



Supplement of

Formaldehyde production from isoprene oxidation across NO_x regimes

G. M. Wolfe et al.

Correspondence to: G. M. Wolfe (glenn.m.wolfe@nasa.gov)

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S1 Evaluation of MVK, MACR and HCHO observations

In this study, we utilize observations of the isoprene oxidation products methyl vinyl ketone (MVK), methacrolein (MACR), their sum and formaldehyde (HCHO) from several different instruments. It has been shown that isoprene hydroxyhydroperoxides (ISOPOOH) can be converted to MVK or MACR on hot metal surfaces (Liu et al., 2013; Rivera-Rios et al., 2014), with HCHO implied as the co-product. All of the instrumentation employed here includes some metal surfaces in the sampling system, which are typically held at temperatures of 30 – 50 °C (though residence times are typically < 1 s). Thus, this mechanism can potentially lead to a measurement artifact. For the analysis presented in the main text, such an interference would artificially increase calculated initial isoprene and thus cause the prompt yield ($y_p = \Delta\text{HCHO}/\Delta\text{ISOP}_0$) to be artificially low (it should not, however, affect calculated background HCHO). Moreover, such an effect would likely be more severe at lower NO_x , where peroxy radical chemistry favors ISOPOOH production.

To use these measurements, we must first try to quantify any potential artifact. It is not possible to do so with observations alone. Here we use a comparison of observations against box model calculations to gain some insight. Box model results are from the steady-state flight simulation described in Sect. 5 of the main text. We examine the correspondence of observed and modeled mixing ratios of MVK, MACR and HCHO as a function of the mixing ratio of $\text{C}_5\text{H}_{10}\text{O}_3$ as measured at 1 Hz by the University of Washington high resolution time of flight chemical ionization mass spectrometer (UW HRTof-CIMS) using iodide-adduct ionization (Lee et al., 2014). The signal for $\text{C}_5\text{H}_{10}\text{O}_3$ is mainly comprised of ISOPOOH but may contain some contribution from isoprene dihydroxyepoxide (IEPOX), which is a product of ISOPOOH oxidation by OH. The uncertainty in absolute $\text{C}_5\text{H}_{10}\text{O}_3$ mixing ratios is $\pm 50\%$, mostly related to calibration accuracy. By using model mixing ratios of MVK, MACR and HCHO as a benchmark, we are assuming that the model does not have a systematic bias that would directly match that of an artifact in the observations.

Figure S1 compares modeled mixing ratios of MVK+MACR against the sum as measured by PTR-MS. The correlation is linear and shows no clear dependence on $\text{C}_5\text{H}_{10}\text{O}_3$ abundance. The model exhibits a high bias of 14% relative to observations on average, inconsistent with the presence of a significant measurement artifact and within the 20%

uncertainty in the measurement. Removing some fraction of the observed $C_5H_{10}O_3$ mixing ratio from the PTR-MS data (to correct for an interference) would further degrade the agreement. Based on these results, we conclude that the $m/z +71$ signal as observed by the PTR-MS during SENEX is predominantly representative of MVK and MACR mixing ratios, and any interference from ISOPOOH conversion is negligible to within measurement precision.

The iWAS instrument speciates MVK and MACR but at reduced sampling frequency relative to the PTR-MS. Comparison against model results shows consistent model biases of -34% in MVK and 17% in MACR, leading to overall model bias of -18% in the sum (Fig. S2). The bias in MACR is close to that seen in the PTR-MS comparison, while that in MVK is much larger and in the opposite direction. Model biases once again do not trend with $C_5H_{10}O_3$ mixing ratios. These results indicate that iWAS observations of MACR are likely accurate, while those of MVK may contain a positive artifact on the order of 34 – 51% (the high end of this estimate assumes an expected bias equal to that of MACR). Correcting MVK down by 50% optimizes agreement between iWAS and PTR-MS observations. The disagreement may be due to an unidentified issue with the box model chemical mechanism or the iWAS sampling system. Both the PTR-MS and the iWAS system were calibrated using the same compressed gas standards, and the two measurement techniques agree well for other species such as isoprene, so a calibration error is unlikely. Production of certain oxygenated VOCs, such as MVK, in ambient air samples collected and aged in stainless steel canisters cannot be ruled out. For example, significant enhancements in MVK (above the 20% uncertainty) have been observed in canisters after aging over ~11 days (Lerner et al., 2015), though for SENEX the typical turn-around time from collection to analysis was 3-4 days. The fact that the model-measurement bias is independent of $C_5H_{10}O_3$, however, suggests that ISOPOOH is not the source of this artifact.

