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 satellited-erived 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 ~ 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

2 Response to Reviewer 2

2.1 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.

2.2 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.

3 Response to Reviewer 3

3.1 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.

3.2 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 ($HO_x \equiv OH + HO_2$)

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 SENEX 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.

Glyoxal yield from isoprene oxidation and relation to formaldehyde: chemical mechanism, constraints from SENEX aircraft observations, and interpretation of OMI satellite data

Christopher Chan Miller[1], Daniel J. Jacob[1,2], Eloise A. Marais[1], Karen Yu[2], Katherine R. Travis[2], Patrick S. Kim[1], Jenny A. Fisher[3], Lei Zhu[2], Glenn M. Wolfe[4,5], Thomas F. Hanisco[4], Frank N. Keutsch[2,6], Jennifer Kaiser[7,a], Kyung-Eun Min[8,9,b], Steven S. Brown[9,10], Rebecca A. Washenfelder[8,9], Gonzalo González Abad[11], and Kelly Chance[11]

[1]Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
[2]School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
[3]School of Chemistry and School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW, Australia
[4]Atmospheric Chemistry and Dynamics Lab, NASA Goddard Space Flight Center, Greenbelt, MD, USA
[5]Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA
[6]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA
[7]Department of Chemistry, University of Wisconsin Madison, Madison, WI, USA
[8]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA
[9]Chemical Sciences Division, NOAA Earth System Research Laboratory, Boulder, CO, USA
[10]Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[11]Harvard-Smithsonian Center for Astrophysics, Cambridge MA, USA
[a]now at: School of Engineering and Applied Sciences, Harvard University, Cambridge MA, USA
[b]now at: School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea

Correspondence to: Daniel Jacob (djacob@fas.harvard.edu)

Abstract.

Glyoxal (CHOCHO) is produced in the atmosphere by the oxidation of volatile organic compounds (VOCs). ~~It is measurable from space by solar backscatter along with~~ Like formaldehyde (HCHO), another ~~oxidation product of VOCs~~VOC oxidation product, it is measurable from space by solar backscatter. Isoprene emitted by vegetation is the dominant source of CHOCHO and HCHO in most of the world. We use aircraft observations of CHOCHO and HCHO from the SENEX campaign over the Southeast US in ~~summer~~ Summer 2013 to better understand the CHOCHO time-dependent ~~yields~~ yield from isoprene oxidation, ~~their dependences~~ its dependence on nitrogen oxides ($NO_x \equiv NO + NO_2$), the behaviour of the CHOCHO-HCHO relationship, the quality of OMI CHOCHO satellite observations, and the implications for using ~~satellite CHOCHO observations~~ CHOCHO observations from space as constraints on isoprene emission. We simulate the SENEX and OMI observations with the GEOS-Chem chemical transport model featuring a new chemical mechanism for CHOCHO formation from isoprene. The mechanism includes prompt CHOCHO formation under low-NO_x conditions following the isomerization of the isoprene peroxy radical ($ISOPO_2$). The SENEX observations provide support for this prompt CHOCHO formation pathway, and are generally consistent with the GEOS-Chem mechanism. Boundary layer CHOCHO and HCHO are strongly correlated in the observations and the model, with some departure under low-NO_x conditions due to prompt CHOCHO formation. SENEX vertical profiles indicate a free tropospheric CHOCHO background that is absent from the model. The OMI CHOCHO data provide some support for this free tropospheric background and show Southeast US enhancements consistent with the isoprene source but a factor of 2 too low. Part of this OMI bias is due to excessive surface reflectivities assumed in the retrieval. The OMI CHOCHO and HCHO seasonal data over the Southeast US are tightly correlated and provide redundant proxies of isoprene emission. Higher temporal resolution in future geostationary satellite observations may enable detection of the prompt CHOCHO production under low-NO_x conditions apparent in the SENEX data.

1 Introduction

Glyoxal (CHOCHO) and formaldehyde (HCHO) are short-lived products of the atmospheric oxidation of volatile organic compounds (VOCs). Both are detectable from space by solar backscatter (Chance et al., 2000; Wittrock et al., 2006). Isoprene emitted by terrestrial vegetation accounts for about a third of the global source of non-methane VOCs (NMVOCs) (Guenther et al., 2012) and drives large enhancements of CHOCHO and HCHO in the continental boundary layer (Palmer et al., 2003; Fu et al., 2008). Satellite observations of HCHO have been widely used as a proxy to estimate isoprene emission (Abbot et al., 2003; Palmer et al., 2006; Millet et al., 2008; Curci et al., 2010; Barkley et al., 2013), but there are uncertainties related to the HCHO yield from isoprene oxidation (Marais et al., 2012) and the role of other NMVOCs as HCHO precursors (Fu et al., 2007). CHOCHO observations from space could provide a complementary constraint (Vrekoussis et al., 2009, 2010; Alvarado et al., 2014; Chan Miller et al., 2014). Here we use CHOCHO and HCHO aircraft observations over the Southeast United States from the Summer 2013 Southeast Nexus (SENEX) campaign (Warneke et al., 2016), interpreted with the GEOS-Chem chemical transport model (CTM), to test understanding of the CHOCHO yield from isoprene oxidation, its dependence on nitrogen oxide radicals ($NO_x \equiv NO + NO_2$), and the combined value of the HCHO-CHOCHO pair measured from space to constrain isoprene emissions and chemistry.

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 (HO_x ~~peroxy radicals~~$\equiv OH + HO_2$) (Peeters and Muller, 2010) and NO_x (Mao et al., 2013; Fisher et al., 2016). Atmospheric oxidation of isoprene by OH takes place on a timescale of less than an hour to produce organic peroxy radicals ($ISOPO_2$). Reaction of $ISOPO_2$ with NO drives production of ozone and of organic nitrates that serve as a reservoir for NO_x (Browne and Cohen, 2012). At lower NO_x levels, $ISOPO_2$ reacts dominantly with HO_2 to produce isoprene epoxydiols (IEPOX) via isoprene peroxides (ISOPOOH) (Paulot et al., 2009b), and from there isoprene SOA (Marais et al., 2016). $ISOPO_2$ can also isomerize to generate HO_x radicals (Peeters et al., 2009; Crounse et al., 2011; Peeters et al., 2014).

The fate of $ISOPO_2$ determines the production rates and overall yields of CHOCHO and HCHO. Several studies have provided insight on the time- and NO_x-dependent yield of HCHO (Palmer et al., 2003; Marais et al., 2012; Wolfe et al., 2016). Under high-NO_x conditions, HCHO production is sufficiently prompt that observed HCHO columns can be locally related to isoprene emission rates (Palmer et al., 2006). This assumption is the basis of many studies that have used satellite HCHO observations to constrain isoprene emissions (Palmer et al., 2006; Fu et al., 2007; Millet et al., 2008; Curci et al., 2010). HCHO production is much slower under low-NO$_x$ conditions, spatially "smearing" the local relationship between isoprene emissions and HCHO columns. This has been addressed by using concurrent satellite data for NO$_2$ columns to correct the isoprene-HCHO relationship (Marais et al., 2012) or by using adjoint-based inverse modeling to relate HCHO columns to isoprene emissions including the effect of transport (Fortems-Cheiney et al., 2012).

Isoprene is estimated to account for about $\sim 50\%$ of global CHOCHO production (Fu et al., 2008), but there is large uncertainty regarding the yield of CHOCHO from isoprene oxidation. Open fires and aromatic VOCs ~~also produce CHOCHO with high yield~~ can also be major sources of CHOCHO (Volkamer et al., 2001; Fu et al., 2008; Chan Miller et al., 2016). Several studies have used the measured CHOCHO-HCHO concentration ratio $R_{GF} = [\text{CHOCHO}]/[\text{HCHO}]$ as an indicator of the dominant VOC precursors. Vrekoussis et al. (2010) found higher R_{GF} values (> 0.04) from GOME-2 satellite observations in regions where biogenic VOCs are dominant, and lower values where anthropogenic VOCs are dominant. However, the opposite behaviour is observed from ground-based studies (DiGangi et al., 2012). 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 NO$_2$ interferences. There remains the question of how observed CHOCHO-HCHO relationships are to be interpreted.

