1 Response to Reviewer 2

1.1 General Comments

Comment 1

The added supplement information is very clear that the AM3 mechanism may have larger yields for wrong reasons. The additional figures are also very helpful. The new supplement makes it a much better paper. There are still three issues I think the authors need to correct. The changes will not require much additional work.

Response

We thank the reviewer for their additional comments for improving our manuscript. Responses to specific comments are given below.

Comment 2

One of my review questions is why there is a strong emphasis on the higher yield under low-NOx condition. It is still unanswered. Since this study and Li et al. both suggested a higher yield under lower NOx conditions (for different reasons), I suppose there must be observation evidence requiring it. But one of the authors? responses stated ?there are only 3 observations with NOx < 100 pptv?. Then there were no observations under really low-NOx conditions. Why would two studies focus on an issue that has not observation support? Can the authors make a clear statement in the paper as to whether or not a higher yield under low-NOx condition (than MCM) is required by the observations? It needs to be stated in the paper?s conclusions. Note that Fig. 6 is not the evidence if most of the missing CHOCHO in the lowest NOx bin is from pinene oxidation. In Fig. 6, the observations do not show an increase R(GF) with NOx (if the lowest NOx bin is not included); in contrast, the model shows the increase for the whole NOx range. The statement in Line 31 (P. 7) ?In both the model and observations there is a subset of low-NOx points with higher RGF values (0.03-0.06)? is very misleading since the model did not simulate the observations of RGF>0.035, which are the majority of 0.03-0.06 data points.

GEOS-Chem predicts that 44% of isoprene is lost through the isomerization and HO_2 pathways during SENEX (Figure 1), indicating that CHOCHO yields via the low-NOx pathways should influence the observations. We have now explicitly stated the reasons for the underestimate in the CHOCHO yield from isoprene in MCMv3.3.1 in the conclusion (P10,L20).

> Underestimated CHOCHO yields from isoprene in MCMv3.3.1 can be explained by missing production via DHDC photolysis, and a lower δ-ISOPO$_2$ equilibrium fraction (3.4% in MCMv3.3.1 vs. 10% in GEOS-Chem).

Although not seen in the binned averages, the observations in Figure 6 do show an increase in R_{GF} with NOx at low t_{OH}, corresponding to OH titration. Under these specific conditions (high isoprene, low OH levels) the isomerization pathway should be the dominant CHOCHO source. This is because (1) The isomerization branching pathway should be higher under low NOx and (2) because CHOCHO production from the other precursors depends on OH. The fact that there is an R_{GF} enhancement is therefore evidence for production from via $ISOPO_2$ isomerization (which is not included in MCMv3.3.1). Although GEOS-Chem does not replicate the R_{GF} magnitude, what is relevant is the trend with t_{OH} (i.e. at lower NOx levels, when t_{OH} decreases we see an enhancement in R_{GF}). There are a few possibilities why the model cannot capture the magnitude of R_{GF} (1) The model cannot resolve the most extreme titration events. (2) The yield via isomerization, or the photolysis rate of DHDC is underestimated - these have both been estimated based on proxies from existing literature (Section S3), and are thus subject to uncertainty.

Comment 3

P. 6, Line 31-32, P.7 Line 1-2. If shallow convection is the reason, why does it not affect MVK+MACR in the observations (Fig. S8)? The model CO bias is larger at 3-4 km than 1-3 km. That cannot be an indication of shallow convection. I think it?s better to acknowledge that the reasons for measured CHOCHO at 2-3 km are not understood.

We have updated the text to better acknowledge the uncertainty for the cause of the transition layer enhancement (P6,L31)

> During SENEX the mixed layer was typically capped by a neutrally stable transition layer of shallow cumulus convection which extended up to 3 km (Wagner et al., 2015), which could suggest that the model underestimates transport via this mechanism. However, the model does not underestimate other isoprene oxidation products in the transition layer, such as MVK+methacrolein (Figure S8). Another possible source of CHOCHO in the transition layer is via heterogeneous aerosol oxidation (Volkamer et al., 2015). However, specific aerosol precursors that produce CHOCHO at yields required to match the SENEX observations are currently unknown (Kaiser et al., 2015).

Comment 4

In the response, the authors stated that "The HCHO scaling was based on a validation of OMI HCHO observations using SEAC4RS 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." This is a fair statement and should be noted in the conclusions of this paper. It will then put a statement like "The HCHO satellite data are better validated"? in the appropriate context.

We have amended the conclusion in response to the reviewers suggestion (P10,L28).

> Recent validation of the HCHO satellite data revealed negative retrieval biases (Zhu et al., 2016), which can be corrected using spatially uniform scaling factors (as done in this study). Since similar biases may exist for the CHOCHO retrieval, the scaled HCHO data should at present be preferentially used as proxy for isoprene emission.