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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Reviewer 2

This paper describes an optimized mechanism for representing the connection between isoprene and formaldehyde, which allows for faster inversions of isoprene emissions from HCHO satellite retrievals. The paper describes the development process, validates against the larger mechanism, and shows an example inversion. The paper is ready for publication after considering the following minor comments.

We thank the anonymous referee for their helpful remarks.

Based on the recommendations of the reviewers, we have made various changes to the chemical mechanism and 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 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 have derived a new set of parameters, which we implemented and tested in MAGRITTE CTM. This new 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 new 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.

General Comments

Would this mechanism also be appropriate for inferring isoprene emissions from isoprene satellite retrievals, or for joint isoprene-HCHO retrieval inversions?

Thanks for the question. The comparison of isoprene columns in Fig. 5b shows differences of 10 to 20% in source regions, which could introduce relatively similar biases in the emission inversion. For inversions using isoprene retrievals, additional care should be taken to model the OH concentration well, as it is the dominant factor in isoprene lifetime. Although there is potential for using SICMA in inversions constrained by isoprene columns, additional improvements could be made to reduce the SICMA bias for isoprene columns. We have added a note on this in the conclusions section.

Specific Comments

L77: What is the justification for filtering low HCHO columns? Does this also mean you are filtering negative values? This would lead to a high bias in the average and is not appropriate when the variability is due to precision (e.g., spectral fitting).

Negative daily columns are retained when calculating monthly means. Filtering is only applied after monthly averaging and therefore does not systematically remove negative retrievals arising from measurement noise. Though this could still lead to a high bias by removing months with low columns, this does not impact the inversion results, as such filtering only affects remote regions (oceans) and very high latitude regions.

L121: Does this procedure inherently assume that the entirety of model-measurement difference is driven by emissions? If so, could errors in chemistry, particularly at low NOx, be misinterpreted in the cost function and lead to erroneous emission estimates?

The referee is correct that the inversion implicitly attributes discrepancies between the modeled and observed HCHO columns to the parameters being optimized, including the isoprene emissions. Consequently, errors in chemistry will propagate to errors in the top-down emissions. The assumption that model-measurement difference is driven by emissions is common to all inverse modelling studies.

However, one of the main objectives of this study is to assess whether SICMA produces different emission estimates with respect to the full MAGRITTEv1.2 chemistry when applied to the same observations and using identical inversion settings. Indeed, the inversions yield somewhat different emission estimates for the two mechanisms despite using the same a priori emissions and HCHO observations, demonstrating that chemical uncertainties can propagate into the inferred emissions. However, the relatively small differences between the SICMA and MAGRITTEv1.2 inversions indicate that the simplification of the isoprene chemistry has only a limited impact on the top-down emissions in our application. We have added a statement to the revised manuscript acknowledging that chemical model errors can translate into emission estimates in HCHO-constrained inversions.L148: Does the model use this weighted average everywhere? Or is the model implementing a temperature-dependent isomerization rate?

The SICMA model uses a temperature-dependent isomerization rate as given in Table 3. This bulk rate is determined based on the weighted average of the different isomerization reactions in MAGRITTEv1.2 in Amazon conditions at 298 K (0.0089 s^{-1}), while using a temperature dependence typical for these isomerization reactions in MAGRITTEv1.2 (i.e. exp(-9000/T)).

L168: The inclusion of monoterpenes is confusing and introduces semi-buried assumptions: namely, that monoterpenes are behaving like isoprene and the molar ratio everywhere matches that in Amazonia. Relative emissions vary widely by phenology and environmental drivers. Please provide some justification for this decision. What would be the consequences of excluding monoterpenes here?

The procedure described in the manuscript makes it possible to directly derive top-down isoprene emissions using SICMA chemistry, without the need to include monoterpene chemistry. We do not assume that monoterpenes behave like isoprene, except for the fact that both isoprene and monoterpenes are short-lived hydrocarbons and generate HCHO at high yields. The manuscript acknowledges and discusses the variations of the molar ratio, as shown in Fig. S1 of the supplement. As

discussed in the revised paper, the assumption of a fixed molar ratio is one of the main sources of discrepancy between SICMA and MAGRITTE in the CTM simulations.

To remove the assumption of the molar ratio in SICMA, additional reactions would be needed. However, this would come at the cost of increased model complexity, which is not always desirable.

If we were to exclude monoterpenes from the box model simulations, SICMA would only represent isoprene oxidation. For the chemistry-transport modelling and emission inversions, the monoterpene chemistry used in the full chemistry of MAGRITTE would have to be added to SICMA, thereby increasing the number of reactions substantially.

L192: are optimized parameters sensitive to initial guesses?

