

Formaldehyde production from isoprene oxidation across NO_x regimes

Wolfe et al., ACP (2015)

Reviewer Responses

We are grateful to all three reviewers for their insightful comments. A number of changes have been made to the manuscript following these reviews, as detailed below. Referee comments are given in **bold**.

Referee 1

The authors present an investigation of HCHO production over the US based on aircraft measurements, and use the comparisons in smart ways to test current chemical models and their representation of NO_x-dependent reaction pathways of isoprene oxidation. The analysis framework is clear and well-thought out, the writing is clear, and overall the work makes a useful contribution to the literature in this area. The paper should be accepted. Below are just a few comments for the authors to consider.

Abstract (and page 31603), “we find that the total organic peroxy radical production rate is essentially independent of NO_x, as the increase in oxidizing capacity with NO_x is largely balanced by a decrease in VOC reactivity. Thus, the observed NO_x dependence of HCHO mainly reflects the changing fate of organic peroxy radicals.”

These points appear to contradict two main findings of a paper just out as an accepted preprint in JGR (Valin et al., “The role of OH production in interpreting the variability of CH₂O columns in the Southeast U.S.”). Regarding the first point, Valin et al. state that the feedbacks of P(OH) on CH₂O removal and production do not offset each other, so that CH₂O is not independent of OH. Regarding the second point above, they state: “the yield of CH₂O at low NO_x concentrations is buffered by high-yield RO₂- RO₂ reactions (. . .) in isoprene-rich regions, the influence of NO_x on CH₂O production is primarily due to its feedback on POH, which controls the rate of RO₂ formation, and less so through its effect on the fate of individual RO₂.” It would be worth adding a discussion of these apparent contradictions.

We thank the reviewer for bringing this important paper to our attention. After considering these discrepancies, we discovered an error in our calculation of total RO₂ production from the box model. This error has been resolved, and we now find that RO₂ production does indeed increase with NO_x. Figure 5 and all text has been updated accordingly. We have also added a paragraph comparing our results to those of Valin et al., and an additional panel to Fig. 5 showing the branching ratios for several RO₂ species. Please note that we have also discussed these findings with

the lead author of Valin et al.. The relevant text in Sect. 5 for the above two changes now reads as follows:

“To disentangle these factors, we extract chemical rates from the diel steady-state UWCM simulations discussed in Sect. 5. Figure 5A shows the gross production rates for total peroxy radicals and HCHO as a function of NO_x. Consistent with our earlier discussion, total HCHO production increases by more than a factor of 3 from low to high NO_x. Total RO₂ production increases by a factor of 2 over this same range, driven primarily by increasing OH. The bulk branching ratio β , calculated as the ratio of HCHO and RO₂ production rates, increases from 0.43 to 0.62 (Fig. 5B). This trend is consistent with NO_x-dependent branching ratios of several major HCHO precursors, including isoprene hydroxyperoxy radicals (ISOPO₂) and methyl peroxy radical (Fig. 5B). Based on this analysis, we conclude that enhanced OH production is the main driver for the NO_x dependence of HCHO production, with variations in RO₂ branching playing a lesser (but still important) role.

Using a combination of regional modeling and satellite observations, a recent study by Valin et al. (2016) also examines the drivers of HCHO production. They concur that OH production exerts a controlling influence on HCHO throughout the Southeast U.S. In contrast to our study, however, they assert that changes in RO₂ branching have a negligible effect on the HCHO-NO_x dependence. There are several potential explanations for this discrepancy. First, Valin et al. (2016) derive an “effective branching ratio” that is analogous to the bulk branching ratio in Eqn. (2) but calculated with reference to production of OH rather than RO₂. Many OH sinks do not form RO₂ radicals (e.g. reaction with CO, HCHO, methanol and NO₂) and thus will not make HCHO. The fractional contribution of such reactants to total modeled OH reactivity increases from 36% to 60% over our NO_x range; thus, using P(OH) instead of P(RO₂) to calculate β from Eqn. (2) would effectively normalize out the actual NO_x dependence of the RO₂ branching ratios (Fig. 5B). Second, these two studies use very different photochemical mechanisms. Valin et al. (2016) use a modified version of the lumped Regional Atmospheric Chemistry Mechanism 2 (Browne et al., 2014; Goliff et al., 2013), while our box model uses the explicit MCMv3.3.1 (Jenkin et al., 2015). In Valin et al. (2016), it is stated that decreasing HCHO production from the RO₂ + NO channel is compensated for by increasing production from RO₂ + RO₂ – an effect that we do not observe. Deeper investigation reveals that the rate constant for reaction of ISOPO₂ with HO₂ in RACM2, which is based on work by Paulot et al. (2009b), is a factor of 2 lower than those used in both MCMv3.3.1 and the AM3 mechanism. Thus, our model predicts a significantly larger contribution of RO₂ + HO₂ (which produces negligible HCHO) to the total RO₂ sink. These differences highlight the importance of carefully evaluating chemical mechanisms before using models to interpret in situ and satellite observations.”

