text.

Your interpretation is correct, the SICMA mechanism assumes a 10:1 emission ratio of isoprene and monoterpenes. As discussed in the manuscript, the impact of this assumption is significant. We acknowledge that this assumption was not clearly indicated, especially when describing the setup of the SICMA chemistry and parameter optimization. We now mention the inclusion of the monoterpene flux at various points throughout the text. Most notably, we include the following paragraph in Sect. 4.2: "*In box model simulations of the MAGRITTEv1.2 full chemistry, we include an emission flux for monoterpenes that is 10 times lower flux than that of isoprene, corresponding to the average monoterpene-to-isoprene molar emission ratio for Amazonia (Sindelarova et al., 2022). Given the similarly short atmospheric lifetimes of isoprene and monoterpenes, the simplified chemistry scheme will therefore represent the total yield of HCHO from combined isoprene and monoterpene emissions, for the typical case of a 10% monoterpene-to-isoprene molar emission ratio. This representation is necessarily simplified and does not explicitly account for differences in emission patterns or chemical degradation pathways between isoprene and individual monoterpene species.*"

Further on this topic, in the CTM evaluation in Section 5 the MAGRITTE v1.2 simulation uses 439 Tg yr^{-1} of isoprene emissions and the 108 Tg yr^{-1} of monoterpene emissions. However, SIMCA has no monoterpene chemistry so only uses the 439 Tg yr^{-1} of isoprene emissions with remaining

108 Tg yr^{-1} "accounted for" by SIMCA's chemistry. Is that correct? If so, this needs to be made clear.

Indeed, the monoterpene emissions are implicitly accounted for by the SICMA chemistry, hence the monoterpene emissions are turned off in the SICMA simulations. The molar emission ratio of 0.1 implies a global contribution of ~88 Tg yr^{-1} for SICMA, which is a bit lower than in MAGRITTE since the ratio was taken based on tropical conditions, where most of the global BVOC emissions take place. We have clarified this point in Sect. 5.

When looking at the boreal OH high bias in SIMCA (relative to MAGRITTE), would it be better correct to saying that SIMCA is effectively underestimating monoterpenes in this region (since, as you say, monoterpene/isoprene emissions >> 0.1 here)? I am surprised that the higher local NO_x, due to lack of isoprene and monoterpene nitrate formation in SIMCA, doesn't lead to higher O_3 in the region since there should be plentiful isoprene. Could you explain this?

Thank you for this question. For the boreal forests, the OH high bias is indeed the result of the combination of too low monoterpenes in SICMA (which would titrate OH), and the overestimated NOx concentrations in the absence of organic nitrate chemistry. We make this clearer now in the text. The NOx is overestimated, however it is not sufficiently high to cause strong ozone formation in the model.

While I broadly agree with the framework for parameter optimisation, the one major omission is the lack of an isoprene nitrate or PAN-type species to act as a surrogate for NO_x-reservoir species. To their credit, the authors highlight in several places the problems this omission causes. I will not ask the authors to redo the optimisation, but it is imperative that they mention in their concluding statements that a high priority for further SIMCA development is the inclusion of a nitrate term.

Indeed, besides the treatment of monoterpenes, arguably the largest source of discrepancy in SICMA is the omission of nitrate chemistry. Again, this is no major issue in the context of BVOC emission inversions. However, with several additional species and reactions, this aspect of the chemical network could be improved considerably. For example, the addition of a long-lived organic nitrate (RONO2) in R3 could carry away nitrogen from source regions, to be then either deposited or oxidized via RONO2 + OH = NO_2. As suggested, we mention potential extensions to the SICMA mechanism in our concluding statements.

The choice to optimise for HCHO production makes sense given that one of the aims of the SIMCA mechanisms is to be used to generate new isoprene emission estimates. However, there are other important species whose performance needs to be evaluated in more detail if the second aim of the SIMCA mechanism, that of being a feasible alternative mechanism to MAGRITTE v1.2 for chemical transport modelling, is to be met. Specifically, the following evaluation should be done as a minimum and included in the revised manuscript's main text.

- Monthly mean tropospheric ozone burden for SIMCA and MAGRITTE v1.2 as a timeseries
- Zonal mean ozone differences (for the whole troposphere) between SIMCA and MAGRITTE v1.2
- Tropospheric ozone column differences between SIMCA and MAGRITTE v1.2 using a latitude-time Hovmoller setup to reveal seasonality
- Methane lifetime in SIMCA and MAGRITTE v1.2

In addition, most researchers would expect the production of ozone or ozone burden to the most useful constraint metric, not formaldehyde production. I am not saying your choice is wrong but please explain in more detail the decision not to use ozone burden/production as a target.