Absolutely. SICMA has a large number of free parameters to optimize, with many correlations between the different parameters. For example, increasing the IOX yields in R2, R3, and R4 followed by a reduction of the HCHO yield in R5 gives similar HCHO (after increasing the OH and reducing the HO_2 regeneration in R5 to keep the HOx balance). The cost function has a broad minimum; hence the cost gradient is very small close to the minimum. A large range of parameters can provide a reasonably good fit for HCHO, OH, and HO_2. Consequently, several initial guesses are needed to find the best-performing solutions in the mechanism. We have clarified these points in Sect. 4.2 of the revised text.

L198: given the high number of tunable parameters, this agreement is not surprising.

While the number of tunable parameters provides flexibility, the optimization simultaneously reproduces cumulative HCHO production, OH and HO_2 concentrations across multiple NO_x regimes and diurnal cycles. Considering the huge reduction of the number of reactions and species, achieving this agreement is not trivial.

L248: decomposing PAN would also lead to HCHO via CH3CO3 reactions.

Further reactions of organic nitrates and PAN indeed also contribute to the HCHO column. This contribution is crudely accounted for in the IOX oxidation reaction.

Technical Comments

L127: anyone printing in black and white won't see the blue font.

We have removed the blue font from the table. Instead, we describe the list of optimizable parameters in the caption of the table and in the running text.

Figure 2: green and orange lines are probably not colorblind-friendly.

We now use the "tableau-colorblind10" color style list in python, instead of the standard matplotlib color list. The colors are now blue for MAGRITTEv1.2 plots, orange for SICMA plots, and gray for the a priori emissions in Fig. 9. TROPOMI columns in Fig. 6 are still depicted in black.

Reviewer 3

This manuscript introduces a drastically reduced isoprene oxidation mechanism "SICMA" for use in chemical transport modeling to minimize the computational cost of chemistry steps within the model. The authors specify a five-reaction, three-isoprene-related-species format for a reaction network meant to mimic the effect of isoprene photooxidation on formaldehyde, OH, and HO2. They then optimize tunable parameters within this framework (including some reaction rates and product yields) to minimize differences between SICMA and a detailed mechanism of concentrations of HCHO, OH, and HO2 using a simple box model setup. Next, they incorporate SICMA into the global MAGRITTE model and show that the reduced mechanism adequately represents outcomes of interest over major isoprene-emitting regions. Finally, they use SICMA to perform a model inversion, deriving isoprene emissions from measured TROPOMI satellite HCHO columns, and find minimal overall differences from an equivalent inversion with complex chemistry.

Overall, the manuscript is very well-written, and the utility of SICMA is made fairly obvious for this specific application of deriving biogenic VOC emissions from formaldehyde columns -- a process that requires substantial computational capacity and for which SICMA is specifically optimized. I recommend the manuscript be published in GMD following minor revisions to address the points raised below. I'd also like to note that my area of expertise does not include the emission inversion process, so hopefully another reviewer is better able to assess those sections.

We thank the anonymous referee for their positive feedback and helpful comments.

Based on the recommendations of the reviewers, we have made various changes to the chemical mechanism and 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 have derived a new set of parameters, which we implemented and tested in the MAGRITTE CTM. This new 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 new 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.

General Comments

First, I believe that the title and abstract moderately over-sell the utility of SICMA; it's very specifically designed to optimize formaldehyde, and does an excellent job as demonstrated here for inversions from formaldehyde observations, but specifically does not optimize NOx or ozone or allow for any isoprene (or monoterpene) derived SOA formation, which severely limits its utility for many other applications in global chemistry transport modeling. I'd recommend specifically referencing formaldehyde, or perhaps formaldehyde and HOx together, in the title to clarify.

Thanks for your comment. The mechanism is specifically designed for BVOC emission inversions using HCHO columns and lacks several key reactions needed for modelling NOy long-range transport (e.g. through organic nitrates), ozone production, and SOA. We therefore made the title of the manuscript more specific: “A simplified isoprene oxidation mechanism for fast formaldehyde-based emission inversion of isoprene”. The revised title reflects more accurately both the intended application and the current limitations of SICMA. We have also made changes in the abstract and throughout the text to make this point more clear.

Second and perhaps most importantly, I find the choice of combining isoprene with monoterpenes in a 10:1 ratio for the mechanism simplification and subsequent inversion very strange and highly limiting. if i'm understanding it right, you've optimized not an isoprene mechanism, but a fixed, specific isoprene + monoterpene combination that therefore doesn't really let you back out isoprene emissions precisely, and doesn't allow for flexibility in the spatial and temporal distribution of the isoprene-to-monoterpene ratio. Would it have been severely limiting to optimize a separate monoterpene + OH --> x*HCHO reaction (or a few reactions to get the NOx dependence right), or to consider the monoterpene-derived formaldehyde fixed and only optimize the mechanism and perform an inversion for isoprene?