31599, when discussing the yields of HCHO from isoprene, please be explicit about the units to avoid confusion (here, ppb/ppb aka mol/mol) as some previous work has used carbon-based yields

We have ensured that units appear on all numbers referring to yields.

31601, 12-18: in the Valin et al. paper referenced above, they argue that a steady-state assumption is justified for HCHO but not for isoprene with respect to its emissions. Does this have a significant bearing on the model application here?

We believe that this finding adds validity to our use of a steady-state 0-D box model to calculate HCHO over the Southeast U.S. We are not assuming that isoprene is in steady state, but rather that HCHO is in steady-state with its sources and sinks. Box model isoprene is constrained by observations.

31601, it would aid the interpretation of Fig 4 to discuss the differences between AM3 and UWCM in terms of the isoprene chemistry implemented in each. To what degree could the discrepancies between the two in Fig 4 reflect mechanistic chemical differences? Or is it just the effect of steady-state versus non-steady-state model frameworks?

Though the two models actually agree quite well in Fig. 4, we have considered differences in their mechanisms. We have added the following paragraph to Sect. 5, along with two new supplementary figures (S6-S7).

“The agreement between AM3 and UWCM-MCMv3.3.1 is consistent with how these mechanisms treat first-generation ISOPO₂ radicals (Figs. S6 and S7). Both models use the same rate constants for reactions of ISOPO₂ with NO and HO₂, which comprise the bulk of ISOPO₂ sink. The AM3 mechanism assigns a 12% yield of HCHO to the reaction of ISOPO₂ with HO₂ (Paulot et al., 2009b), while the MCM assumes 100% production of peroxides for this channel. This may explain some of the discrepancy in the prompt yield at low NO_x (Fig. 4A), though neither mechanism is consistent with the current experimental HCHO yield of ~6% HCHO (Liu et al., 2013). There are also two key differences in the minor reaction channels. First, the rate constant for reaction of ISOPO₂ with other RO₂ is an order of magnitude lower in AM3 compared to MCMv3.3.1 (1.54 vs 12 – 16 × 10⁻¹³ cm³ s⁻¹, the latter depending on the ISOPO₂ isomer distribution). This reaction can produce HCHO with yields comparable to that of ISOPO₂ + NO and may be an important source in very-low NO_x regimes. Second, AM3 assumes a constant ISOPO₂ isomer distribution and thus under-predicts the isomerization rate relative to MCMv3.3.1, especially at mid to high NO_x (Fig. S7D). AM3 also includes HCHO and other small oxidized VOC as direct products of isomerization rather than producing hydroperoxyaldehydes and other large products, which influences the timescale of HCHO production and thus the partitioning between prompt and background HCHO. The impact of the RO₂ reaction and isomerization channels on HCHO yields is likely minor but depends significantly on the RO₂/HO₂ ratio (at low NO_x) and on the overall ISOPO₂ lifetime, which affects the ISOPO₂ isomer distribution. For the particular model conditions in Fig. S3B, ISOPO₂ lifetimes for the two mechanisms can differ by as much as 25% at the lowest NO_x values (Fig. S7E). Regardless of these differences, the results shown in Fig. 4 confirm that both the condensed AM3 and explicit MCMv3.3.1 mechanisms perform similarly with regard to overall HCHO production.”

