

1 **Formaldehyde production from isoprene oxidation across** 2 **NO_x regimes**

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1

2 **Abstract**

3 The chemical link between isoprene and formaldehyde (HCHO) is a strong, non-linear
4 function of NO_x ($= \text{NO} + \text{NO}_2$). This relationship is a linchpin for top-down isoprene emission
5 inventory verification from orbital HCHO column observations. It is also a benchmark for
6 overall photochemical mechanism performance with regard to VOC oxidation. Using a
7 comprehensive suite of airborne *in situ* observations over the Southeast U.S., we quantify
8 HCHO production across the urban-rural spectrum. Analysis of isoprene and its major first-
9 generation oxidation products allows us to define both a “prompt” yield of HCHO (molecules
10 of HCHO produced per molecule of freshly-emitted isoprene) and the background HCHO
11 mixing ratio (from oxidation of longer-lived hydrocarbons). Over the range of observed NO_x
12 values (roughly 0.1 – 2 ppbv), the prompt yield increases by a factor of 3 (from 0.3 to 0.9
13 ppbv ppbv⁻¹), while background HCHO increases by a factor of 2 (from 1.6 to 3.3 ppbv). We
14 apply the same method to evaluate the performance of both a global chemical transport model
15 (AM3) and a measurement-constrained 0-D steady state box model. Both models reproduce
16 the NO_x dependence of the prompt HCHO yield, illustrating that models with updated
17 isoprene oxidation mechanisms can adequately capture the link between HCHO and recent
18 isoprene emissions. On the other hand, both models under-estimate background HCHO
19 mixing ratios, suggesting missing HCHO precursors, inadequate representation of later-
20 generation isoprene degradation and/or under-estimated hydroxyl radical concentrations.
21 Detailed process rates from the box model simulation demonstrate a 3-fold increase in HCHO
22 production across the range of observed NO_x values, driven by a 100% increase in OH and a
23 40% increase in branching of organic peroxy radical reactions to produce HCHO.

24

25 **1 Introduction**

26 Formaldehyde (HCHO) is a ubiquitous byproduct of volatile organic compound (VOC)
27 oxidation. While methane is the principal HCHO precursor in remote regions, larger VOC are
28 the main source over continents. HCHO is also directly emitted via biomass burning (Lee et
29 al., 1997), fossil fuel combustion (Luecken et al., 2012), natural gas flaring (Knighton et al.,
30 2012), ethanol refining (de Gouw et al., 2015), possibly vegetation (DiGangi et al., 2011) and
31 agricultural activity (Kaiser et al., 2015a), but chemical production dominates the global
32 budget (Fortems-Cheiney et al., 2012). Photolysis and reaction with OH destroy HCHO with

1 a characteristic lifetime of several hours during midday, implying that the HCHO abundance
2 reflects recent VOC oxidation.

3 Globally, isoprene is the main precursor of near-surface HCHO. A highly reactive
4 diene emitted by vegetation, isoprene comprises roughly one third of all non-methane VOC
5 emissions (Guenther et al., 2012). Oxidation of isoprene in the presence of nitrogen oxides
6 ($\text{NO}_x = \text{NO} + \text{NO}_2$) stimulates the production of ozone (Trainer et al., 1987) and organic
7 aerosol precursors (Xu et al., 2015), impacting air quality and climate in many continental
8 regions. Biogenic emission inventories struggle to accurately represent the spatiotemporal
9 variability of isoprene emissions, with model-measurement discrepancies and differences
10 among emission inventories approaching a factor of 2 or more (Carlton and Baker, 2011;
11 Warneke et al., 2010). Such differences directly impact predicted ozone and aerosol
12 distributions (Hogrefe et al., 2011).