I hesitate to suggest that the authors reformulate their mechanism or rerun any simulations, but at least acknowledging this detail of the mechanism in the abstract and discussing the implications for inversions and for forward modeling in the conclusions (beyond the cursory acknowledgment of the "crude" accounting on L 326) seems necessary to again avoid overselling the utility of this mechanism. The prospects for improving monoterpene representation in future versions of SICMA should also be discussed.

The SICMA mechanism indeed assumes a monoterpene emission source equal to 10% of the isoprene molar flux. This has been made clearer throughout the text. Including monoterpene species into the mechanism would have been possible, although not straightforward, at the cost of several additional species and reactions. However, SICMA was designed to be as compact as possible, with the use case of an adjoint-based isoprene emission inversion using HCHO data. For this use case, it was desirable to have a minimum number of reactions, with a focus on isoprene, which has been the topic of intensive research in the last decades and for which kinetic uncertainties are lower than for the monoterpenes. Though currently one of the major sources of discrepancy is the variation of the monoterpene-to-isoprene emission ratio, we argue that the main goal of isoprene emission inversion, focused on tropical ecosystems, can be achieved with this crude representation of monoterpenes.

Nonetheless, the addition of monoterpene chemistry to SICMA could broaden the applicability of the mechanism. We have added a note on the prospect of extending SICMA to monoterpenes in the concluding section.

Further more minor concerns and comments are provided (mostly with line numbers refering to the original manuscript preprint) below:

• Can you provide quantitative evidence of the reduction in computational cost with the SICMA mechanism relative to MAGRITTE for forward and inverse global modeling runs?

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. Consequently, the reduction in computational cost of the simplified isoprene mechanism cannot be isolated directly from the computation time of the forward and inverse modelling runs.

Instead, we have calculated the reduction in computational time in the box model simulations 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 comment on the difference in computational time in the box model simulations in Sect. 4.

• L 139-140: if both HO2 and isomerization contribute in the same environments, why is it necessary to separate them out into two reactions? Are their contributions spatially and temporally heterogeneous enough for this to matter?

The HO_2 and isomerization reactions can contribute similarly in some environments, yet different in others. This depends on the local HO_2 concentrations, which in turn depend on many environmental factors like NO_x and ozone concentrations, temperature, radiation, and humidity. In high-NOx conditions, the ISOPO2 + NO pathway generally dominates, whereas in low-NOx conditions, the reaction with HO_2 and the isomerization can both be important.

Our experience in testing a version of SICMA without the isomerization reaction in the CTM showed poor results, particularly for HOx and NOx concentrations. The isomerization is also an important sink for the isoprene peroxy radical ISOPO2, which would otherwise always be forced to react with either HO_2 or NO. By including the isomerization reaction, the fate of ISOPO2 is much closer to that of the analogous compounds in the MAGRITTEv1.2 chemistry.

• L 146-147 & 155-156: Isomerization being applied to all RO2, instead of just the fraction of RO2 radicals able to undergo 1,6 H-shifts, seems like it should introduce a lot of potential for deviation from the main mechanism. Is this satisfactorily ameliorated by fitting the other parameters? Why not scale the isomerization rate to the fractional abundance of the isomers that are able to undergo the 1,6 H shift? And similarly, why not optimize the yields of OH and HO2 in these reactions? Are they really so well-constrained with actual experimental evidence that they merit this fixed treatment?

The isomerization reaction rate already represents a bulk rate considering the fraction of peroxy radicals able to undergo the 1,6 H-shift, as is suggested in your comment. The MAGRITTEv1.1 mechanism itself is

not explicit (which would require far too many species for a 3-dimensional model) and incorporates bulk isomerization rates for two different pools of peroxy radicals, as described in detail in Müller et al. (2019). Based on the (bulk) isomerization reactions in the MAGRITTE chemistry, SICMA remains an even more condensed representation.

We thank the reviewer for the excellent suggestion to optimize the OH and HO_2 yields in these reactions. The HOx coefficients in reaction R4 were initially fixed to limit the number of free parameters in SICMA, leading to inaccuracies. In the revised version of SICMA, we optimize the HOx parameters of the isomerization reaction.

• L 163: This fixed value for O3 seems relatively low, as though it might underestimate the contribution of ozonolysis in many actual ambient conditions, and the fixed value for water vapor seem would also impose a limitation on the actual variability of formaldehyde yields from that ozonolysis. Can you estimate how much potential error this introduces to the mechanism by excluding an ozonolysis reaction, and how big a deal it would be if your simulations designed for mechanism optimization has higher ozone concentrations?