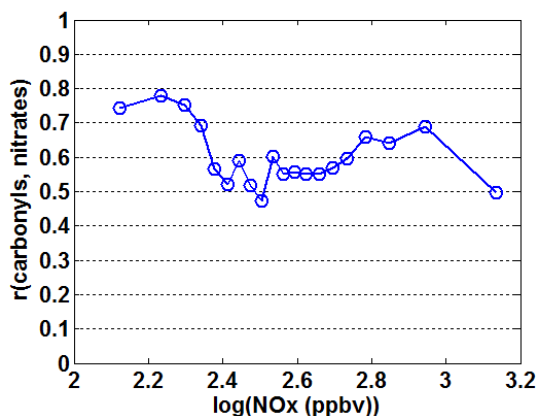
Referee 2

Wolfe and colleagues have analyzed formaldehyde observations made in regions with large isoprene fluxes as a function of NO_x levels. They find that the ‘prompt’ (e.g. within one day) yield of formaldehyde varies with NO_x in a fashion consistent with photochemical theory. Subsequent HCHO formation (e.g. ‘background levels’), however, are larger than can be explained, suggesting that formation from longer-lived organic compounds may not be described accurately by current photochemical theory. Finally, they suggest that in regions with high isoprene emissions, the formation rate of peroxy radicals remains largely constant with NO_x. This is a nice analysis; the manuscript is well written. I suggest publication in ACP following a few suggested modifications / tests.

1. The behavior of the UWCMv2.2 illustrated in Figure S4 suggests that below 200 ppt, RO₂ + RO₂ chemistry is a non-significant contributor to MVK and MACR (especially the latter). Is there support for the importance of RO₂+RO₂ chemistry in the field data? Although not unrelated to point 2 below, I suggest an analysis of the isoprene nitrates (C₅ + C₄ second generation) may be illustrative. If RO₂ + RO₂ becomes a dominant source of MVK+MACR, we anticipate that at low NO_x, the nitrates and carbonyls will no longer be correlated.

Having the best possible estimate for MVK and MACR yields is important as it affects the calculation of initial isoprene and thus the “prompt yield”, so we thank the reviewer for these comments. First, we have recalculated the MVK and MACR yields using MCMv331. In the newer mechanism at low NO_x, the MVK yield increased and the MACR yield decreased.

Regarding the sources of MVK and MACR (and the possible role of RO₂+RO₂), we have looked at the model sources of these compounds for NO values of 20 and 200 ppt (5th and 95th percentiles of observed NO, see green lines above). At 200 pptv NO, ISOP₂ + NO dominates the sources of both, as we expect. At 20 pptv NO, RO₂ + RO₂ comprises 20% of the ISOP_{BO} source (precursor to MVK) and 48% of the ISOP_{DO} source (precursor to MACR). As the reviewer points out here and in item (4) below, this may be less representative of reality due to the fixed OH concentrations in the simulation giving rise to excess RO₂ at low NO_x.

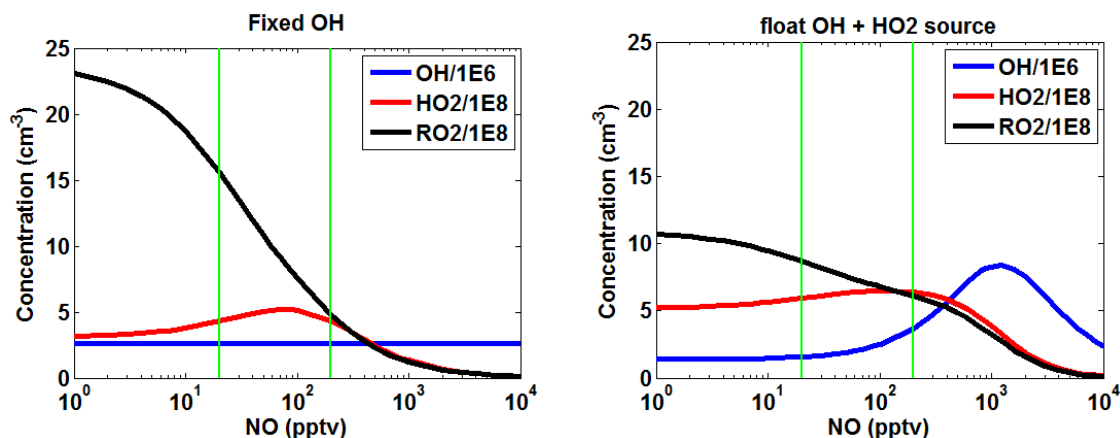


carbonyls here. Assuming that this correlation is driven by the fate of RO₂, this is also consistent