13 Numerous studies have applied satellite-based HCHO column observations as a top-
14 down constraint on isoprene emissions (see Kefauver et al. (2014) for a review). Typically, a
15 chemical transport model is employed both to supply *a priori* HCHO vertical distributions for
16 satellite retrievals (González Abad et al., 2015) and to relate HCHO column concentrations to
17 isoprene emission strength. Early studies utilized linear steady-state relationships (Palmer et
18 al., 2003), while recent computational advances have permitted full inversions that more fully
19 account for transport, multiple sources and varying chemical regimes (Fortems-Cheiney et al.,
20 2012). Such techniques have informed isoprene emission inventories in North America
21 (Abbot et al., 2003; Millet et al., 2008; Millet et al., 2006; Palmer et al., 2006; Palmer et al.,
22 2003), South America (Barkley et al., 2013; Barkley et al., 2008), Europe (Curci et al., 2010;
23 Dufour et al., 2009), Africa (Marais et al., 2012), Asia (Fu et al., 2007; Stavrou et al.,
24 2014), and globally (Fortems-Cheiney et al., 2012; Shim et al., 2005; Stavrou et al., 2009).
25 Future geostationary observations, such as the NASA Tropospheric Emissions: Monitoring of
26 Pollution (TEMPO, <http://science.nasa.gov/missions/tempo/>) mission, will permit an even
27 more detailed investigation of the spatial and temporal variability of isoprene emissions and
28 other VOC sources.

29 Chemistry dictates the relationship between HCHO columns and underlying isoprene
30 emissions. Many of the above-listed studies apply 0-D box model calculations to evaluate the
31 yield of HCHO from isoprene as a function of oxidation time, NO_x regime and chemical
32 mechanism. In all cases, it is found that NO_x enhances both the production rate and ultimate

1 yield of HCHO. Slower production at lower NO_x can lead to “smearing,” whereby HCHO
2 production is displaced relative to the isoprene source. Palmer et al. (2003) define a
3 characteristic smearing length scale, which can range from 10 to 100 km or more.
4 Furthermore, accumulation of oxygenated VOC over multiple generations of isoprene
5 degradation can contribute to substantial background HCHO production, which is not directly
6 linked with fresh isoprene emissions. Long-lived primary anthropogenic or biogenic
7 emissions, like methane and methanol, can also contribute to this background. Background
8 column concentrations are typically on the order of $5 \times 10^{15} \text{ cm}^{-2}$, equal to 20% or more of the
9 isoprene-driven HCHO column enhancement (Barkley et al., 2013; Millet et al., 2006). A
10 wave of recent theoretical (Peeters et al., 2014; Peeters and Müller, 2010; Peeters et al.,
11 1999), laboratory (Crouse et al., 2012; Crouse et al., 2011; Paulot et al., 2009a; Paulot et
12 al., 2009b) and field (Mao et al., 2012) research has highlighted shortcomings in low-NO_x
13 isoprene oxidation schemes. Such issues translate directly into top-down emission estimates;
14 for example, Marais et al. (2012) report an uncertainty of 40% in satellite-derived African
15 isoprene emissions at high-NO_x and 40-90% at low-NO_x. Coarse resolution of averaged
16 satellite observations and model simulations (typically $1^\circ \times 1^\circ$ or more) has partly mitigated
17 these problems in prior work, as variability in NO_x-dependent smearing and background
18 production is averaged out. A more careful treatment will be needed to harness the enhanced
19 resolution of near-future orbital observations (e.g., $8 \times 4.5 \text{ km}^2$ for TEMPO), especially since
20 these measurements will include diurnal variability.

21 Here, we use a comprehensive set of *in situ* observations to quantify the impact of NO_x
22 on the isoprene-HCHO chemical link. Using isoprene and its unique first-generation products,
23 we segregate HCHO into two categories. The first, defined as “prompt” HCHO, is produced
24 from fresh isoprene emissions (on a timescale of less than a day) and retains the signature of
25 isoprene emission source strength. The second category is “background” HCHO stemming
26 from oxidation of longer-lived isoprene oxidation products and other VOC. We examine the
27 NO_x dependence of both quantities. Applying the same method to 0-D and global model
28 simulations, we evaluate the ability of current chemical mechanisms to replicate the observed
29 trends. Box model results are also used to elucidate the mechanistic underpinnings of the NO_x
30 influence on HCHO production.