Thanks for this comment. We note that ozone is not fixed in the box model runs. Its initial concentration reflects low-NOx tropical environments. We have included the evolution of ozone concentration in Fig. 2. Despite the low initial ozone, conditions in the box model lead to a strong variation of ozone throughout the 5-day simulation. Nonetheless, we have tested varying the initial ozone concentration and humidity in the model, and found negligible impact on the results. Furthermore, as discussed above, we have included the ozonolysis reaction in the revised SICMA. It has a significant impact on nighttime HCHO production, HOx generation, and isoprene concentration. Although its reaction rate is relatively low, this reaction is important for the diurnal abundances of the relevant compounds.

• L 167: Imposing a peak of 1 ppb of isoprene and continuous emissions means that your mechanism is optimized for early-generation, short-term formaldehyde production; could this be why you have lower formaldehyde columns over the ocean in comparison to MAGRITTE (fig 4)? Could this be fixed by optimizing against a time series that allows for longer durations, and either (a) adding a third generation, or (b) allowing the IOX + OH reaction to produce a small amount of IOX, or of another formaldehyde precursor already contained in the mechanism?

The HCHO column underestimation over the ocean is likely not related to the long-range transport of VOC intermediates. Instead, its major cause is the absence of long-lived organic nitrates, which can release NOx in remote regions. This then leads to higher OH and more background HCHO production through methane oxidation in MAGRITTEv1.2 compared to SICMA, as already discussed in Sect. 5.2.

We thank the reviewer for the helpful comment on the fixed isoprene profile in the box model runs. We updated the box model setup, which now includes a diurnal isoprene emission source and a 4.5-day simulation period. This captures both the early HCHO generation and the delayed production through the formation of IOX. We found that the optimized parameter set of SICMA leads to a good agreement with MAGRITTE after 7 days, suggesting that the delayed production is sufficiently well captured. A third-generation product could make slight improvements, but was not considered given the already good performance of the current mechanism. Regenerating IOX is an interesting idea, though we have not tested this in the mechanism.

• L 197-202: Can you comment / speculate on what causes these differences, and potentially how to fix them in future SICMA versions? It seems in particular that a midday difference would be problematic for comparison with a midday satellite...

The nighttime differences in OH and HO_2 were mainly caused by the absence of the ozonolysis reaction. After including this reaction in the revised SICMA version, the nighttime OH and HO_2 concentrations have improved considerably (see Fig. 2 of the revised paper). There is still a small midday difference for HCHO in the box models, with higher HCHO concentrations in SICMA. This is likely due to a higher noontime HCHO production in combination with lower morning and evening HCHO production.

It is unclear what the exact reasons are for this discrepancy, but it is likely related to the simplistic representation of IOX, with only one reaction (IOX + OH) and a single rate (k_5). In MAGRITTEv1.2, isoprene oxidation leads to a long series of oxidation steps involving many intermediate species which can react in various ways and at different rates. A different evolution of HCHO production is therefore to be expected.

• Fig 3: Why does Figure 3 show the best HCHO agreement midday if that's when Figure 2 showed the worst agreement?

With the inclusion of the ozonolysis reaction, the diurnal cycle of SICMA is improved, especially during nighttime. However, we still see a larger nighttime production of HCHO in MAGRITTEv1.2, and in the absence of a strong HCHO sink, the HCHO difference builds up until the end of the night. During daytime, both HCHO production and loss rates increase substantially, primarily due to the stronger photochemical activity and increased OH concentrations. The resulting faster chemistry gradually reduces the HCHO concentration difference inherited from nighttime, and the two mechanisms converge toward similar daytime HCHO concentrations. Consequently, the agreement between SICMA and MAGRITTEv1.2 is best around midday, despite the larger differences that developed during the preceding night.

• L 220-221: Is it important to also evaluate regions beyond the emission hotspots? Genuine question -- maybe if you're just trying to optimize total gross emissions, the answer's no, but it also seems like the potential for the reduced mechanism to deviate from the main one would increase in places either downwind from emissions, where the temporal evolution of the oxidation chain matters, or where you have a mixture of different emission sources

Currently, we have indeed evaluated the diurnal cycles only in emission hotspots. However, Figs. 4 and 5 show global maps of the differences in the CTM simulations, where the differences downwind can be observed. Since these are relative differences, large impacts can be seen in more pristine environments. Figure 5 suggests that the long-range transport of NOx reservoirs impacts chemical composition downwind.