Figure S3 shows the comparison with HCHO observations from the NASA ISAF instrument. The model-measurement agreement is excellent. Mean model bias is -7%, less than the stated measurement accuracy of 10%. Again, the bias is uncorrelated with observed $C_5H_{10}O_3$. This result is consistent with a negligible interference in ISAF observations.

Laboratory work is ongoing to more robustly characterize the potential for an ISOPOOH interference in these measurements. Recent results from chamber experiments suggest an upper limit of a few percent conversion of ISOPOOH to HCHO in the ISAF sampling system (J. St.

Clair, personal communication, 2015). We caution that our findings here are specific to the SENEX instrument configurations.

S2 Model Calculation of MVK, MACR and HCHO yields

In Section 3 of the main text, we utilize model-derived first-generation yields of MVK and MACR to infer initial isoprene mixing ratios. Yields are calculated using the University of Washington Chemical Box Model (UWCMv2.2, described further in Sect. 5) driven by the Master Chemical Mechanism (MCMv3.3, (Jenkin et al., 2015)). The model is set up to simulate a series of pseudo-chamber experiments as follows. Meteorology is set to typical daytime conditions ($P = 1000$ mbar, $T = 298$ K, $RH = 75\%$, solar zenith angle = 10°). Mixing ratios/concentrations of CO, O₃ and OH are respectively held constant at 120 ppbv, 50 ppbv and 2.7×10^6 cm⁻³. Mixing ratios of isoprene, HO₂ and NO₂ are respectively initialized at 5 ppbv, 20 pptv and $4 \times [\text{NO}]$ and allowed to evolve in time. NO mixing ratios are held fixed at one of 37 different values ranging from 1 pptv to 10 ppbv. For each NO value, the model is integrated forward for one hour (equivalent to the lifetime of isoprene at the prescribed OH concentration). First-generation yields for MVK, MACR and HCHO are calculated as the slope of the relationship between isoprene lost and product gained, i.e. $y = \Delta[\text{product}]/\Delta[\text{isoprene}]$. The fitting window is restricted to minutes 5 – 10 of the simulation to minimize contamination from model spin-up and multi-generation chemistry. Resulting yield curves are shown in Fig. S4. Model-derived yields of MVK and MACR are consistent with recent lab-derived yields at both high (Liu et al., 2013) and low (Fuchs et al., 2013) NO_x.

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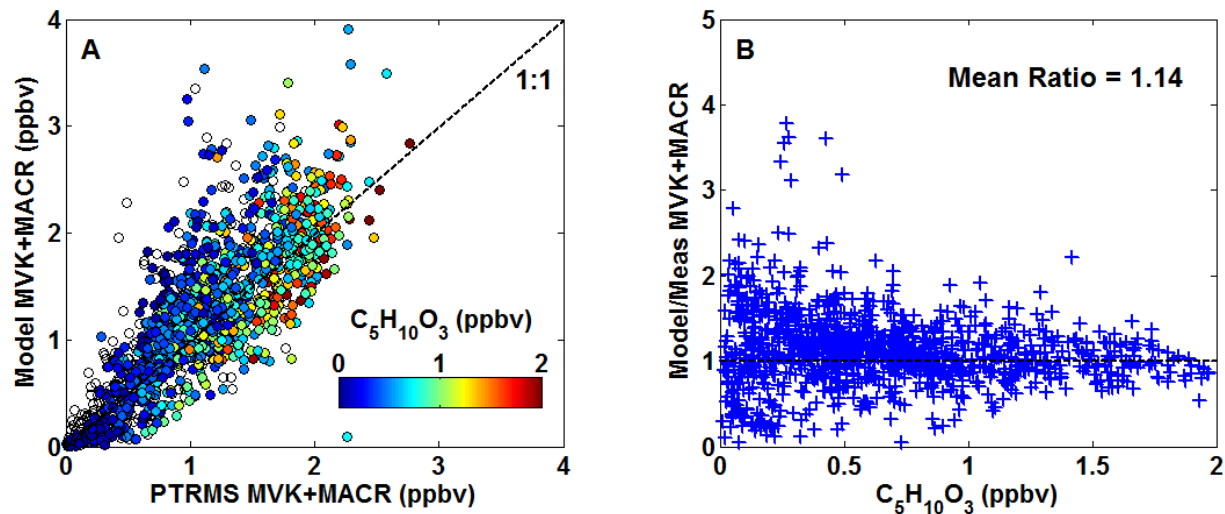


Figure S1. Comparison of box-modeled and observed (PTR-MS) mixing ratios of the sum of MVK and MACR to identify potential measurement interferences. (A) Scatterplot of all daytime boundary layer results, colored by mixing ratios of the $C_5H_{10}O_3$ (roughly equal to the sum of ISOPOOH and IEPOX) as observed by the UW iodide CIMS. Dashed line shows a 1:1 correlation. (B) Ratio of modeled to measured mixing ratios as a function of observed $C_5H_{10}O_3$. Dashed line denotes a ratio of 1. The mean ratio for all data is also given.