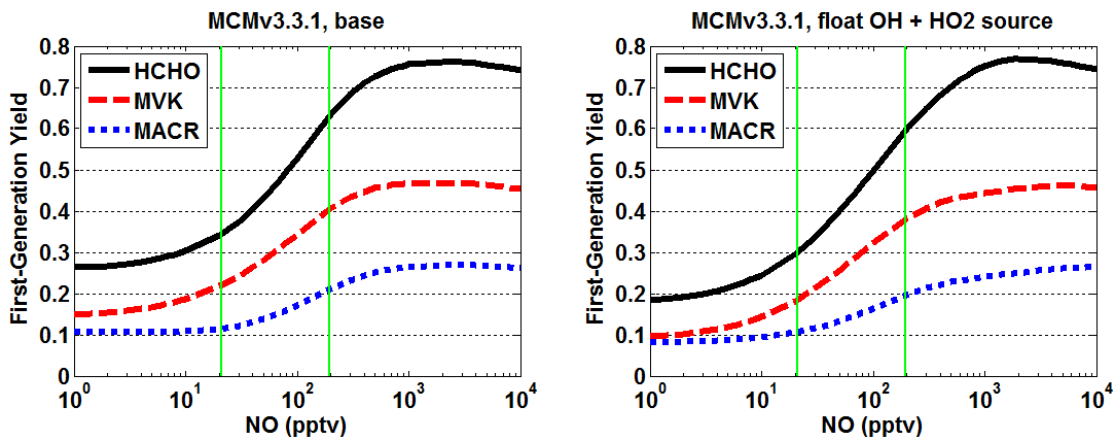
Following the reviewer’s suggestion, we have examined the correlation of MVK+MACR (PTRMS) with isoprene nitrates (UW CIMS, C₅H₉O₄N₁+C₄H₇O₅N₁) as a function of NO_x. Here we use the same procedure as that used for the linear fitting shown in Fig. 3 of the main text. The figure to the left shows the correlation coefficient for these two observations when grouped by NO_x. The two measurements are most well correlated at low NO_x, consistent with RO₂+RO₂ not being a dominant source of

with the MVK+MACR observations NOT having a significant interference from ISOPOOH (discussed further below); if ISOPOOH were a significant contributor to the MVK+MACR signal, we would expect this correlation to degrade at lower NO_x where ISOPO₂ + HO₂ is favored.

In light of these issues, we have modified the yield simulations to better represent the distribution of RO₂ sinks by allowing OH to be determined by the conditions in the simulation. In this case, these conditions are taken from NOAA P-3 observations over the SOAS Centreville site on June 10, 2013 (CO = 120 ppbv, O₃=50 ppbv, SZA = 10 degrees, RH = 75%). In addition, we add a source of HO₂, equivalent to photolysis of 5 ppbv HCHO, to compensate for HO₂ sources not included in pseudo-chamber simulation. The figures below show RO_x concentrations in the old and new simulations (both using MCMv3.3.1). At 20 pptv NO, OH and RO₂ decrease by 40% and HO₂ increases by 40%. OH and HO₂ concentrations are comparable to those observed during SOAS, and the HO₂/RO₂ ratio is within the range of values calculated in the full steady-state simulation.



This results in a general lowering of the yield curves, though the effects are relatively minor over the range of NO_x values relevant to this study (vertical green lines denote 5th and 95th percentiles of data).



We believe that this is the best possible representation of the NO-dependent yields that we can gain with the available information, and we use the “MCMv3.3.1 + floatOH + HO₂ source” yields in the

subsequent calculation of initial isoprene. We have also added a plot of ROx concentrations to Fig. S3. Please note that, despite these modifications, our main results (Figures 3 and 4) are essentially unchanged.