The Southeast Nexus (SENEX) aircraft campaign was conducted over the Southeast United States in June-July 2013. The aircraft had a detailed chemical payload including in situ CHOCHO (Min et al., 2016) and HCHO (Cazorla et al., 2015). Thirteen daytime flights were conducted over the campaign with extensive boundary layer coverage. ~~A previous comparison of~~ (Li et al., 2016) recently used the SENEX observations to evaluate CHOCHO formation from isoprene in the AM3 CTM~~simulations highlighted the CHOCHO yield uncertainty in current isoprene oxidation mechanisms (Li et al., 2016)~~. They found that the AM3 mechanism had closer agreement with observations than the explicit Master Chemical Mechanism v3.3.1 (MCMv3.3.1) (Jenkin et al., 2015), and suggested that CHOCHO yields from isoprene epoxydiols are underestimated in MCMv3.3.1. Here we take a more rigorous look at potential missing pathways in MCMv3.3.1. In doing so, we present an improved chemical mechanism for CHOCHO formation from isoprene for the GEOS-Chem CTM~~. We use~~ , and evaluate it against the SENEX observations~~to evaluate the CHOCHO formation pathways from isoprenein the new mechanism and in the Master Chemical Mechanism v3.3.1 (Jenkin et al., 2015). Wolfe et al. (2016) used their SENEX HCHO observationsto analyze the HCHO yield from isoprene and its~~ , including the time- and NO$_x$-dependence ~~. We apply here some of the same methods to analyze the CHOCHO yield~~of the CHOCHO yield from isoprene. We discuss the implications of the new mechanism for the interpretation of satellite observations, and present a first validation of the CHOCHO retrieval from the OMI satellite instrument (Chan Miller et al., 2014).

2 GEOS-Chem Model Description

2.1 General Description

We use the same version of GEOS-Chem v9.2 (http://www.geos-chem.org) that has been used previously to interpret chemical observations from the NASA SEAC^{4}RS aircraft campaign conducted in the same Southeast US region in August-September 2013 ~~(Toon et al., 2016)~~(Travis et al., 2016; Fisher et al., 2016). The model is driven by assimilated meteorological data with $0.25° \times 0.3125°$ horizontal resolution from the Goddard Earth Observing System (GEOS-FP) reanalysis product (Molod et al., 2012). The native $0.25° \times 0.3125°$ resolution is retained in GEOS-Chem over the North American domain ($130° - 60°$W, $9.75° - 60°$N), nested within a global simulation at $2° \times 2.5°$ resolution (Kim et al., 2015). Isoprene chemistry in GEOS-Chem v9.2 is as described by Mao et al. (2013), but the SEAC^{4}RS simulation includes a number of updates described by Travis et al. (2016) and Fisher et al. (2016). The simulation presented here includes further modifications relevant to CHOCHO, listed in the supplementary material (Table S1), and summarized below. Evaluation of the model with SEAC^{4}RS observations has been presented by Kim et al. (2015) for aerosols, Travis et al. (2016) for ozone and NO_x, Fisher et al. (2016) for organic nitrates, Marais et al. (2016) for isoprene SOA, and Zhu et al. (2016) for HCHO including satellite validation.

Isoprene emissions in the model are from MEGANv2.1 (Guenther et al., 2012) with a 15% reduction (Kim et al., 2015), and NO_x emissions are as described by Travis et al. (2016) including a 50% decrease in the anthropogenic source relative to the ~~2013~~ 2011 National Emission Inventory of the U.S. Environmental Protection Agency. Yu et al. (2016) pointed out that isoprene and NO_x emissions in the Southeast US are spatially segregated and show that the $0.25° \times 0.3125°$ resolution of GEOS-Chem is adequate for separating the populations of high- and low-NO_x conditions for isoprene oxidation.

2.2 CHOCHO ~~Formation~~ formation from ~~Isoprene~~ isoprene and ~~Loss Pathways~~loss

Figure 1 shows the CHOCHO formation pathways from isoprene oxidation by OH (the main isoprene sink) as implemented in this work. Oxidation is initiated by OH addition to the terminal carbons of the isoprene double bonds (positions 1 and 4, Figure 1). Isoprene peroxy radicals ($ISOPO_2$) are formed by O_2 addition to the carbon either in β or δ to the hydroxyl carbon. $ISOPO_2$ reacts with NO and HO_2, and also isomerizes. Together these pathways represent 92% of $ISOPO_2$ loss, with the remainder due to reactions with organic peroxy radicals.

Under high-NO_x conditions, CHOCHO is produced promptly via products of the δ isomers (HC5, DIBOO) (Paulot et al., 2009a; Galloway et al., 2011). CHOCHO production via the β isomers is slower, due to the intermediary production of methylvinylketone (MVK) followed by glycolaldehyde (GLYC). GEOS-Chem originally had a fixed δ vs. β branching ratio of 24% for the reaction of $ISOPO_2 + NO$, based on the chamber experiments of Paulot et al. (2009a). However recent work has shown that O_2 addition to the isoprene-OH adducts is reversible (pink pathway, Figure 1), allowing interconversion between β and δ $ISOPO_2$ isomers (Peeters et al., 2009; Crounse et al., 2011; Peeters et al., 2014). β isomers are heavily favoured at equilibrium, accounting for $\sim 95\%$ of $ISOPO_2$ (Peeters et al., 2014). The experimental conditions in Paulot et al. (2009a) used high NO concentrations (~ 500 ppbv). This implies short $ISOPO_2$ lifetimes, and thus may not reflect the degree of isomer interconversion seen at ambient oxidant levels. Here we adopt a $\delta{-}ISOPO_2$ ~~branch~~ branching ratio of 10%, following Fisher et al. (2016), to match SEAC^{4}RS observations of organic nitrates produced through the $\delta-\mathrm{ISOPO_2}+\mathrm{NO}$ pathway.

CHOCHO forms under low-$\mathrm{NO_x}$ conditions through isoprene epoxydiols (IEPOX) and through the $\mathrm{ISOPO_2}$ isomerization pathway. IEPOX forms as a second-generation non-radical product of isoprene oxidation via ISOPOOH, and thus represents a slow CHOCHO formation pathway. IEPOX isomer fractions in GEOS-Chem are based on equilibrium δ/β $\mathrm{ISOPO_2}$ branching ratios (Bates et al., 2014; Travis et al., 2016). At low $\mathrm{NO_x}$ levels the $\mathrm{ISOPO_2}$ lifetime is sufficiently long for equilibrium to be reached (Peeters et al., 2014). $\mathrm{ISOPO_2}$ isomerization in the previous GEOS-Chem mechanism of Travis et al. (2016) produced solely hydroperoxyaldehydes (HPALDs), but here we also include the formation of dihydroperoxy α-formyl peroxy radicals (di-HPCARPs) (Peeters et al., 2014) following ~~the Master Chemical Mechanism v3.3.1 (~~MCMv3.3.1~~) (Jenkin et al., 2015)~~. di-HPCARPs in MCMv3.3.1 have a low CHOCHO yield, but here we introduce a (1,5)H-shift isomerization of di-HPCARPs that could be competitive with the (1,4)H-shift isomerization due to the presence of the terminal-peroxide functional group (Crounse et al., 2013). The resulting di-hydroperoxide dicarbonyl compound (DHDC) product quickly photolyzes to produce CHOCHO, analagous to the mechanisms proposed for HPALDs (Peeters et al., 2014) and carbonyl nitrates (Müller et al., 2014). ~~We~~ As shown below, we find that this pathway can explain SENEX observations of prompt CHOCHO production under low-$\mathrm{NO_x}$ conditions.