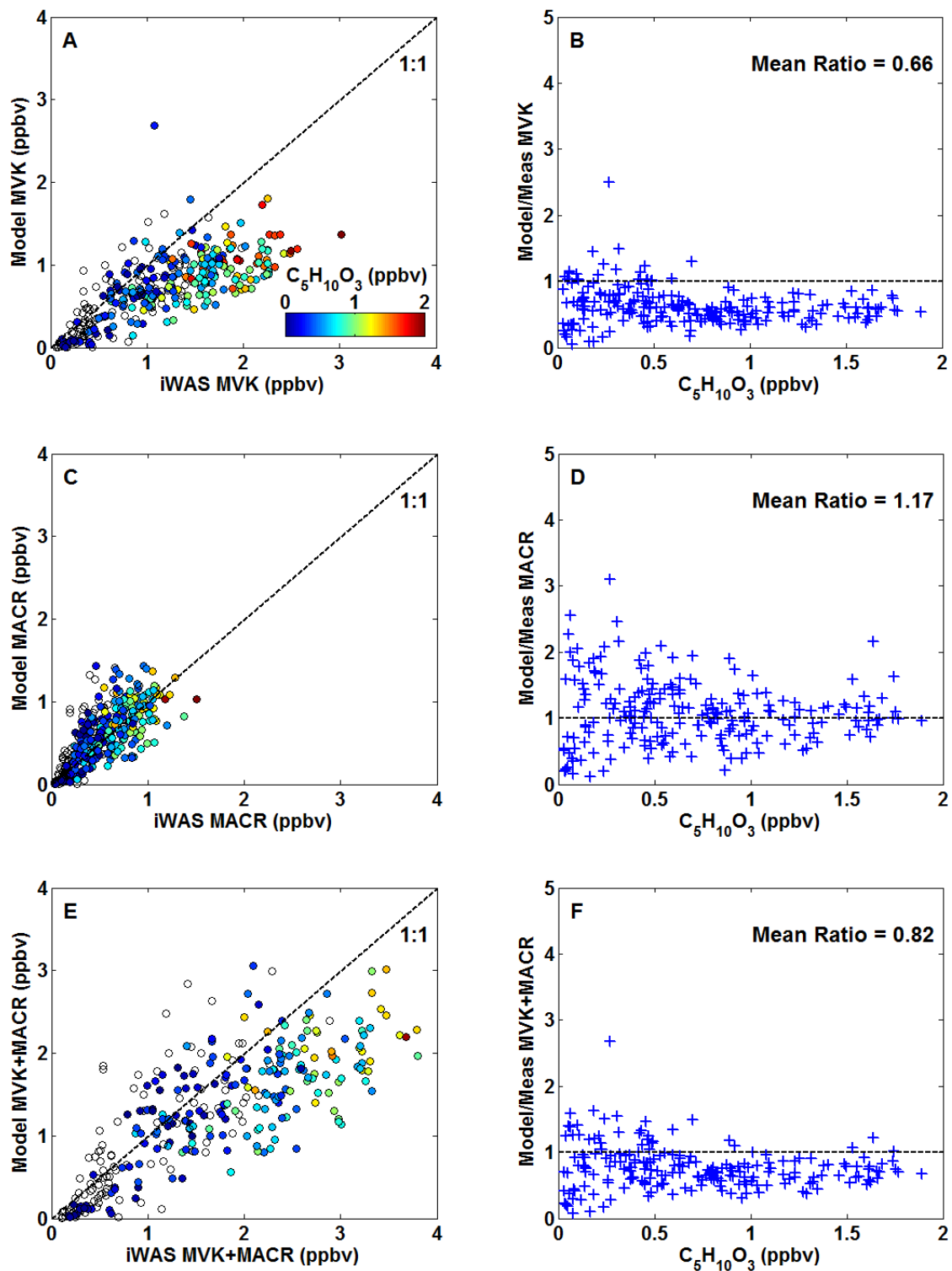


Figure S2. As in Fig. S1 but for iWAS observations of MVK (A,B), MACR (C,D) and their sum (E,F).