Is the fate of the RO2s different between AM3 and UWCM? A figure in the supplement showing the branching ratios vs NOx would be welcome.

Yes. Please see Figures S7 and S8 in the SI, as well as our above response to Referee 1 on this subject.

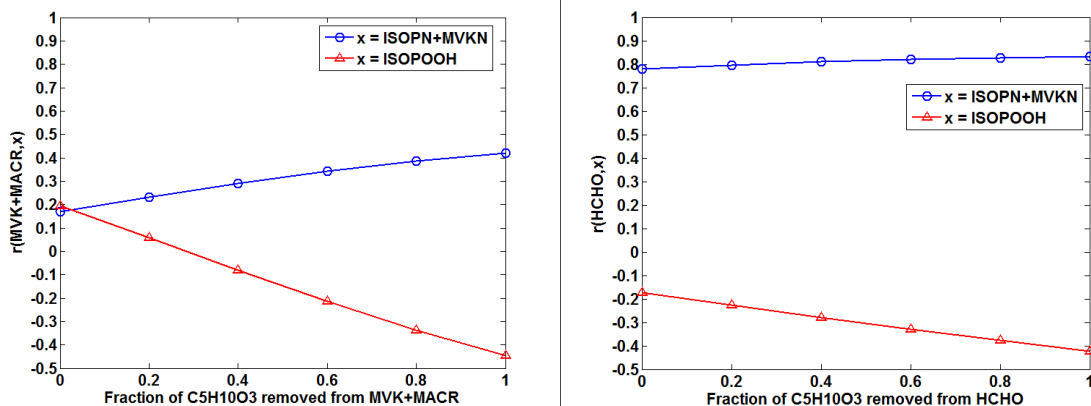
2. I am surprised that the NOAA PTRMS would not convert ISOPOOH to MVK/MACR. Has this been verified with standards of ISOPOOH? Are there differences between the drift tube used by the European groups and NOAA that might explain why there is minimal conversion in the NOAA CIMS? I find the analysis presented in S1 and S2 to be less than compelling. In the SEAC4RS data, ISOPOOH is anticorrelated with MVK+MACR (while IEPOX is uncorrelated) as might be expected from the photochemical mechanism. Does C5H10O3 show such an anticorrelation (From S1 it appears not)? During the Caltech FIXCIT experiments, the Colorado State I- CIMS was found to be more sensitive to IEPOX than ISOPOOH. Is that also the case for UW I- CIMS? If so, perhaps the analysis described in the supplement is less compelling of a test. In the SEAC4RS data, we find that $(m/z79 - 0.8*ISOPOOH)$ is very highly correlated with ISOPN+MVKN while the correlation with $m/z79$ alone is much more scattered. We have interpreted that to suggest that the conversion is high. In light of the substantial non-NO production of MVK+MACR suggested by S4, perhaps this may be a fortuitous result. It would be interesting to see a similar analysis for SENEX.

The NOAA PTRMS has not been tested for interferences with an ISOPOOH standard, thus we cannot definitively rule out an interference or develop a correction factor. We do not, however, feel that this is cause to discard the data as unusable; moreover, our key findings are robust against even a substantial interference, as discussed further below. First, we note that recent lab experiments have confirmed a low conversion rate (<5% of ISOPOOH) for the HCHO instrument used during SENEX, and we have added a reference to the appropriate paper (St. Clair et al., in preparation, 2016) in the text.

Regarding the NOAA PTRMS: The NOAA and European (Wisthaler group) instruments are both derived from IONICON and thus likely have similar drift tubes, though the inlet systems may be different. The NOAA inlet is 1/8" OD silcosteel, heated to ~30C, with a typical residence time of <1 second from ambient to instrument. To our knowledge, there is no published work yet that has sufficiently characterized the details of ISOPOOH conversion in these instruments, and it is not clear how the conversion might depend on flow rates, electric fields, etc. Thus, such comparisons should be viewed with caution.