~~GEOS-Chem includes CHOCHO loss via photolysis and oxidation by OH. Pressure-dependent CHOCHO photolysis rates are computed using the FAST-JX radiative transfer model (). CHOCHO loss via aerosol reactive uptake does not significantly alter daytime CHOCHO concentrations because the CHOCHO lifetime against OH and photolysis is short (1-2 h). Since we only consider daytime observations (10-17 local), our model evaluation is not~~ The mechanism presented here differs substantially from the AM3 mechanism previously used by Li et al. (2016) to analyze the SENEX observations. Li et al. (2016) tested branching ratios of 22% and 0% for $\delta-\mathrm{ISOPO_2}+\mathrm{NO}$, with the latter intended to reflect $\mathrm{ISOPO_2}$ isomer interconversion. The 10% branching ratio in this study is constrained by SEAC^{4}RS organic nitrate observations (Fisher et al., 2016). Li et al. (2016) report a CHOCHO yield from GLYC oxidation (Section S1), which is mainly due to a lower CHOCHO yield from $\mathrm{GLYC}+\mathrm{OH}$ (13% vs. 20%). Their yield of CHOCHO from IEPOX is 28%, much higher than can be accommodated by yields of hydroxyacetone derived from IEPOX oxidation chamber experiments (Bates et al., 2014) (the expected coproduct of CHOCHO via this pathway, Section S2). Following Travis et al. (2016), we set the CHOCHO yield from IEPOX to the corresponding hydroxyacetone yields reported by Bates et al. (2014) (8.5% via $\mathrm{HO_2}$ and 8.8% via NO). Finally AM3 assumes 25% CHOCHO yield from HPALD photolysis following Stavrakou et al. (2010), which has been used in many past studies (Mao et al., 2013; Marais et al., 2016). However HPALD photolysis is not expected to yield CHOCHO (Section S3). The CHOCHO formation pathway via DHDC proposed here can be justified from existing literature (Section S3). Inclusion of DHDC increases the yield of CHOCHO via $\mathrm{ISOPO_2}$ isomerization by 18%, which is comparable to the AM3 yield.

Li et al. (2016) found that CHOCHO concentrations are sensitive to aerosol reactive uptake~~, in contrast with a previous CTM comparison to SENEX by Li et al. (2016)where no time filtering was applied.~~. Our standard model simulation does not include this uptake, but we conducted a sensitivity simulation with a reactive uptake coefficient $\gamma = 2\times10^{-3}$ 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.

2.3 Time- and $\mathrm{NO_x}$-dependent CHOCHO and HCHO yields from isoprene

Understanding the time- and $\mathrm{NO_x}$-dependent yields of CHOCHO and HCHO from isoprene oxidation is critical for interpreting observed CHOCHO and HCHO columns from space in terms of isoprene emissions. Here we examine time-dependent CHOCHO and HCHO molar yields in the GEOS-Chem and MCMv3.3.1 chemical mechanisms using the ~~DSMACC~~ Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) box model (Emmerson and Evans, 2009). Simulations are initiated at 9am local time with 1 ppbv isoprene, 40 ppbv $\mathrm{O_3}$, and 100 ppbv CO. $\mathrm{NO_x}$ concentrations are held at fixed values. Photolysis rates are calculated for clear-sky with the TUV radiative transfer model (Madronich, 1987). To correct for differences in time-dependent yields associated with differences in OH concentrations, we reference GEOS-Chem and MCMv3.3.1 results to a common "OH exposure time" variable (t_{OH});

$$t_{OH} = \frac{1}{[OH]_{ref}} \int_0^t [OH](t')dt' \qquad (1)$$

Here $[OH](t)$ is the OH concentration simulated in the box model, and $[OH]_{ref} = 4 \times 10^6$ molecules cm^{-3} is a reference OH concentration representative of summer daytime conditions over the Southeast US (Wolfe et al., 2016). For a fixed [OH]$=4 \times 10^6$ molecules cm^{-3}, t_{OH} represents the actual time.

Figure 2 shows the time- and $\mathrm{NO_x}$-dependent cumulative molar yields of CHOCHO and HCHO in GEOS-Chem and MCMv3.3.1. The branching ratio of $\mathrm{ISOPO_2}$ as a function of $\mathrm{NO_x}$ is also shown. The time-dependent HCHO yields in both mechanisms are similar under high-$\mathrm{NO_x}$ conditions. Additional confidence in the HCHO yield under these conditions is offered by the ability of GEOS-Chem to reproduce the observed correlation between HCHO and isoprene organic nitrates (Mao et al., 2013; Fisher et al., 2016). The HCHO yield is lower under low-$\mathrm{NO_x}$ conditions in both mechanisms, and overall the difference between them is minor.

There is far more disagreement between the two mechanisms for CHOCHO yields. Under high-$\mathrm{NO_x}$ conditions, GEOS-Chem produces CHOCHO rapidly in the first two hours due to its higher $\delta\mathrm{-ISOPO_2+NO}$ branching ratio (10% in GEOS-Chem vs. 3.4% in MCMv3.3.1). This is compensated at longer OH-exposure times by higher GLYC yields from isoprene in MCMv3.3.1. GEOS-Chem produces higher ultimate yields of CHOCHO under low-$\mathrm{NO_x}$ conditions mainly due to DHDC formation and subsequent photolysis, neither of which are included in MCMv3.3.1. The $\mathrm{NO_x}$-dependence of the CHOCHO yield in MCMv3.3.1 is similar to that of HCHO, implying that CHOCHO and HCHO observations would provide redundant information on isoprene emissions. The SENEX observations indicate that CHOCHO yields under low-$\mathrm{NO_x}$ conditions are too low in MCMv3.3.1, as discussed below. In GEOS-Chem, by contrast, the CHOCHO and HCHO yields show opposite dependences on $\mathrm{NO_x}$, implying that they could provide complementary information on isoprene emissions.

3 Constraints from SENEX observations

Figure 3 shows the observed and simulated median vertical profiles of CHOCHO, HCHO, and $\mathrm{NO_x}$ concentrations along the SENEX flight tracks. Figure 4 shows maps of concentrations below 1 km altitude (above ground level) taken as the mixed layer. Here and elsewhere we only include daytime observations (10-17 local) and exclude targeted sampling of biomass burning plumes (diagnosed by acetonitrile concentrations above 200 pptv). CHOCHO, HCHO and $\mathrm{NO_x}$ were measured by the Airborne Cavity Enhanced Spectrometer (ACES) (Min et al., 2016), In-Situ Airborne Formaldehyde (ISAF) instrument (Cazorla et al., 2015), and the NOAA chemiluminescence instrument (Ryerson et al., 1999; Pollack et al., 2010), with stated accuracies of 6%, 10%, and 5% respectively.

Simulated median $\mathrm{NO_x}$ concentrations in the mixed layer are within 10% of observations, supporting the 50% reduction in EPA NEI $\mathrm{NO_x}$ emissions previously inferred from the analysis of SEAC^{4}RS observations by Travis et al. (2016), also included here (Section 2.1). Half of isoprene oxidation in the model under the SENEX conditions takes place by the low-$\mathrm{NO_x}$ pathways (Figure 1). Simulated median CHOCHO and HCHO concentrations in the mixed layer are within 20% of observations, but the model is too low at higher altitudes. 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), suggesting that transport via this mechanism is underestimated in the model. Modeled CO concentrations are also negatively biased above the mixed layer (Figure S8), providing further support that convective transport in the model is underestimated.

The CHOCHO observations in the free troposphere (> 3 km) have to be treated with caution since they are ~~close to the instrument detection limit (Kaiser et al., 2015)~~below the reported instrument precision (32 pptv, Kaiser et al. (2015)). It is therefore difficult to determine whether the bias is due to a missing CHOCHO source in the model or instrument artifact. Elevated CHOCHO concentrations above the boundary layer have also been observed in previous campaigns over the Southeast US (Lee et al., 1998), California (Baidar et al., 2013), and the remote Pacific (Volkamer et al., 2015). There could be a free tropospheric source missing in the model, but it is unclear what this source could be, and correlative analysis ~~in the SENEX observations~~ of observed free tropospheric CHOCHO with other species measured in SENEX offer no insight ($r < 0.3$ for all observed VOCs).

The mixed layer concentrations maps in Figure 4 show that the model captures some of the horizontal variability in the observations. The spatial correlation for HCHO is high ($r = 0.75$) as in SEAC^{4}RS ($r = 0.64$, Zhu et al. (2016)), and reflects isoprene emission patterns. Correlation for CHOCHO is also relatively strong ($r = 0.51$). ~~Average mixed layer~~ Temporally averaged CHOCHO and HCHO concentrations simulated by the model for the SENEX period (background in Figure 4) are much more uniform than those sampled along the SENEX flight tracks ~~, as shown in the GEOS-Chem panels of Figure 4. This is~~ because of day-to-day variability in isoprene emissions, mostly driven by temperature (Zhu et al., 2016).

