1 Response to Reviewer 1

1.1 General Comments

Comment 1

The authors present a studying using GEOS-Chem and box model simulations to understand and interpret observations of glyoxal and formaldehyde from the SENEX aircraft campaign over the Eastern US. In addition, they compare results to satellitederived formaldehyde and glyoxal columns to determine if there is separate information about isoprene emissions that can be obtained from each species (which they do not find). The manuscript is well written and should be published after addressing the following minor comments.

Response

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

1.2 Specific Comments

Comment 2

Beta vs delta isoprene RO2 isomers: Can you clarify the yield of beta vs delta RIO2 isomers separately from the RIO2+NO ISOPN yield from each isomer? Table S1 indicates the authors recommend an update to the RIO2+NO → ISOPNB and ISOPND yields. I wonder how much of that update is due to the different isomer distribution and how much is due to the yield of ISOPN from each isomer. Note that in older versions of the isoprene chemistry, the yield of beta-RIO2+NO to produce ISOPNB and deltaRIO2+NO to produce ISOPND were different. Fisher et al., 2016 updated them to both be 9%. The 10% yield of delta isomers indicated in Figure 1 is higher than MCM (3.4%, page 5 line 29).

Response

The finalized isoprene organic nitrate yield (ISOPNB+ISOPND, both 9%) from Fisher et al. (2016) was not pushed to the simulation shown here, but should be included in the revised mechanism to properly simulate isoprene-derived organic nitrates. The scaling in our paper preserved the organic nitrate yields from the beta and delta pathways from the original mechanism (6.2% and 10%). This leads to a slight decrease in the MVK and HC5 yields (1.7% and 0.2% respectively). Based on Figure 1 of our paper, this will lead to a minor decrease in CHOCHO production ($\sim 1.2\%$ over the southeast US).

To avoid confusion about recommendations, we have included the Fisher et al. (2016) in the revised mechanism, and added a footnote to the table with the reaction used here.

Comment 3

The Li et al. paper is only cited twice despite using a very similar data set and working on a similar issue. More synthesis of results in the context of Li et al. would be helpful. For example, do both models agree in terms of the role of RO2 isomerization and its contribution to glyoxal? Comparing Figure 1 of Li et al. to Figure 1 in this paper indicates Li et al. predict a much larger role for RO2+HO2 relative to isomerization in producing glyoxal (but the figures are not directly comparable, so it is not clear).

Response

We now include more discussion about the differences between the GEOS-Chem and AM3 chemical mechanisms (Section 2.2). The justifications for our particular choices of CHOCHO precursor yields are further expanded on in the supplementary material (Sections S1-3). Section S2 addresses the difference in RO2+HO2. Our CHOCHO yield via this channel is approximately 3 times lower than in AM3, due to differences in the yield from IEPOX. Our CHOCHO yields via ISOPO2 isomerization are similar (Section S3) however the pathways generating CHOCHO are different (DHDC photolysis in GEOS-Chem vs. HPALD photolysis in AM3). To our knowledge there is currently no obvious mechanism for HPALD photolysis to produce CHOCHO, and no details were provided in the paper cited by Li et al. (Stavrakou et al. (2010)).

Comment 4

Page 5, line 6-7. How was it determined that the model was not sensitive to aerosol reactive uptake? Was that through a simulation or estimated lifetime against uptake? The authors note that a background/free tropospheric source of glyoxal may be missing from the model. Have the authors considered whether or not reversible uptake of glyoxal, particularly if it is formed in the boundary layer and repartitions to glyoxal in the free troposphere, may provide this missing source?

Response

Originally this was based on a sensitivity simulation with and without CHOCHO aerosol uptake, using a reactive uptake coefficient of 10^{-3} (average of the Li et al. rates) at the OMI overpass time (13-14 pm local). However, this time period is where the OH and photolysis sinks should be strongest, and will overestimate their importance at times with less light.

