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.