31

1 2 SENEX Observations

2 The Southeast Nexus (SENEX) mission was an airborne campaign designed to examine the
3 interaction of natural and anthropogenic emissions (Warneke et al., 2016). During June and
4 July of 2013, the NOAA WP-3D aircraft logged about 120 flight hours over 20 research
5 flights in a range of environments throughout the Southeast United States, including urban
6 centers, power plant plumes, natural gas extraction regions, agricultural areas and forests. The
7 payload included a suite of gas- and particle-phase instrumentation. Here we utilize
8 observations of HCHO, isoprene, methyl vinyl ketone (MVK), methacrolein (MACR), NO
9 and NO₂. HCHO was measured at 1 Hz by the NASA In Situ Airborne Formaldehyde (ISAF)
10 instrument, which utilizes the laser-induced fluorescence technique and has an accuracy of
11 ±10% (Cazorla et al., 2015). Isoprene, MVK and MACR were measured by both a quadrupole
12 proton transfer reaction mass spectrometer (PTR-MS) and the NOAA improved whole-air
13 sampler (iWAS) with offline gas chromatography. The PTR-MS (de Gouw and Warneke,
14 2007) has a stated accuracy of 20% and sequentially sampled masses for isoprene (m/z +69)
15 and the sum of MVK and MACR (m/z +71) for 1 s each with a duty cycle of 14 s. The iWAS
16 (Lerner et al., 2016) collected 72 canister samples each flight, which were analyzed offline
17 with gas chromatography – mass spectrometry 3-4 days post-flight. iWAS measurement
18 uncertainty is 20% for speciated MVK and MACR and 27% for isoprene. NO and NO₂ were
19 measured at 1 Hz via chemiluminescence coupled with a photolytic NO₂ converter (Pollack et
20 al., 2010; Ryerson et al., 1999) with an accuracy of 5%. Data are filtered to include only
21 daytime boundary layer conditions (solar zenith angle < 60°, radar altitude < 1 km). Influence
22 from biomass burning (acetonitrile > 210 pptv and CO > 300 ppbv) is also removed. This
23 procedure, along with the disjunct nature of the PTR-MS measurement, excludes 50% of all
24 fast (1 Hz) data. After accounting for data gaps, we retain 8435 1 Hz data points and 81 iWAS
25 samples.

26 Measurements of MVK and MACR may include a positive bias from conversion of
27 isoprene hydroxyhydroperoxides (ISOPOOH) on hot metal surfaces in the sampling system
28 (Liu et al., 2013; Rivera-Rios et al., 2014). ISOPOOH mixing ratios up to 2 ppbv were
29 observed by the University of Washington Iodide high-resolution time-of-flight chemical
30 ionization mass spectrometer during SENEX. Neither the NOAA PTR-MS nor the iWAS
31 have been tested for this interference with an ISOPOOH standard, thus we cannot definitively
32 rule out such artifacts or develop a correction factor. To our knowledge, it is not yet clear how

1 the putative interference depends on instrument configuration (flow rates, electric fields, etc.).
2 Thus, caution is warranted when comparing the SENEX systems to similar, but not identical,
3 instruments. Theoretically, this mechanism could give rise to an analogous artifact in HCHO
4 observations. Recent laboratory tests, however, indicate that the ISOPOOH-to-HCHO
5 conversion efficiency in ISAF is less than 5% (St. Clair et al., 2016).

6 We cannot unambiguously quantify the ISOPOOH artifact using observations alone,
7 but we can gain some insight from comparing PTR-MS and iWAS data. On average, iWAS
8 observations of MVK+MACR are ~40% higher than those from the PTR-MS (Figs. S1 and
9 S2), suggesting a systematic bias in one or both measurements. Both instruments were
10 calibrated using the same gas standards, and the two techniques agree well for other species
11 such as isoprene (Lerner et al., 2016; Warneke et al., 2016), so a calibration error is unlikely.
12 Production of oxygenated VOC in ambient air samples collected and aged in stainless steel
13 canisters cannot be ruled out. Enhancements in MVK and MACR (above the 20%
14 uncertainty) have been observed in canisters after aging over ~11 days (Lerner et al., 2016),
15 though this is significantly longer than typical turn-around times for SENEX. To evaluate the
16 potential for ISOPOOH conversion to explain this discrepancy, we plot the ratio and
17 difference of the PTR-MS and iWAS measurements as a function of ISOPOOH in Fig. S2.
18 While the ratio is essentially constant (iWAS/PTR-MS ~1.43), the absolute difference
19 exhibits a strong positive correlation with ISOPOOH ($r^2 = 0.43$). The slope of this relationship
20 implies that a conversion of 50% of ISOPOOH to MVK and/or MACR in the iWAS system
21 would explain the difference in the two measurements. Correcting total iWAS MVK+MACR
22 for such an artifact reduces the slope of the iWAS-PTR-MS correlation from 1.48 to 1.24
23 (Fig. S1B), bringing agreement to well with combined measurement uncertainties. In practice,
24 we cannot apply such a correction to the speciated iWAS observations as the conversion
25 efficiency may be different for each isomer. This result does not exclude the possibility of an
26 artifact in the PTR-MS measurement, though it does suggest an upper limit ISOPOOH
27 conversion efficiency of 50% for the PTR-MS (which would imply a conversion of 100% for
28 the iWAS). The analysis presented in Sections 3 and 4 primarily relies on PTR-MS data due
29 to its greater temporal coverage. Our key conclusions are not impacted by a 50% ISOPOOH
30 correction to the PTR-MS data, thus we use the data without correction.