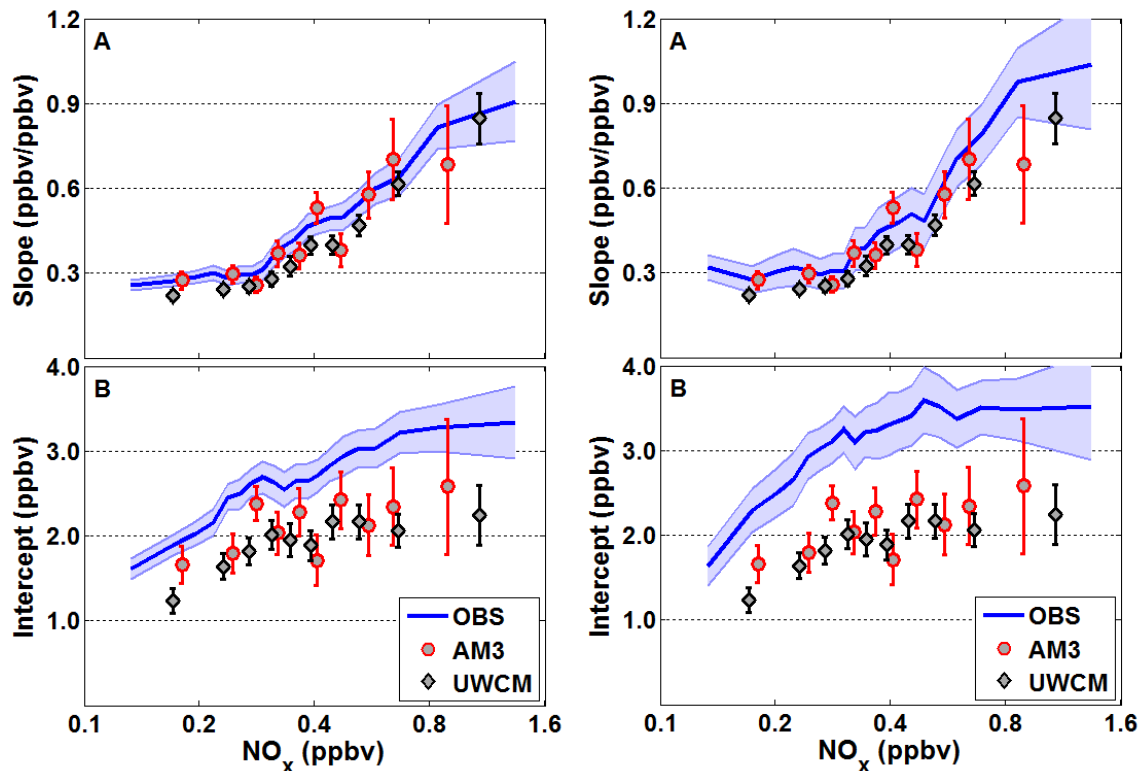
Regarding the UW-CIMS: For the C5H10O3 mass, the UW-CIMS as flown on SENEX is ~8.5 times more sensitive to ISOPOOH than to IEPOX (B. Lee, personal communication, 2016). During SEAC4RS, the Caltech triple-quad observed, on average, equal amounts of ISOPOOH and IEPOX in the SEUS. Thus, we expect that this mass is primarily representative of ISOPOOH.

Regarding correlation of MVK+MACR with other oxidation products: We assume here that the reviewer intended to write m/z 71 (the PTRMS mass for MVK+MACR) rather than m/z 79 in the above comment. For a clear view of the NO_x dependence of RO₂ fates, we look at a single SENEX flight on 20130616 in the Atlanta area. In power plant plumes, we typically find that nitrates are elevated and ISOPOOH is depleted; MVK+MACR can go up or down, but the variability and limited time resolution of this signal makes it difficult to distinguish clear trends. We examined the correlation coefficients between MVK+MACR and both nitrates and ISOPOOH, looking at how these change as fractions of the C₅H₁₀O₃ signal are subtracted from the PTRMS m/z 71 signal.



The plot on the left shows that the correlation with nitrates increases while that with ISOPOOH decreases, as the reviewer noted. As a check, we performed this same calculation with HCHO. Here we find similar trends, though somewhat less in magnitude than for the MVK+MACR case. Also, the trend in $r(\text{MVK+MACR}, \text{ISOPN+MVKN})$ would continue to increase even when subtracting more than 100% of the C₅H₁₀O₃ signal from m/z 71. Thus, it is not clear that such correlations are an unbiased diagnostic of potential interferences.

