

1 Response to Reviewer 2

1.1 General Comments

Comment 1

Dear Authors,

Thank you for your response to Reviewer 2's further comments. Most of the comments have been addressed adequately. I have some further comments about Figure 6. It appears that even with the higher yields (than MCM), GEOS-CHEM still cannot capture the magnitude of the high RGF values in the observed data. Regarding comment 2 from the reviewer, I agree that 1) page 7 line 31 should be modified to more accurately reflect the difference in observation and model results, 2) an explicit statement on whether a higher yield (than MCM) under low-NO_x condition is required by the observations should be included in the manuscript (and further justifications can be included if necessary). These will improve the clarity of the manuscript. Once these are considered and addressed, the manuscript will be accepted for publication in ACP.

Best, Sally

Thanks Sally,

We have amended the discussion of Figure 6 to more accurately reflect the model/observation difference (P7,L33)

The observations contain a subset of low-NO_x points with higher RGF values (0.03-0.06). The model also produces a subset of enhanced RGF values under low-NO_x conditions, although peak RGF values are lower than the observations. In both cases, the enhanced RGF values coincide with short OH exposure times, which are caused by OH titration by isoprene. The high RGF reflects the relatively faster production of CHOCHO than HCHO in the early stage of isoprene oxidation under low-NO_x conditions as shown by Figure 2. The presence of that population in the observations provides support for fast glyoxal production from the isomerization pathway of isoprene oxidation (Figure 1) that is present in GEOS-Chem but not in MCMv3.3.1. The model may not capture the highest observed RGF values due to uncertainties in the yield of DHDC from isoprene and its photolysis rate, both of which have been estimated based on literature proxies (Section S3).

We have added an explicit statement about the impact of missing DHDC on the MCMv3.3.1 yield in the conclusions (P10,L16)

Mixed layer (< 1 km) observations show a strong CHOCHO-HCHO relationship that is reproduced in GEOS-Chem and is remarkably consistent across all conditions except at very low NO_x where the [CHOCHO]/[HCHO] ratio (RGF) can be unusually high. This reflects prompt formation of CHOCHO under low-NO_x conditions, which was missing from MCMv3.3.1 and is now simulated in our updated GEOS-Chem mechanism by DHDC photolysis. A previous model

comparison to SENEX showed that MCMv3.3.1 underestimates the CHOCHO yield from isoprene (Li et al., 2016). Our work shows the missing DHDC production pathway can explain approximately 60% of this underestimate, with the remainder caused by an underestimate of the δ -ISOPO₂ branching ratio (3.4% in MCMv3.3.1 vs. 10% in GEOS-Chem).