

Interactive comment on “Glyoxal yield from isoprene oxidation and relation to formaldehyde: chemical mechanism, constraints from SENEX aircraft observations, and interpretation of OMI satellite data” by Christopher Chan Miller et al.

Anonymous Referee #2

Received and published: 29 December 2016

The analyses of CHOCHO and HCHO in this paper have many interesting components, three models (GEOS-Chem, DSMACC, and a parcel model), two mechanisms (GEOS-Chem and MCM), SENEX in situ observations, and OMI retrievals. A casual reading would suggest it is a publishable paper. But in the more careful second-round reading, I found many problems. I cannot recommend publishing this paper in its present form. Substantial changes are required.

This work was probably done during the same period as Li et al. (2016, Observational constraints on glyoxal production. . .). The publication of that paper makes it necessary

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that differences between the two papers are resolved in this paper. Very little was done in this paper. Many differences were not mentioned. For example, Li et al. (2016) showed some effects of aerosol loss of CHOCHO in the mixed layer. Their budget shows that aerosol loss is 26% of total CHOCHO loss in the boundary layer, which is quite significant. The justification for not including this loss given in line 4-8 on P. 5 did not provide either the details on aerosol loss modeling or the results.

Many analyses in this paper are similar to Li et al. (2016), but the results are different. The implications of these differences were not considered in this paper. The omission of comparing the simulation of isoprene to the observations, which was done by Li et al., may be an indication that the submission of this paper was rushed. Looking at the results of this paper and Li et al. (2016), I cannot find enough support for the main conclusions in this paper.

1. P. 1, line 10-11, line 15; P. 2, line 4; P. 10, line 9-10, line 11-16

The emphasis on the prompt CHOCHO production under low NO_x conditions is not explained well. Fig. 2 shows that the new GEOS-Chem mechanism has similar cumulative molar yields to MCM (although a little higher) for low- and high-NO_x conditions. The increase of the yield at low NO_x conditions is not higher than at high-NO conditions. Why is the yield increase at low-NO_x conditions singled out? It is also unclear to me how in situ or satellite data can be used to separate prompt production of the GEOS-Chem mechanism from slower production of MCM at low NO_x conditions when isoprene emissions are continuous over large regions in daytime. Tracking air parcels is impractical in this environment (see the later comments on section 3).

The much bigger problem is that Li et al. (2016) showed a factor 2-3 higher CHOCHO yields at low-NO_x than high-NO_x conditions, while the new GEOS-Chem mechanism and MCM have a factor of 3-4 lower yields at low-NO_x than high-NO_x conditions. A simple scaling of Fig. 1 by Li et al. and Fig. 2 of this paper gives a factor of 5-10 difference between the two studies at 0.01 ppbv NO_x. This difference is much larger

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than that between the new GEOS-Chem mechanism and MCM. If in situ and satellite observations can be used to constrain CHOCHO yields, this large difference between the two studies can surely be resolved.

Comparing Fig. 3 of this paper to Fig. 2 of Li et al., CHOCHO in this paper is close to 0 above 2 km while Li et al. showed CHOCHO concentrations within the range of the observations. Not looking at the details, one would think that the in situ observations suggest CHOCHO yields at low-NO_x conditions are in line of Li et al. and are much higher than the new GEOS-CHEM mechanism or MCM. The 0-1 km data in Fig. 7 of this paper also suggest the model CHOCHO yields can be higher at low-NO_x conditions.

Fig. 7 will be more clear if the arithmetic NO_x binning is changed to a logarithmic scale. 0-250 pptv covers both low- and mid- NO_x conditions. Fig. 2 shows that CHOCHO cumulative yields do not change much for 0.5-1.5 ppb NO_x, so it's not surprising that the changes of [CHOCHO]/[CHO] ratio in Fig. 7 are small. These are not "low" NO_x conditions. I would not consider 200 ppt NO_x as "low-NO_x" either. A clear definition of low NO_x is needed in the discussion. Fig. 2 shows that 200 ppt NO_x, the cumulative CHOCHO yield is about 60% of 1 ppb NO_x. I'd suggest adding a panel of the cumulative HCHO yield distribution in Fig. 2 to compare to CHOCHO.

HCHO has a background from CH₄ oxidation. CHOCHO can have a background from oxidation of C₂H₂ but it is small and has a weak altitude dependence from 2 to 5 km. The observed CHOCHO decrease by a factor of 5 from 2 to 5 km in Fig. 3 does not look like a "background". I do not think that the unspecified instrument detection limit (line 20 on P. 6) can explain this type of altitude dependent decrease.

2. It is possible that the CHOCHO yields at low-NO_x conditions are not the problem if simulated isoprene has large low biases. The suggestion of lacking shallow cumulus convection in the model (line 17-18 on P. 6) is a good reason to expect such a bias. Isoprene, MVK and MACR observations were used in section 3. Why are they not compared to model results in Fig. 3? PTRMS MVK+MACR data may have high biases.

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Can WAS data be used to correct PTRMS data?

I suggest adding the comparisons of simulated isoprene, MVK+MACR, ozone, and CO to the observations in Fig. 3. It will be useful to see the spatial distributions of NO_x, isoprene, MVK+MACR, and ozone in comparison to the observations, which Li et al. did not show. I suggest adding the model-observation comparisons of these species in Fig. 4.

3. P. 1 line 15; P. 2, line 1-4; P. 10, line 18-24

The OMI data used in section were June-August 2006-2007. Are the model simulations for the same period? The discussion in line 20-25 in section 4 (P. 9) seems to suggest that the model results are for the SENEX period. I think that GEOS-Chem results for June-August 2006-2007 are needed to support these rather tenuous conclusions.

Show Figs. 9 and 10 only for the high isoprene emitting SE region not the eastern US. The relatively high CHOCHO at 2-5 km is presumably due to isoprene oxidation unless one can show that VOCs other than isoprene (and its oxidation products) can produce that much CHOCHO at 2-5 km. There is no point of looking for this “background” CHOCHO over regions with low isoprene emissions.

The averaged model-OMI biases shown in Fig. 8 are not that large. How do these biases compare to retrieval uncertainties? OMI HCHO columns were increased by x1.67. What are the reasons? Why are CHOCHO retrievals not affected as HCHO retrievals?

4. Section 3

I do not think the parcel model analysis can be published. Below 1 km, air mass is actively mixed with continuous emissions in daytime over the Southeast. The assumption of air parcels isolated from emissions, i.e., Eqs (1) and (2), cannot be justified. The concept of “initial” isoprene is inappropriate in this context. Observed CHOCHO below 1 km is the result of oxidation of isoprene continuously emitted during an integrated

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time period.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1042, 2016.

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