We agree that Figures S1 – S3 are not compelling and have removed them from the supplement. Instead, we have opted for a more careful comparison of the iWAS and PTR-MS to get some handle on the potential for an interference in either measurement. Through this analysis (see text below), we surmise that the conversion efficiency of ISOPOOH in the PTR-MS is likely no more than 50%. As a sensitivity test, apply such a correction and rerun all calculations with these new MVK+MACR concentrations. The plots below compare Figure 4 from the main text using MVK+MACR as observed (left) and with this correction (right). There is clearly some increase in the variability of observation-based slopes and intercepts, and the intercept increases faster at mid-NO_x values; however, the overall trends are robust.



To summarize: we cannot conclusively rule out ISOPOOH conversion in the PTRMS and iWAS instruments. To our knowledge, there is also no way to unambiguously quantify such interferences using the available observations. Furthermore, our key conclusions are robust against a substantial assuming conversion rate of 50%. We have made a number of changes to the text, including deleting section S1 and Figures S1-S3, adding two new figures to the supplement (now S1 and S2), and adding substantial text to Section 2 of the main paper, which reads as follows.

“Measurements of MVK and MACR may include a positive bias from conversion of isoprene hydroxyhydroperoxides (ISOPOOH) on hot metal surfaces in the sampling system (Liu et al., 2013; Rivera-Rios et al., 2014). ISOPOOH mixing ratios up to 2 ppbv were observed by the University of Washington Iodide chemical ionization mass spectrometer during SENEX. Neither the NOAA PTR-MS nor the iWAS have been tested for this interference with an ISOPOOH standard, thus we cannot definitively rule out such artifacts or develop a correction factor. To our knowledge, it is not yet clear how the putative interference depends on instrument configuration (flow rates, electric fields, etc.). Thus, caution is warranted when comparing the SENEX systems to similar, but not identical, instruments. Theoretically, this mechanism could give rise to an analogous artifact in HCHO observations. Recent laboratory tests, however, indicate that the ISOPOOH-to-HCHO conversion efficiency in ISAF is less than 5% (St. Clair et al., 2016).

We cannot unambiguously quantify such interferences using observations alone, but we can gain some insight from comparing PTR-MS and iWAS data. On average, iWAS observations of MVK+MACR are 40% higher than those from the PTR-MS (Figs. S1 and S2), suggesting a systematic

bias in one or both measurements. Both instruments were calibrated using the same gas standards, and the two techniques agree well for other species such as isoprene (Lerner et al., 2016; Warneke et al., 2016), so a calibration error is unlikely. Production of oxygenated VOC in ambient air samples collected and aged in stainless steel canisters cannot be ruled out. For example, enhancements in MVK (above the 20% uncertainty) have been observed in canisters after aging over ~11 days (Lerner et al., 2016), though this is significantly longer than typical turn-around times for SENEX. To evaluate the potential for ISOPOOH conversion to explain this discrepancy, we plot the ratio and difference of the PTR-MS and iWAS measurements as a function of ISOPOOH in Fig. S2. While the ratio is essentially constant (iWAS/PTR-MS ~1.43), the absolute difference exhibits a strong correlation with ISOPOOH ($r^2 = 0.43$). The slope of this relationship implies that a conversion of 50% of ISOPOOH to MVK and/or MACR in the iWAS system would explain the difference in the two measurements. Correcting total iWAS MVK + MACR for such an artifact reduces the slope of the iWAS-PTR-MS correlation from 1.48 to 1.24 (Fig. S1B). In practice, we cannot apply such a correction to the speciated iWAS observations as the conversion efficiency may be different for each isomer. This result does not exclude the possibility of an artifact in the PTR-MS measurement, though it does suggest an upper limit ISOPOOH conversion efficiency of 50% for the PTR-MS (in which case, the conversion would be 100% for the iWAS). The analysis presented in Sections 3 and 4 primarily relies on PTR-MS data due to its greater temporal coverage. Even when applying a 50% ISOPOOH correction to the PTR-MS data, we find only minor differences in our key results; thus, we use the data without correction.”