Figure 5 compares simulated and observed CHOCHO vs. HCHO relationships in the mixed layer color coded by $\mathrm{NO_x}$ concentrations. Correlation between the two species is strong~~, and model and observations are consistent. This might suggest that CHOCHO and HCHO provide redundant information for constraining isoprene emissions. However, examination of Figure 5 indicates some sensitivity, which will be discussed further below.~~

~~Measurements of isoprene (ISOP) and total methylvinylketone + methacrolein (MVK+MACR) made by proton transfer mass spectrometry from the SENEX aircraft (de Gouw and Warneke, 2007) allow some evaluation of GEOS-Chem CHOCHO and HCHO yields by using the parcel model of Wolfe et al. (2016) to infer initial isoprene and OH exposure time t_{OH}. The evolution of ISOP and MACR concentrations within the parcel is given by~~

$$ISOP + OH \xrightarrow{k_1} Y_{MACR}(NO)MACR$$

$$MACR + OH \xrightarrow{k_2} products \qquad (2)$$

~~Here $Y_{MACR}(NO)$ is the -dependent yield of MACR from isoprene, and k_1~~. The model better captures the observed slope (0.028 modeled vs. 0.024 observed) compared to the AM3 CTM (0.045 and 0.035 with and ~~k_2 are the rate constants for the reactions of with and respectively, all given by Wolfe et al. (2016). Whole air samples (Lerner et al., 2016) during SENEX indicated a uniform ratio of 2.3 ± 0.2 mol mol^{-1} so that the MACR concentrations can be inferred from the higher-frequency MVK+MACR measurement. For an air parcel initially containing only isoprene we derive the following expression for the ratio of MACR to isoprene as sampled by the aircraft.~~

$$\frac{[MACR]}{[ISOP]} = \frac{Y_{MACR}(NO)k_1}{k_2 - k_1}\left(1 - \exp\left((k_1 - k_2)\cdot[OH]_{ref}t_{OH}\right)\right)$$

~~We use equation 2 to calculate t_{OH} from the observed ratios and from there to infer the initial isoprene concentration =exp($k_1 t_{OH}$). The calculation is applied to the ensemble of SENEX data below 1 km altitude and yields t_{OH} in the range of 0.25 - 1.5 h.~~

~~Figure **??** shows the observed relationships of CHOCHO and HCHO concentrations vs. initial isoprene color coded by concentrations. High-and low-conditions can be separated by envelopes using linear regression fits to the data with concentrations above 800 pptv and below 200 pptv respectively (Figure 2). The observed slopes increase by at least a factor of two for both CHOCHO and HCHO in the transition from low- to high-conditions. This is well reproduced by~~ without CHOCHO production from $\delta{-}\mathrm{ISOPO_2} + \mathrm{NO}$ respectively) (Li et al., 2016). Inclusion of aerosol uptake further reduces the bias to the observed slope (0.026, Figure S10). On average, CHOCHO is produced more promptly in AM3 compared to GEOS-Chem, ~~even though the model CHOCHO yield is -independent over~~ which may lead to the higher slope. In the first few hours of ~~isoprene oxidation (Figure 2). The higher CHOCHO under high-conditions in GEOS-Chem~~ oxidation this is due to ~~longer photochemical aging, as OH concentrations increase with increasing . Overall the comparison in Figure **??** provides support for the CHOCHO and HCHO yields computed by GEOS-Chem and their dependences on~~ a higher CHOCHO yield from $\mathrm{ISOPO_2}$ isomerization. Beyond the initial stages of isoprene oxidation, CHOCHO is produced faster in AM3 because of the increased fraction of CHOCHO produced from IEPOX over GLYC oxidation (Figure 1).

~~Previous studies have used the~~

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}~~=ratio~~

~~as an indicator for different VOC precursors (Vrekoussis et al., 2010; DiGangi et al., 2012). In the Southeast US, isoprene is the dominant source of both. In this case variations in R_{GF} would be expected to reflect differences in the chemical environment for isoprene oxidation, and the information may be useful for relating satellite column observations to isoprene emission~~) at low-NO_x concentrations, not captured by GEOS-Chem. Figure 6 shows the R_{GF} ratio as a function of NO_x below 1 km in the SENEX observations and as simulated by GEOS-Chem. Points are color coded by OH exposure time t_{OH} (Equation 1), derived from ~~the parcel model~~PTR-MS observations of the methylvinylketone + methacrolein-to-isoprene ratio (de Gouw and Warneke, 2007) following Wolfe et al. (2016). The median and interquartile R_{GF} values binned in 250 pptv NO_x increments are also shown. The observed median R_{GF} values (0.02 to 0.024 mol mol^{-1}) show no significant dependence on NO_x, while GEOS-Chem shows a weak dependence. In both the model and observations there is a subset of low-NO_x points with higher R_{GF} values (0.03-0.06). These correspond to short OH exposure times and are caused by OH titration by isoprene. The high R_{GF} 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.

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 timescale of days (Figure S11).

4 Implications for satellite observations

Knowledge gained from SENEX enables an improved interpretation of CHOCHO and HCHO column observations from space in isoprene dominated environments. We use for this purpose June-August 2006-2007 observations of CHOCHO, HCHO, and tropospheric NO_2 columns from the Ozone Monitoring Instrument (OMI). OMI was launched onboard the NASA Aura satellite in July 2004, and provides daily global coverage in sun-synchronous orbit with an equatorial crossing time of 13:40 LT. The CHOCHO data are from the Smithsonian Astrophysical Observatory (SAO) retrieval described in Chan Miller et al. (2014) and hereby referred to as OMI SAO. The HCHO and NO_2 data are from the OMI Version 3 product release (González Abad et al., 2015; Bucsela et al., 2013). Retrievals are in the 435-461 nm spectral range for CHOCHO, 328.5-356.5 nm for HCHO, and 405-465 nm for NO_2. We use 2006-2007 data because 2013 data for CHOCHO are very noisy (Figure ~~S1~~S12), possibly because of sensor degradation. The OMI observations are compared to a GEOS-Chem simulation covering the same period, at $2^\circ \times 2.5^\circ$ horizontal resolution.

Slant columns along the optical path of the backscattered solar radiation are fitted to the observed spectra and converted to vertical columns by division with an air mass factor (AMF) that accounts for the viewing geometry, atmospheric scattering, and the vertical profile of the gas (Palmer et al., 2001):

$$AMF = \int_{0}^{\infty} w(z)s(z)dz \tag{3}$$

Here $w(z)$ is the scattering weight measuring the sensitivity of the retrieval to the gas concentration at altitude z, and $s(z)$ is a normalized vertical profile of gas number density. Here we recomputed the AMFs for the three retrievals using vertical profiles from GEOS-Chem, as it is necessary for comparing simulated and observed vertical columns (Duncan et al., 2014).

We remove observations impacted by the row anomaly (http://www.knmi.nl/omi/research/product/rowanomaly-background.php), and those with cloud fractions over 20%. Previous validation of the OMI HCHO retrievals with SEAC^{4}RS aircraft observations revealed a 43% uniform low bias (Zhu et al., 2016), corrected in the data shown here.

Figure 7 compares CHOCHO and HCHO vertical columns from GEOS-Chem and OMI, and Figure 8 shows spatial correlations over the eastern US. Excellent agreement is found for HCHO, providing an independent test of the correction to the OMI HCHO retrieval inferred from the SEAC^{4}RS data (Zhu et al., 2016). ~~CHOCHO~~ 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. CHOCHO from OMI is highly correlated with GEOS-Chem (~~$r = 0.76$~~$r = 0.81$), indicative of the isoprene source. However OMI CHOCHO shows a higher continental background and a factor of 2 weaker enhancement over the Southeast US.

Zhu et al. (2016) suggested that errors in the assumed surface reflectivities affecting the AMFs were an important source of the bias in the OMI HCHO retrievals. CHOCHO retrievals are even more sensitive to surface reflectivity because of the longer wavelengths. Russell et al. (2011) previously pointed out that the OMI surface reflectivities used in the standard NO_2 retrievals (Kleipool et al., 2008) were too high and replaced them with high resolution ($0.05° \times 0.05°$) reflectivity observations from MODIS (Schaaf and Wang, 2015) to produce the Berkeley High-Resolution (BEHR) OMI NO_2 retrieval. CHOCHO and NO_2 are retrieved at similar wavelengths so the sensitivity to surface reflectivity should be similar. Figure 7 (bottom right) shows the mean CHOCHO scattering weights computed from the OMI-SAO and BEHR. The lower BEHR surface reflectivity values result in a lower AMF and hence a higher vertical column (Figure 7, bottom left panel). The slope of the regression between GEOS-Chem and OMI CHOCHO columns increases from ~~0.46 to 0.57~~0.48 to 0.62, improving but not reconciling the differences.

