1 Response to Reviewer 2

1.1 General Comments

Comment 1

The analyses of CHOCHO and HCHO in this paper have many interesting components, three models (GEOS-Chem, DSMACC, and a parcel model), two mechanisms (GEOSChem 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 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.

Response

We thank the reviewer for their time reading the paper. To clarify the differences between Li et al. and our paper, we have added a thorough comparison of the differences in CHOCHO formation pathways from isoprene (Section 2.2). Responses to specific comments are given below.

1.2 Specific Comments

Comment 2

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 NOx 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-NOx conditions. The increase of the yield at low NOx conditions is not higher than at high-NO conditions. Why is the yield increase at low-NOx 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 NOx 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).

Response

The comparison was intended to discuss the differences between GEOS-Chem and MCMv3.3.1. For the quote in question

> In GEOS-Chem, by contrast, the CHOCHO and HCHO yields show opposite dependences on NO_x, implying that they could provide complementary information on isoprene emissions.

The comment does not imply we are tracking air parcels. The idea is that if the time- and NOx-dependence of CHOCHO and HCHO production from isoprene only differed by a scaling factor (as is approximately true in MCMv3.3.1), then the associated CHOCHO and HCHO spatial distributions would also only differ by a scaling factor. Hence CHOCHO would provide redundant information for an isoprene emissions inversion.

Comment 3

The much bigger problem is that Li et al. (2016) showed a factor 2-3 higher CHOCHO yields at low-NOx than high-NOx conditions, while the new GEOS-Chem mechanism and MCM have a factor of 3-4 lower yields at low-NOx than high-NOx 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 NOx. This difference is much larger 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.

Response

The minimum mixed layer observed NOx concentration (with concurrent CHOCHO observations) was 87 pptv. The in-situ observations therefore do not provide a constraint on the differences between our mechanisms at NOx levels of 10 pptv.

Comment 4

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-NOx 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 CHCHO yields can be higher at low-NOx conditions.

Response

Concentrations above 2 km in Li et al. are also close to zero, but appear to be larger because the horizontal axis starts at -50 pptv. Whilst the SENEX data may support a modest increase in prompt low-NO_x CHOCHO formation in our mechanism, they do not appear to support the extremely high yields at low-NOx production shown in Li et al. (2016) (Figure 4 in Li et al. (2016) shows large differences between the binned average R_{GF} for the lower NO_x bins).

Comment 5

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

Response

There are not enough points at the values discussed for the suggested logarithmic binning to be robust (there are only 3 observations with NOx $<$ 100 pptv). The CHOCHO yield in Figure 2 shows that it is higher in GEOS-Chem at low-NO_x. Also the cumulative HCHO yield distribution is already shown in Figure 2.

Comment 6

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.

Response

The section in question only refers to the observations above 3 km (and thus does not include the steep decrease between 2-3 km). We have amended the text with the precision stated by

Kaiser et al. (2015) (**P7, L3**)

> The CHOCHO observations in the free troposphere (> 3 km) have to be treated with caution since they are below the reported instrument precision (32 pptv, Kaiser et al. (2015)).

Comment 7

2. It is possible that the CHOCHO yields at low-NOx 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. Can WAS data be used to correct PTRMS data?

Response

We have added profile comparisons of isoprene, MVK+MACR, CO and O3 to the supplementary information. We do not see large low biases in simulated isoprene (Figure S8). Wolfe et al. (2016) show a detailed comparison between iWAS and PTRMS MVK+MACR data. iWAS observations are biased high relative to the PTRMS data, possibly due to larger inlet conversion of ISOPOOH, or production within the canisters, with the latter explanation deemed less likely.

Comment 8

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 NOx, 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.

Response

Figure 4 already shows NO_x. We have added the comparisons of isoprene, MVK+MACR, O3 and CO to the supplementary material (Figure S8 and S9).

Comment 9

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.

Response

The model simulations are also from June-August 2006-2007. This simulation is from the model as described in the main text, except that it was performed globally at $2^\circ \times 2.5^\circ$ resolution. We have amended the main text to make this clearer (**P8, L15**).

> The OMI observations are compared to a GEOS-Chem simulation covering the same period, at $2^\circ \times 2.5^\circ$ horizontal resolution.

Comment 10

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.

Response

Both the CHOCHO and HCHO retrievals derive offset corrections over specific target regions where the column's values are assumed known. As such, the absolute value of the columns is less robust than the relative differences between columns. Looking at the spatial correlation, including both the low-isoprene region and the SE US isoprene hotspot, provides a means to validate the difference in satellite and model backgrounds.

Comment 11

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?

Response

The random uncertainties in the retrievals can be assesed from spectrum fitting residuals, and are negligible after the spatiotemporal averaging applied in Figure 8 (e.g. for CHOCHO these are less than 2×10^{13} molecules cm^{-2}). A bottom up estimate of the retrieval precision is much more difficult. Figure 9 is an attempt to indirectly assess the retrieval precision, which we have clarified in the text (**P8, L28**).

> Excellent agreement is found for HCHO, providing an independent test of the correction to the OMI HCHO retrieval inferred from the SEAC4RS data (Zhu et al., 2016). Since GEOS-Chem can also replicate the HCHO-CHOCHO correlation in the SENEX data, the simulated CHOCHO columns can be used to indirectly validate the OMI CHOCHO observations.

The HCHO scaling was based on a validation of OMI HCHO observations using SEAC^{4}RS HCHO observations by Zhu et al. (2016). The reasons for the bias are presently unknown, and we do not claim that the CHOCHO retrievals are not subject to similar error sources.

Comment 12

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 time period.

Response

We have removed the comparison between initial isoprene and CHOCHO/HCHO based on the reviewers concerns. The parcel model is still used to derive the t_{OH} values in Figure 6 of the revised manuscript, as low MACR+MVK/ISOP ratios should still be a qualitative indicator for OH titration.