The SICMA chemistry was developed with the goal to perform BVOC emission inversions with a strongly reduced mechanism. As such, many simplifications and assumptions were made, and we do not expect to find good results for the metrics you request, since ozone is not our target. As described in the previous point, several alterations should be made in order to improve the performance of SICMA for ozone. One aspect is the inclusion of separate reactions for monoterpene chemistry. The addition of the ozonolysis reaction has limited impact on ozone, as this reaction is quite slow and is only important during nighttime conditions. Additional peroxy radicals might be needed to account for NO-to-NO_2 conversions. Finally, a representation of isoprene nitrate chemistry and PAN would be needed.

We have modified the title of the paper to reflect more carefully that SICMA is focused on the production of HCHO, with the goal of conducting isoprene emission inversions. We have also added an additional note in the conclusions regarding the use of SICMA to model ozone: "More generally, the current version of SICMA is not intended for applications requiring accurate ozone chemistry, as the oversimplifications of the mechanism (e.g., omission of explicit organic nitrate and lack of peroxy radicals) lead to underestimated ozone concentrations."

While you note that the inversion-derived emissions are very similar using the SIMCA and MAGRITTE v1.2 scheme and that they are 30% higher than the MEGAN emissions, there is no further analysis on the reason for this difference. Given that it is very large, I would like to see some explanation for why both mechanisms need a lot more isoprene to optimise HCHO column performance. Could it potentially be a bias in the NO_x emissions being used?

Bottom-up and top-down isoprene emission inventories are very uncertain, hence large differences in total emissions are not uncommon. In terms of bottom-up emissions based on MEGAN, large uncertainties come from the emission factors associated with different plant functional types, the leaf-area index distribution, and even meteorology (Arneth et al., 2011; Guenther et al., 2012). Top-down studies, like in this work, suffer from biases in satellite observations, modelling errors, etc. A 30% higher emission source is significant, but it results in a slightly higher global emission than in recent TROPOMI-constrained inversion studies such as Sfendla et al. (2026) and Li et al. (2026). A large increase in VOC emissions is needed to accommodate the bias-corrected formaldehyde observations. We have expanded the discussion on the inversion results in the paper.

I also think more explanation should be given to the spatial differences in the estimated emissions using the SIMCA and MAGRITTE mechanisms. While the global totals are very similar, the spatial differences are substantial in fractional, and in some places like the Congo or western Amazonia, in absolute terms.

The spatial differences in the top-down emissions between MAGRITTE and SICMA reach up to 15%. These differences can be directly linked to the HCHO column differences, as they are opposite (i.e., where SICMA HCHO columns are higher, the top-down isoprene emissions will be lower). The differences in the HCHO columns are described in Sect. 5.2 for the forward simulations. They are mainly attributed to the monoterpene-to-isoprene molar emission ratio assumed in SICMA, and the lack of organic nitrates, which

impact NOx and HOx concentrations. The over- and underestimations of the SICMA emission cancel out when computing the global total, although larger differences are found regionally.

Minor Comments

Line 21 - please make it clear to what "its" corresponds. I suspect it is isoprene but the preceding sentence references biogenic VOCs.

We have modified this sentence.

Figure 6 - I think there is a standard from term (e.g. x 10^{15}) missing on the y axis.

Thank you for spotting this, 10^{15} was indeed missing from the label. This has been corrected now.

Please add the equivalent of Figure 7 for the SIMCA inversion, i.e. specifically 7(b) and 7(c) so that a side by side comparison can be made. Also make clear the bwr colourbar has a logarithmic scale and consider if you can "zoom" in (i.e. I don't think it is necessary to go from 0.1 to 10) so that the magnitude of changes are easier to identify.

We have made these adjustments to the figure. In the previous version we had omitted the SICMA emission maps due to their similarity with the reference simulation, but we agree that it is better to show the SICMA top-down emissions too. We have adjusted the scale of the emission enhancements to 0.2 – 5.

Please give an indication of the decreases to model runtime and compute on switching from MAGRITTE v1.2 to SIMCA.

In our CTM simulations, we have retained the full set of VOC species and reactions to ensure an identical treatment of anthropogenic and pyrogenic VOC chemistry in both simulations, since these VOC categories share many species with isoprene and monoterpenes. We can therefore not evaluate the decrease in model runtime from the CTM simulation itself. Instead, we have calculated the reduction in computational time in the box models between the MAGRITTE and SICMA chemistry. Here, we find a reduction of 83% in computational cost for a simulation of 14 days. We have added a discussion of the difference in computational time in the box models in Sect. 4.

On line 228 you reference Fig 2c for OH but OH is Fig 2d. I note also that Fig 2d, as it is right now doesn't present evidence for lower nighttime OH as all OH lines are ~ zero. You will need a log plot to make this argument.

We have corrected the reference to the figure in the text. Additionally, we have changed the figure axis in the OH plot of Figure 2 to log-scale, so the nighttime differences can be discerned.

References:

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Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471–1492, https://doi.org/10.5194/gmd-5-1471-2012, 2012.

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