As pointed out above, SENEX and other observations suggest that GEOS-Chem may be missing a background source of CHOCHO~~in the free troposphere (Figure 3), although it is not clear what this source might be~~. Integration of the median CHOCHO profile above 2 km in Figure 3 shows a negative model bias of 1.3×10^{14} molecules cm^{-2}, comparable to the continental background intercept in Figure 8 (~~1.7×10^{14}~~ 1.9×10^{14} molecules cm^{-2}). The nonzero intercept may in part reflect an underestimate of CHOCHO concentrations caused by a missing CHOCHO source over the Southeast US, such as monoterpenes (Section 3). The presence of free tropospheric CHOCHO would further impact the AMF calculation under continental background conditions since the retrieval sensitivity as measured by the scattering weights increases with altitude. Thus the retrieved continental background would be overestimated.

Figure 9 shows CHOCHO vs. HCHO relationships for OMI (using the BEHR scattering weights) and GEOS-Chem, color coded by tropospheric NO_2 columns. Individual points are seasonal averages (data points from Figure 7) in order to limit noise. The slope is steeper in GEOS-Chem because the CHOCHO columns are higher. Since GEOS-Chem reproduces the aircraft CHOCHO-HCHO relationship without bias (Figure 5), this is further evidence of bias in the OMI CHOCHO observations. The CHOCHO-HCHO relationship is tight in both OMI (~~$r = 0.83$~~$r = 0.86$) and GEOS-Chem ($r = 0.99$), with no indication of a separate population of low-NO_x points with high R_{GF} as there was in the SENEX data. It thus appears from the OMI data that satellite observations of CHOCHO and HCHO in isoprene-dominated environments are redundant. This may reflect the higher NO_x levels in 2006-2007 compared to 2013 (Russell et al., 2012). However since median R_{GF} shows no significant variation with NO_x in the SENEX data (Figure 6), the required temporal averaging of satellite observations is a more likely explanation for the tight correlation. Finer-scale and more temporally resolved data, as will be available from the TEMPO geostationary instrument to be launched in the 2018-2020 time frame (Zoogman et al., 2016), may provide new perspectives of the utility of the CHOCHO retrieval.

5 Conclusions

We have used aircraft observations of glyoxal (CHOCHO), formaldehyde (HCHO), and related species from the SENEX aircraft campaign over the Southeast US together with OMI satellite data to better understand the CHOCHO yield from isoprene and the complementarity of CHOCHO and HCHO observations from space for constraining isoprene emissions. This work includes a first validation of the CHOCHO retrieval from the OMI satellite instrument.

We began with an analysis of the time- and NO_x~~dependent~~ -dependent CHOCHO and HCHO yields from isoprene oxidation in the GEOS-Chem chemical transport model and in the Master Chemical Mechanism (MCMv3.3.1). The GEOS-Chem mechanism features several updates relevant to CHOCHO formation. These include a decrease in the $\delta{-}ISOPO_2 + NO$ branching ratio leading to prompt CHOCHO production under high-NO_x conditions, and a proposed low-NO_x pathway for prompt CHOCHO formation ~~from a (~~by photolysis of a di-hydroperoxide dicarbonyl compound (DHDC) product from (1,5)H-shift isomerization of dihydroperoxy α-formyl peroxy radicals ~~formed through~~ in the $ISOPO_2$ isomerization pathway (~~proposed here~~Figure 1). GEOS-Chem and MCMv3.3.1 show similar HCHO yields from isoprene, increasing with increasing NO_x. CHOCHO yields from isoprene in MCMv3.3.1 show behavior similar to HCHO but GEOS-Chem has a higher yield at low-NO_x from the $ISOPO_2$ isomerization pathway.

Comparison of GEOS-Chem to the SENEX observations of CHOCHO and HCHO shows good agreement in the boundary layer but a negative CHOCHO model bias in the free troposphere. This could reflect an instrument artifact but may also imply a missing background source in the model. 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 (R_{GF}) can be unusually high. This reflects prompt formation of CHOCHO under low-NO_x conditions, which ~~the model attributes to the new pathway via isomerization followed~~ was missing from MCMv3.3.1 and is now simulated in our updated GEOS-Chem mechanism by DHDC photolysis~~proposed here (Figure 1)~~.

The SENEX observations enable indirect validation of the OMI CHOCHO satellite data using GEOS-Chem as an intercomparison platform. The OMI data show a continental background that is consistent with the SENEX free tropospheric observations, and an enhancement over the Southeast US that is consistent with the isoprene source. However this enhancement is a factor of 2 too low in the OMI data. A partial explanation is that surface reflectivities assumed in the standard OMI retrieval are too high. The satellite data show strong CHOCHO-HCHO correlation consistent with the model and imply that the two gases provide redundant information for constraining isoprene emissions in regions where isoprene is their dominant precursor. This redundancy may reflect the seasonal averaging in the OMI data required to reduce noise~~, which still may permit observation of oxidation pathway-driven changes in the CHOCHO-HCHO relationship from future geostationary missions~~. The HCHO satellite data are better validated (Zhu et al., 2016) and should therefore be preferentially used as proxy for isoprene emission. Future geostationary observations from TEMPO (Zoogman et al., 2016) will require less temporal averaging and this may reveal the utility of CHOCHO observations for estimating isoprene emissions under low-NO_x conditions when isoprene oxidation is titrated.