In the revised version we have estimated the potential impact of aerosol uptake in the model via a steady state assumption (Section S4) that should resolve this shortcoming. The impacts of aerosols on the mean are now discussed in Section 2.2 (**P5,L17**).

> Li et al. (2016) found that CHOCHO concentrations are sensitive to aerosol reactive uptake. Our standard model simulation does not include this uptake, but we conducted a sensitivity simulation with a reactive uptake coefficient $\gamma = 2 \times 10^{-3}$ from Li et al. (2016). We find that CHOCHO concentrations decrease by only 10% on average (Section S4) because competing CHOCHO sinks from reaction with OH and photolysis are fast.

Comment 5

Page 8, near line 5 and Figure 7: The model shows a population of points with R(GF) $<$ 0.01 while observations do not indicate such low R(GF) at any time. Do you know the cause of these low modeled R(GF)?

Response

The small number of low model R_{GF} values may be due to a missing background source, similar to that missing in the free troposphere. Monoterpenes are a potential candidate, as MCM predicts that they produce CHOCHO in high yield. We have added this to the discussion of Figure 7 (**P8,L1**)

> Figure 6 also shows that there are is a small subset of points in GEOS-Chem with RGF values less than 0.01, reflecting low CHOCHO values in the model that are not found in the observations where the concentration floor is 0.05 ppbv (Figure 5). There may be a CHOCHO background missing from the model, possibly contributed by monoterpenes; MCMv3.3.1 predicts that the total CHOCHO yield from common monterpenes is high (Kaiser et al., 2015), and that they produce CHOCHO over a 5 timescale of days (Figure S11).

Comment 6

5. Page 9, line 26-27 indicates finer scale, more temporally resolved data may provide valuable glyoxal data from satellite? Are the authors hypothesizing that R(GF)s may be more variable? Can GEOS-Chem predictions be used to test that theory?

Response

That is the idea, however as shown in Figure 7, GEOS-Chem can capture the trend, but not the magnitude of the high R_{GF} values associated with prompt low-NOx production. This may be for a variety of reasons. Perhaps the resolution does not capture the high-isoprene low-NOx conditions seen in the observations (the nominal spatial resolution of TEMPO will be $\sim$ 5 times higher). A higher yield, or faster photolysis rate of DHDC will also lead to higher R_{GF} values in the model. These are both uncertain, and we have done our best based on available literature to estimate them.

Comment 7

Figure 6: Is the influence of NOx due to the effect on RO2 branching or OH?

Response

It is a combination of the two. High NOx increases OH and therefore increases isoprene photochemical processing. Increased photochemical processing has two main impacts. The slope will increase from higher isoprene production, but will be partially offset by additional removal of CHOCHO and HCHO by higher OH concentrations. Since the CHOCHO yields in GEOS-Chem are approximately constant for the first few hours of OH exposure time (t_{OH}), the 3 times increase between the low- and high-NOx slopes probably suggests that photochemical processing is more important.

Figure 6 has now been removed from the manuscript due to concerns from another reviewer.

1.3 Technical Corrections

Comment 8

Second sentence of abstract could be reworded as it is not clear if HCHO is also measureable from space via the same technique as glyoxal or not.

Response

The sentence has been amended to

> Like formaldehyde (HCHO), another VOC oxidation product, it is measurable from space by solar backscatter.

Comment 9

Page 3, line 12: ?is in better agreement? than Vrekoussis?

Response

We now cite the retrievals we are referring to in the text (**P3, L10**).

> Our recent CHOCHO retrieval from the OMI satellite instrument (Chan Miller et al., 2014) is in better agreement with surface observations of CHOCHO and R_{GF} (Kaiser et al., 2015) compared to those from GOME-2 (Vrekoussis et al., 2010) and SCIAMACHY (Wittrock et al., 2006) as a result of improved background corrections and removal of NO2 interferences.

Comment 10

Page 4, line 15: delta "vs beta" branching ratio

Response

Fixed

Comment 11

Page 4, line 15: forms as "a" second-generation

Response

Fixed