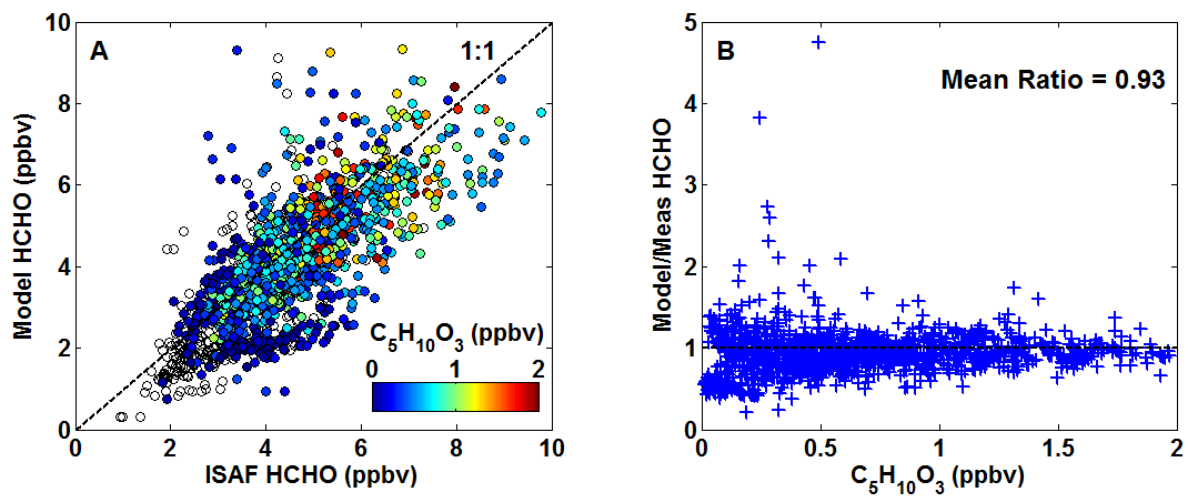


Figure S3. As in Fig. S1 but for ISAF HCHO observations.

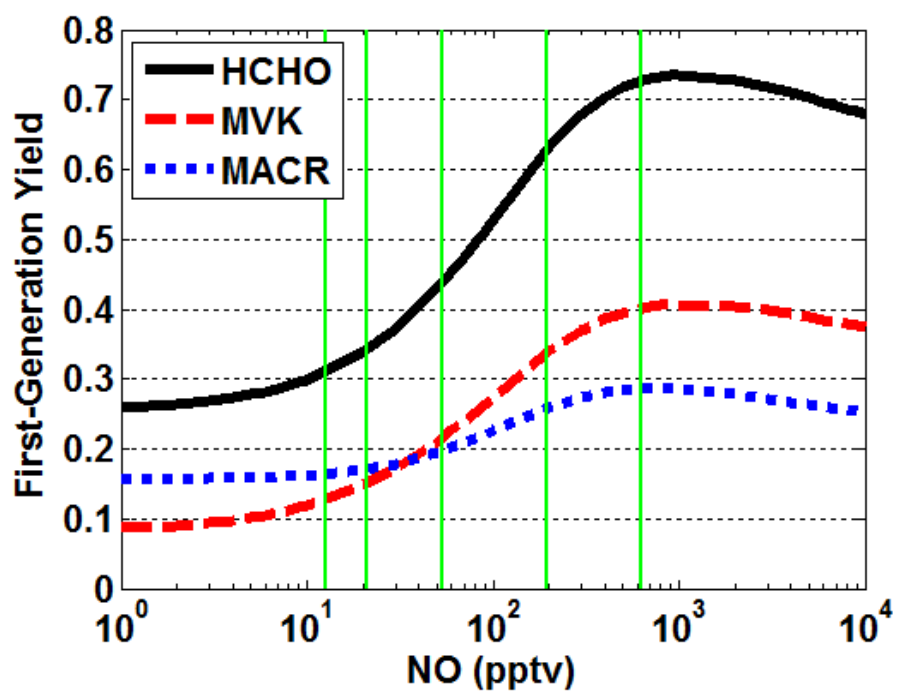


Figure S4. NO dependence of the first-generation yields of HCHO, MVK and MACR from isoprene oxidation. Yields are derived from box model calculations using MCMv3.3 chemistry as described in the SI text. Thin green vertical lines denote, from left to right, the 1st, 5th, 50th, 95th and 99th percentiles of daytime boundary layer NO observed during SENEX.