3. The update to the isoprene chemistry in MCM (used in UWCMv2.2) has now been published in ACP as version 3.3.1. I suggest updating UWCMv.2.2 to this version which is now the standard MCM.

We have used MCMv3.3.1 in both the calculation of product yields and in the full diel steady state simulation. All figures and text have been updated. The most notable impact of this mechanism is that the theoretical isoprene daughter/parent relationship now falls directly on the observed relationship in Fig. 2. Our overall conclusions, however, are unaffected.

4. Related to 1, the analysis shown in S4 has the production rate is ISOPOO constant across NO_x. I expect that the fate of these RO₂s is sensitive to the rate of their production in the low NO regime. An analysis exploring this sensitivity would be welcome.

Please see the above discussion of item (1). By altering the yield simulation to more faithfully represent atmospheric conditions, we hope that this issue has been addressed and further sensitivity tests are unnecessary.

Small points:

1. Pg. 31589; In 5, add ‘photochemical’ before mechanism

Done.

2. Pg. 31589; In 22, does ‘increase in oxidizing capacity’ here just mean [OH]? If so, please substitute.

This text has been altered following reviewer 1's comments.

3. Pg. 31590; In 25. Such models are also needed to provide vertical distribution of HCHO as the averaging kernel of the remote sensed columns is strongly altitude dependent.

This sentence has been modified to read as follows: *“Typically, a chemical transport model is employed both to supply a priori HCHO vertical distributions for satellite retrievals (González Abad et al., 2015) and to relate HCHO column concentrations to isoprene emission strength.”*

4. Pg. 31594; In 24. The focus here is solely on daytime chemistry. I suggest a few words (perhaps with use of the AM3) to demonstrate the lack of sensitivity to nighttime chemistry in your conclusions.

We have added the following text to the bottom of this paragraph: *“HCHO, MVK and MACR are also high-yield products of isoprene ozonolysis (Atkinson and Arey, 2003), but as noted above this reaction is relatively slow. Nighttime oxidation of isoprene by NO₃ radical is also likely a negligible source of these carbonyls (Brown et al., 2009). Yields are small (Atkinson and Arey, 2003; Kwok et al., 1996), and the lifetimes of these compounds is sufficiently short that any nighttime production should not influence the midday considered here.”*

5. Pg. 31602; In 8-10. A brief description of just how different the isoprene chemistry is between AM3 and the UW model would be helpful. Are they really that different (for this chemistry)?

Please see our above response to Reviewer 1 on this topic.

Referee 3

Wolfe et al. introduce airborne observations of formaldehyde and isoprene, a main precursor for formaldehyde. Utilizing box and global models, they examine formaldehyde yields in a wide NO_x spectrum. A comprehensive observational dataset on NOAA P-3 during the SENEX campaign is utilized to observationally constrain the box model. The presented quantitative information about formaldehyde background concentrations and formation rates/yields could be used for critical information in interpreting satellite datasets as the authors argued. As a constellation of geostationary satellites will be launched for air composition monitoring, this work will provide highly valuable constraints to retrieve isoprene emission rates using an inverse modelling scheme. I recommend publishing this manuscript in ACP after the considerations of a couple of suggestions

1) Page 31593: As the ISOPOOH interferences on MVK and MACR in the conventional analytical techniques are still controversial and relatively new, I would recommend including the justification for the conclusion of negligible ISOPOOH interferences on PTR-MS and whole air sample-GC-MS techniques in the main text rather than in the supplementary material

We have heavily modified our discussion of this topic, and all the relevant discussion is now included in the main text. Please see our response to Reviewer #2 on this subject.

2) It would be helpful to discuss about what is the implications of the recently reported faster than expected dry deposition rates (e.g. Nguyen et al. 2015 PNAS) in this study.

We do not expect the findings of Nguyen et al. (2015) to have a significant impact on our work. Faster deposition for oxidized VOC would potentially remove some precursors of HCHO, and if this is not accurately represented in AM3 or UWCM then we would potentially expect some over-prediction of HCHO. From Figure 4, however, it is evident that both models are missing HCHO. Moreover, the photochemical lifetimes of most of the compounds discussed in Nguyen et al. are sufficiently short that deposition should be a minor contribution to their sink.