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Figures

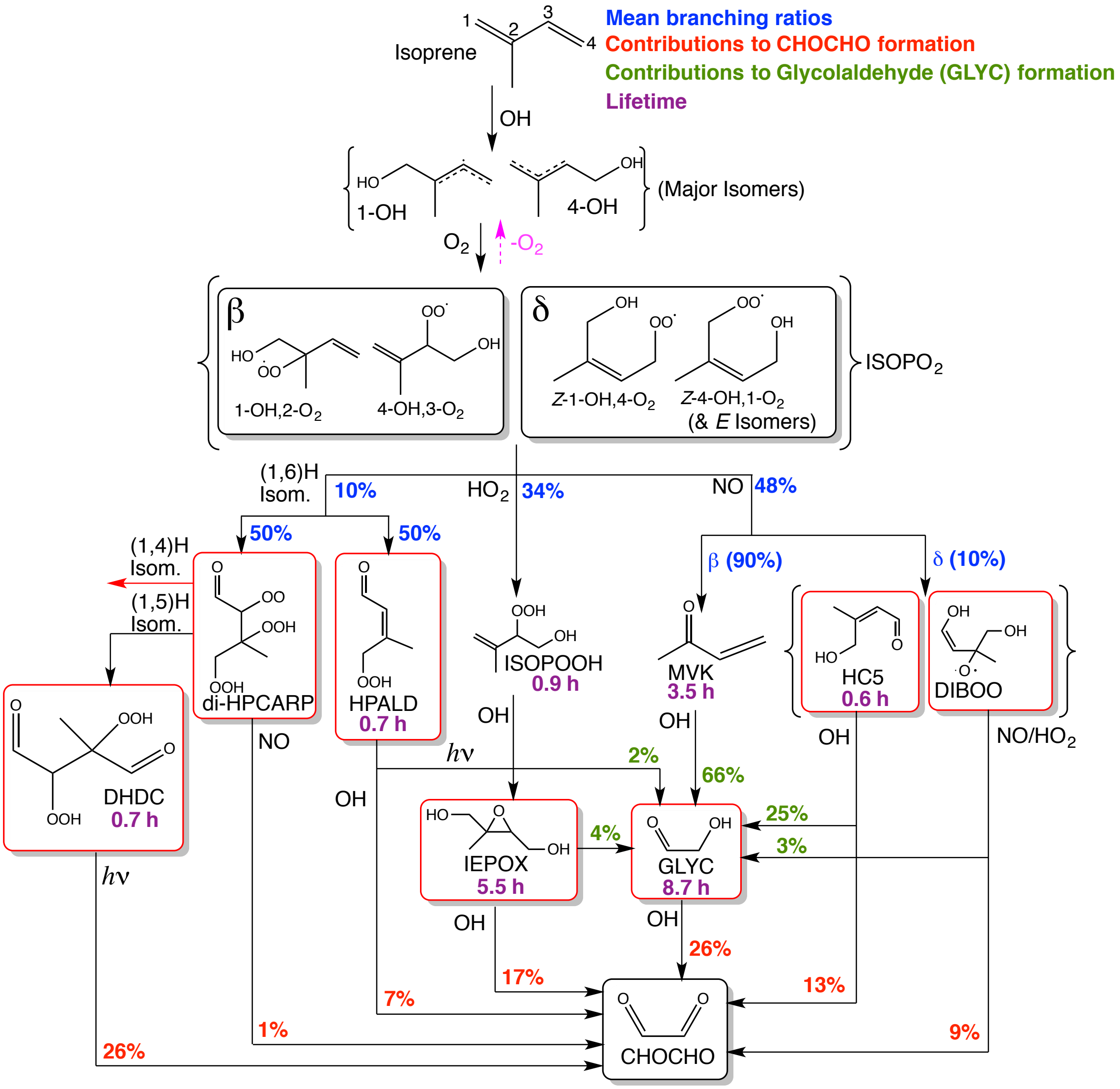

Figure 1. Pathways for glyoxal (CHOCHO) formation from isoprene oxidation in GEOS-Chem as implemented in this work. Only species relevant to CHOCHO formation are shown. Branching ratios, species lifetimes, and contributions to glyoxal and glycolaldehyde (GLYC) formation from each boxed species are mean values over the Southeast United States (96.25 − 73.75°W, 29 − 41°N) during the SENEX campaign (June 1st - July 10th 2013). Species lifetimes are shown for an OH concentration of 4×10^6 molecules cm^{-3}.

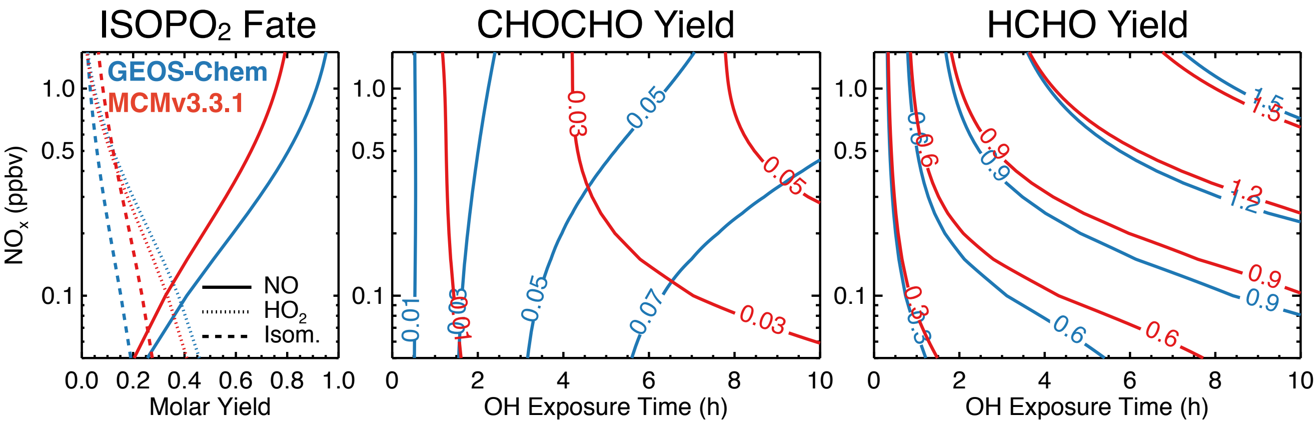

Figure 2. Cumulative time- and NO_x dependent molar yields of CHOCHO and HCHO from isoprene oxidation in the GEOS-Chem and MCM3.3.1 chemical mechanisms. Results are from box model simulations with fixed NO_x concentration as described in the text, and are presented as functions of the imposed NO_x concentration (vertical axis). The left panel shows the isoprene peroxy radical ($ISOPO_2$) branching ratios for reaction with NO, HO_2, and isomerization. The middle and right panels show the time-dependent cumulative yields of CHOCHO and HCHO, where time is normalized by OH exposure (Equation 1). "OH exposure time" is equivalent to time for a constant $[OH] = 4 \times 10^6$ molecules cm^{-3}.

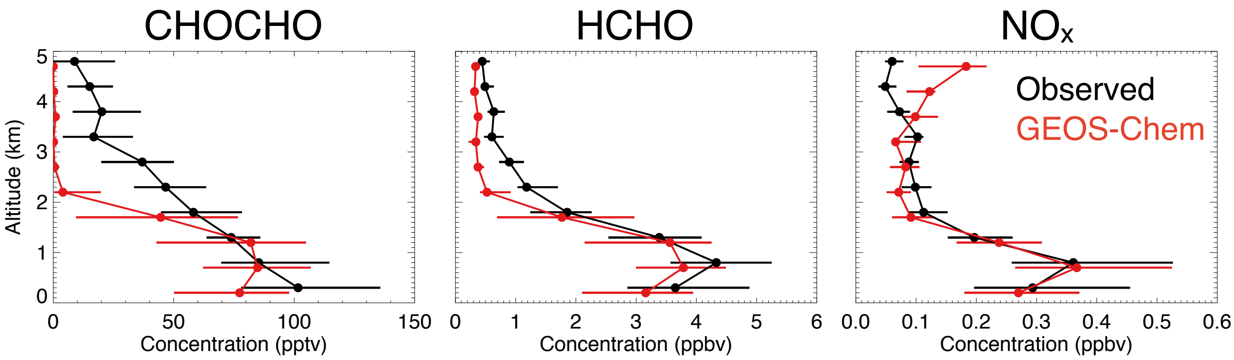

Figure 3. Median vertical profiles of CHOCHO, HCHO, and NO_x concentrations during SENEX (June 1 - July 10 2013). Observed concentrations (Min et al., 2016; Cazorla et al., 2015; Pollack et al., 2010) are compared to GEOS-Chem model values sampled along the flight tracks. Horizontal bars indicate interquartile range. Altitudes are above ground level (AGL).

~~!hRelationships of mixed layer CHOCHO and HCHO concentrations in SENEX to initial isoprene as derived from a parcel model. Observations are compared to the corresponding GEOS-Chem model values sampled along the aircraft flight tracks. Points are color coded by concentration. Dashed lines are reduced major axis regression fits to data below 200 pptv and above 800 pptv . The slopes from the regressions are indicated next to the dashed lines.~~

