

1 Response to Reviewer 3

1.1 General Comments

Comment 1

This paper presents a new chemical mechanism for glyoxal (CHOCHO) production from isoprene oxidation that is used in the GEOS-Chem global chemical transport model. The glyoxal and formaldehyde (HCHO) yields from this mechanism are compared to those of the Leeds Master Chemical Mechanism (MCM v3.3.1) under different NOx conditions. The performance of this mechanism is then evaluated using CHOCHO and HCHO observations from the NOAA SENEX campaign, as well as 2006-2007 retrievals of HCHO and CHOCHO from the NASA Ozone Monitoring Instrument (OMI). The later is the first validation exercise for the OMI CHOCHO retrieval. This is a well-written paper on an important topic in atmospheric chemistry, specifically the oxidation chemistry of isoprene and the ability to use satellite observations to infer isoprene emissions in important regions such as the southeast US. The methods seem reasonable and are described well, and the conclusions are generally supported by the results. All of my comments detailed below are minor or technical in nature, so I recommend publication after minor revisions to address them.

Response

We thank the reviewer for their helpful comments. Our responses to their specific comments are shown below, including corresponding changes to the manuscript.

1.2 Specific Comments

Comment 2

P2, L21: HOx is usually defined as OH + HO₂, not plus all peroxy radicals, right? Why are you including organic peroxy radicals here?

Response

We have corrected this in the revised version (**P2, L20**).

Isoprene impacts air quality and climate as a precursor to ozone (Geng et al., 2011) and secondary organic aerosol (SOA) (Carlton et al., 2009), and also affects concentrations of hydrogen oxide radicals ($\text{HO}_x \equiv \text{OH} + \text{HO}_2$)

Comment 3

P4, L5: There is no 2013 NEI ? Do you mean the 2011 NEI with growth/control factors applied to simulate 2013?

Response

The scaling is relative to the 2011 NEI. We have corrected the sentence (**P4, L6**).

NOx emissions are as described by Travis et al. (2016) including a 50% decrease in the anthropogenic source relative to the 2011 National Emission Inventory of the U.S. Environmental Protection Agency.

Comment 4

P5, L2: This sentence is really a conclusion, and so is out of place here. I'd suggest rephrasing to say that you explore if this pathway is consistent with SENEX observations of CHOCHO production in low NOx conditions in Section 3.

Response

The sentence was intended to reflect the motivation for including this pathway (which is not in MCMv3.3.1). It was not in our original mechanism, but rather it was motivated by discrepancy made apparent by the SENEX observations. We have modified the wording to try and convey this (**P5, L2**)

As shown below, we find that this pathway can explain SENEX observations of prompt CHOCHO production under low- NO_x conditions.

Comment 5

P6, L18-19: Do you have any evidence from more conserved species, like CO or aerosols, that vertical transport is underestimated?

Response

We have included a profile of CO in the supplement (Figure S8), and have updated the main manuscript (**P7, L1**)

Modeled CO concentrations are also negatively biased above the mixed layer (Figure S8), providing further support that convective transport is underestimated.

Comment 6

P6, L24: It's not clear what you mean by ?correlative analysis in the SENEX observations offer no insight.? What analyses did you attempt?

Response

To test for any obvious influences, we looked at the correlation coefficients (and rank correlations for robustness) for observations above 3 km, between 10-17 hours local time, for all VOC species measured during the campaign. We have updated the sentence to reflect this (**P7, L8**).

There could be a free tropospheric source missing in the model, but it is unclear what this source could be, and correlative analysis of observed free tropospheric

CHOCHO with other species measured in SENEK offer no insight ($r < 0.3$ for all observed VOCs).

Comment 7

P7, L1-2: I can see the NOx sensitivity in the GEOS-Chem plot in Figure 5 (perpendicular to the regression line), but I can't see it in the observations. Am I missing something?

Response

The relationship to NOx, HCHO and CHOCHO is clearer when looking at R_{GF} (Figure 6 in the revised manuscript). We have changed the text in the revised manuscript (**P7, L24**).

The strong correlation between CHOCHO and HCHO might suggest that they provide redundant information for constraining isoprene emissions. However, examination of Figure 5 indicates higher observed CHOCHO-to-HCHO ratios (R_{GF}) at low-NO_x concentrations, not captured by GEOS-Chem.

There is much less scatter in the GEOS-Chem points in Figure 5 due to the fact that transport by turbulent eddys is parameterized as diffusion (which removes variability associated with isoprene photochemical processing).

Comment 8

Typos:

P3, L32: need a space before "Travis"

P5, L12: Expand "DSMACC"

P5, L20: I think you need a comma before tOH

P10, L3: I think you need to hyphenate "NOx-dependent"

Response

The typos have been fixed in the revised manuscript.