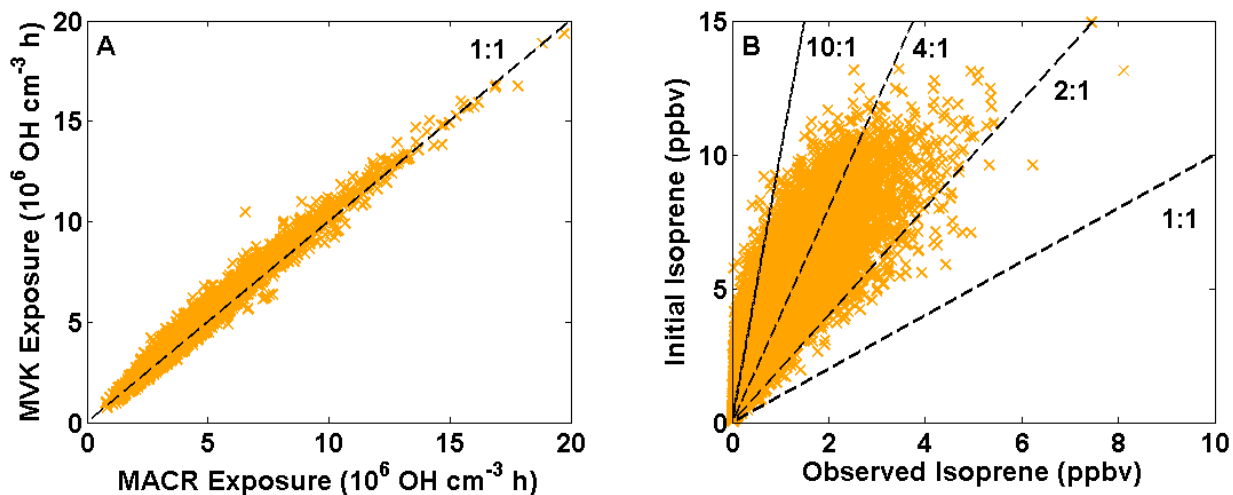


Figure S5. (A) Photochemical exposures (product of OH concentration and reaction time) derived from PTR-MS observations of the sum and MVK and MACR as described in Sect. 3 of the main text. PTR-MS measurements are partitioned into MVK and MACR using the MVK/MACR ratio derived from a 0-D box model simulation. The dashed line denotes a 1:1 relationship. (B) Comparison of observed and initial isoprene mixing ratios. Dashed lines denote slopes for different ratios of initial to observed isoprene.

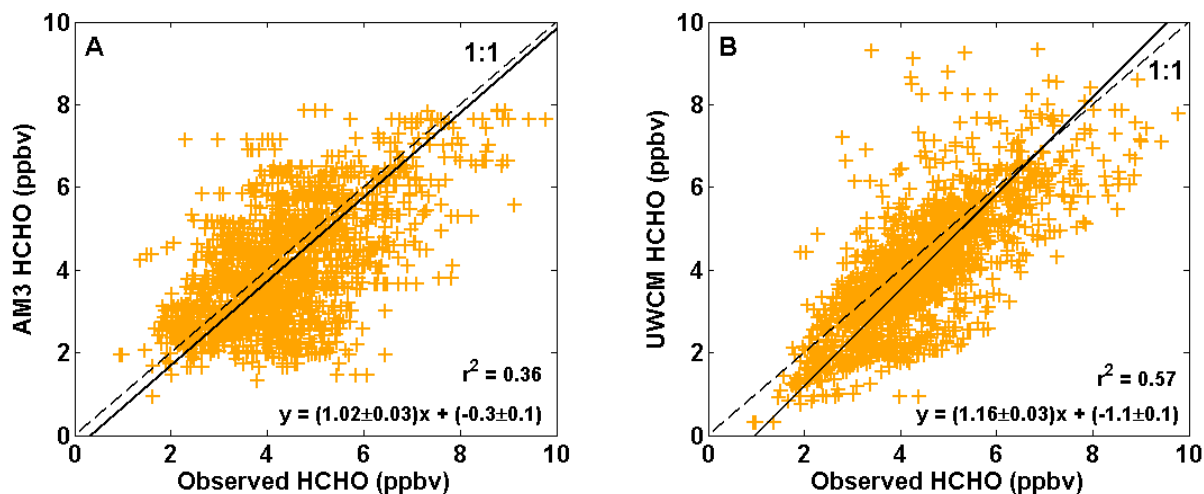


Figure S6. Comparison of observed and modeled HCHO mixing ratios for (A) the AM3 global chemical transport model and (B) the UWCM 0-D box model. Observations and model results are averaged/simulated at 1-minute resolution and filtered to only include daytime, boundary layer, non-biomass burning regions. Dashed lines represent the 1:1 correlation, and solid lines represent major axis least-squares fits. Corresponding slopes, intercepts and coefficients of determination (r^2) are also shown with their 1σ fitting uncertainty.