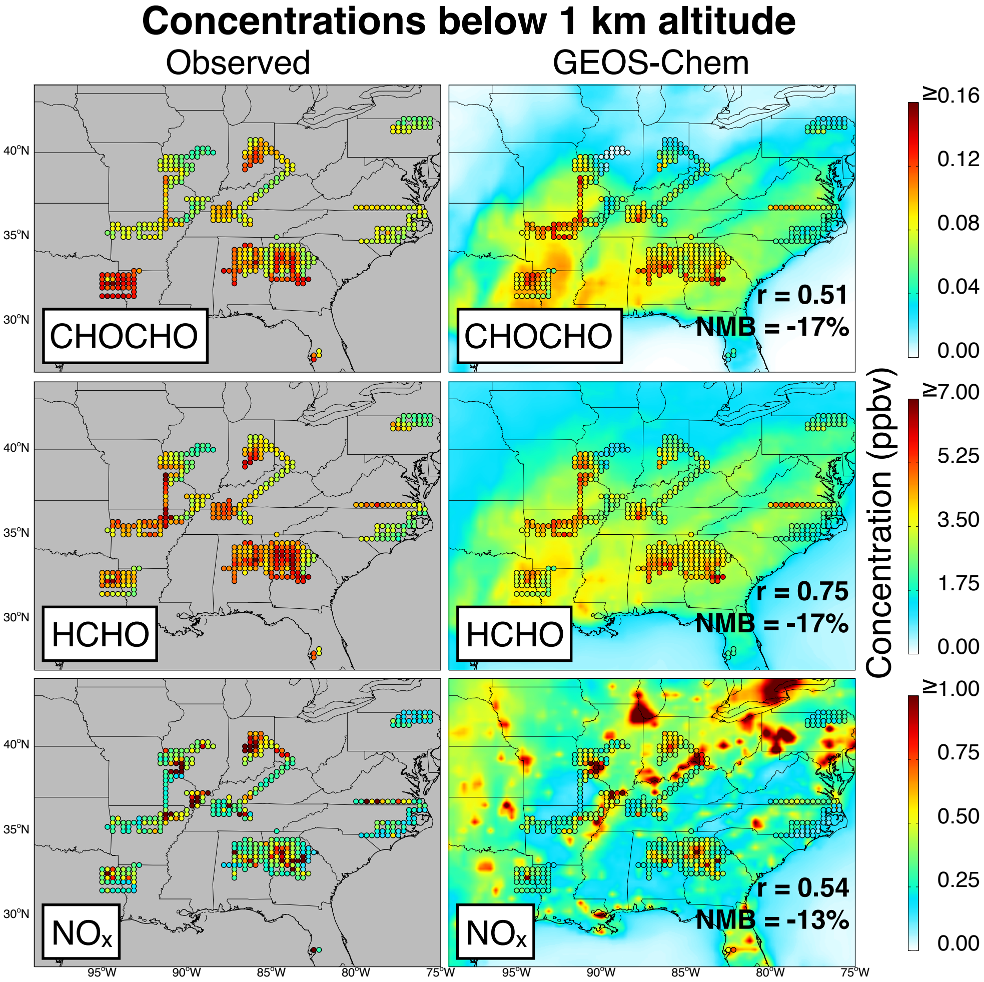

Figure 4. CHOCHO, HCHO, and $\mathrm{NO_x}$ concentrations below 1 km AGL during SENEX (June 1 - July 10 2013). The grid squares show daytime aircraft observations compared to the colocated GEOS-Chem model values on the $0.25^\circ \times 0.3125^\circ$ model grid. Background contours in the right panels show the average model-simulated concentrations at 13 - 14 local time for the SENEX period. Comparison statistics between model and observation grid squares are shown as the correlation coefficient r and the normalized mean bias (NMB). Correlation statistics for $\mathrm{NO_2}$ exclude urban plumes in the observations ($[\mathrm{NO_x}] > 4$ ppb) as these would not be resolved at the scale of the model.

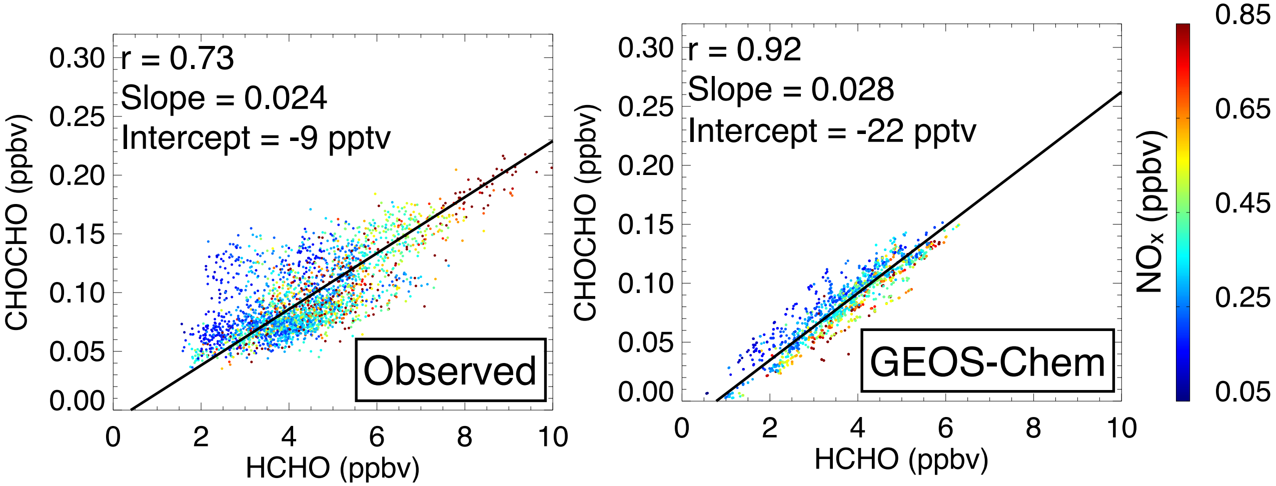

Figure 5. Relationship between CHOCHO and HCHO concentrations in the mixed layer (< 1 km AGL) during SENEX (June 1 - July 10 2013), color coded by NO_x concentration. Observed concentrations (Min et al., 2016; Cazorla et al., 2015) are compared to GEOS-Chem model values sampled along the flight tracks. Lines and reported slopes are from reduced major axis regressions.

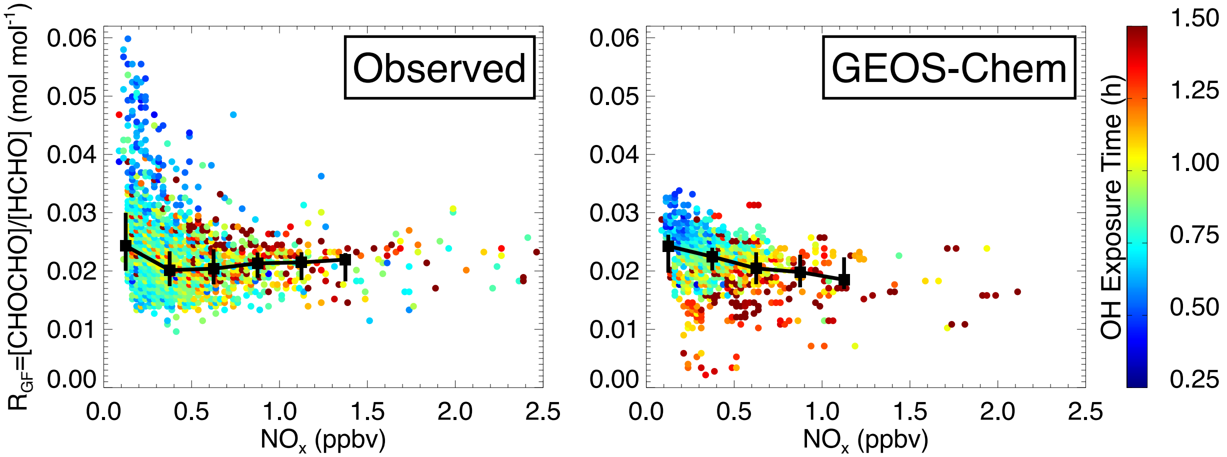

Figure 6. Dependence of the CHOCHO-to-HCHO ratio R_{GF} on NO_x concentrations for the SENEX conditions. Observations below 1 km altitude (left) are compared to GEOS-Chem model values sampled along the flight tracks (right). Points are color coded by the OH exposure time t_{OH} (Equation 1). Binned median and interquartile R_{GF} values in increments of 250 pptv NO_x for bins with more than 20 values are also shown.

