

***Interactive comment on* “Formaldehyde production from isoprene oxidation across NO_x regimes” by G. M. Wolfe et al.**

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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

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

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 and the 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.

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.

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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.

Small points:

1. Pg. 31589; In 5, add 'photochemical' before mechanism
2. Pg. 31589; In 22, does 'increase in oxidizing capacity' here just mean [OH]? If so, please substitute.
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.
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.
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)?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 31587, 2015.

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