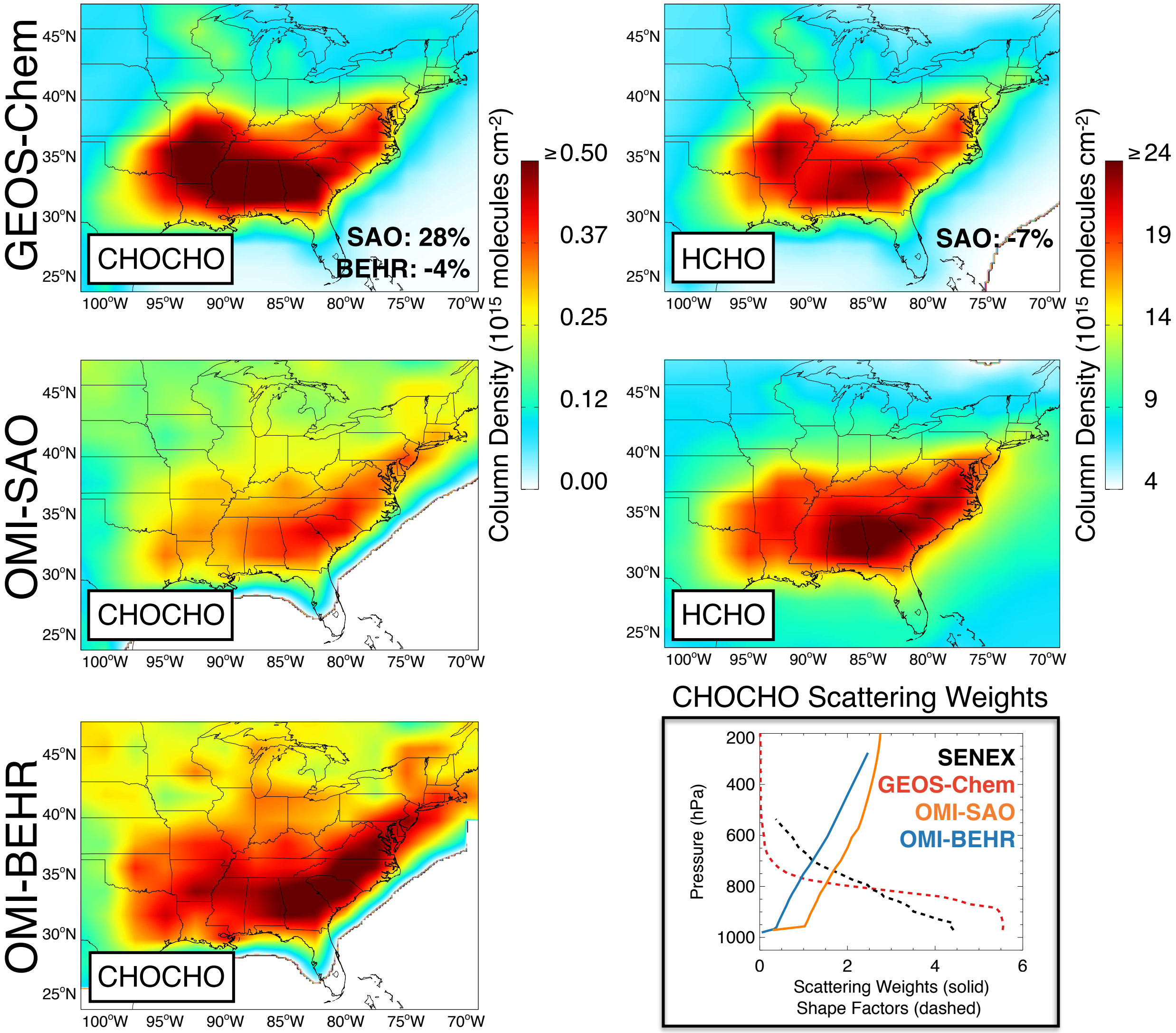

Figure 7. Mean CHOCHO and HCHO columns in summer (JJA) 2006-2007. GEOS-Chem model values (top) are compared to OMI satellite observations (middle and bottom). OMI-SAO is the standard operational product (Chan Miller et al., 2014; González Abad et al., 2015). The OMI-BEHR product for CHOCHO uses tropospheric scattering weights from the BEHR $\mathrm{NO_2}$ retrieval (Russell et al., 2011; Laughner et al., 2016). The OMI HCHO observations have been scaled up by a factor of 1.67 to correct for retrieval bias (Zhu et al., 2016). The normalized mean bias (NMB) between GEOS-Chem and OMI in the Southeast US ($75^\circ - 100^\circ$W, $29.5^\circ - 37.5^\circ$N) is shown within the GEOS-Chem panels. The bottom right panel shows the mean CHOCHO scattering weights (w) from the OMI-SAO and OMI-BEHR retrievals and the vertical shape factors (s) over the Southeast US from the SENEX observations and GEOS-Chem in the Southeast US from a typical orbit (10114, 9 June 2006).

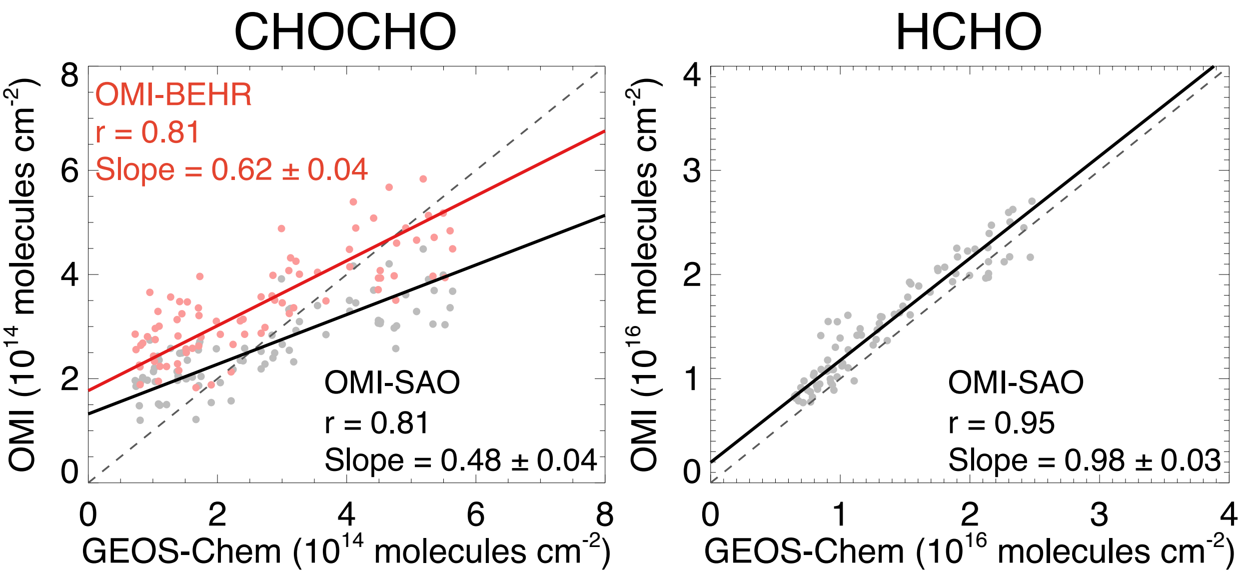

Figure 8. scatter plots of OMI vs. GEOS-Chem CHOCHO and HCHO columns over the eastern US (75° – 100°W, 29.5° – 45°N). Values are seasonal means for JJA 2006-2007 as plotted in Figure 7. OMI observations for CHOCHO are from the standard SAO retrieval (Chan Miller et al., 2014) and using BEHR scattering weights (Russell et al., 2011; Laughner et al., 2016). Correlation coefficients and reduced-major-axis (RMA) regressions are shown.

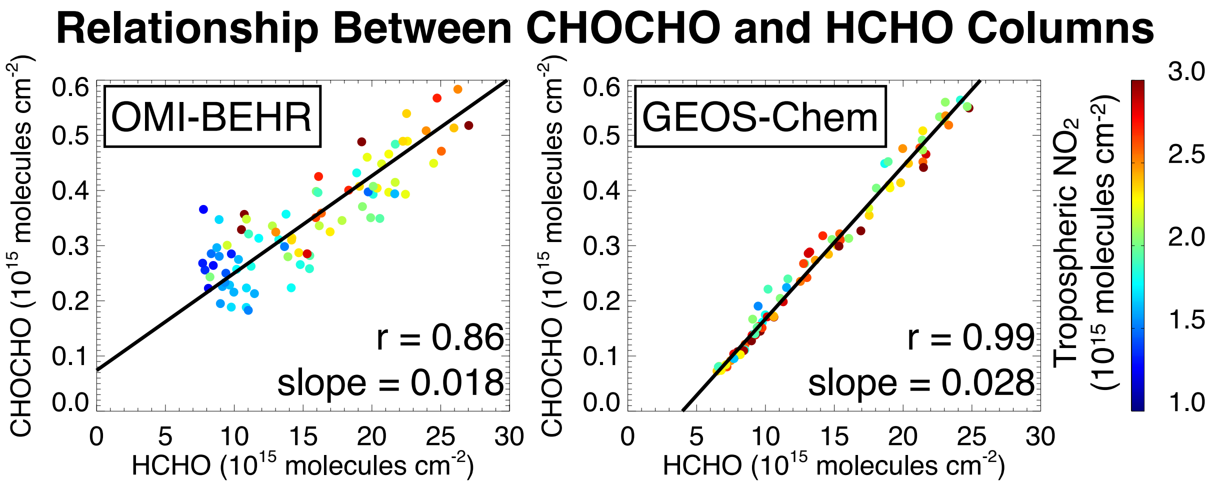

Figure 9. Relationship between CHOCHO and HCHO vertical columns over the eastern US (75° – 100°W, 29.5° – 45°N) in June-August 2006-2007 color coded by tropospheric NO_2 columns. OMI values with CHOCHO AMFs computed from BEHR scattering weights are compared to GEOS-Chem values. Lines and reported slopes are from reduced major axis regressions.