31 SENEX sampled a wide spectrum of chemical regimes (Figure 1). For the daytime
32 boundary-layer observations presented here, maximum 1 Hz isoprene and NO mixing ratios

1 respectively reach 8.1 and 95 ppbv, while minima are less than a few pptv. The distributions
2 of both isoprene and NO observations are approximately log-normal (top and right panels of
3 Fig. 1), peaking at 1.5 ppbv and 50 pptv, respectively. Though these distributions may be
4 biased towards areas of urban influence, the range of environments encountered during
5 SENEX is representative of the Southeast U.S. summertime boundary layer. The long tail at
6 the low end of the isoprene distribution is mostly associated with regions lacking significant
7 tree cover where isoprene emissions are lower, notably Illinois and Indiana. The NO
8 distribution spans four orders of magnitude (< 10 to $\sim 10^4$ pptv), over which radical chemistry
9 changes markedly. At NO mixing ratios of a few hundred pptv or more, organic peroxy
10 radicals (RO_2) react mostly with NO. At low NO (10's of pptv or less), reaction with HO_2 ,
11 other RO_2 and isomerization dominate the RO_2 fate. The bulk of the NO distribution lies in a
12 transition region for radical chemistry, making this dataset ideal for probing the
13 anthropogenic influence on biogenic VOC oxidation.

14 HCHO mixing ratios (color shading in Fig. 1) range from 0.8 to 14 ppbv with a mean
15 of 4.3 ppbv. HCHO is most abundant in regions where both isoprene and NO_x are elevated.
16 High NO_x is often accompanied by increased concentrations of anthropogenic VOC; however,
17 constrained box-model calculations demonstrate that isoprene is the dominant HCHO
18 precursor even in these cases (Sect. 5). Thus, changes in radical cycling and partitioning (and
19 not co-variance of NO_x and anthropogenic VOC) drives the observed NO_x dependence of
20 HCHO abundance.

21

22 **3 Linking Observed and Emitted Isoprene**

23 The isoprene photochemical cascade is a multi-step process. Isoprene oxidation is initiated via
24 reaction with the hydroxyl radical (OH), ozone, or the nitrate radical (NO_3). In the Southeast
25 U.S., typical daytime levels for OH, ozone and NO_3 are $4 \times 10^6 \text{ cm}^{-3}$, 50 ppbv and 0.1 pptv,
26 respectively (OH and NO_3 are estimated from median box model output, see Sect. 5). The
27 corresponding isoprene lifetimes at 298K are 0.7 h, 17 h and 160 h, respectively. Thus,
28 reaction with OH typically constitutes 95% or more of the total daytime isoprene sink in this
29 environment. Addition of OH and reaction with O_2 generates one of several isoprene
30 hydroperoxy radicals (ISOPO_2). ISOPO_2 isomers interconvert rapidly due to reversible O_2
31 addition (Peeters et al., 2009) but are eventually destroyed via reaction with NO, hydroperoxy
32 radical (HO_2), other organic peroxy radicals (RO_2) or isomerization. Most branches have the

1 potential to produce HCHO, with varying yields. The laboratory-derived first-generation
 2 HCHO yield from the NO pathway is ~0.6 (Atkinson and Arey, 2003), though this value may
 3 be less representative of the real atmosphere due to the very high isoprene concentrations (and
 4 very short RO₂ lifetimes) in early chamber experiments. The first-generation yield from the
 5 HO₂ pathway is ~0.06 (Liu et al., 2013). Isomerization chemistry is less well understood; the
 6 1,5-H-shift is believed to produce HCHO with a unity yield, while the much faster 1,6-H-shift
 7 should not produce any HCHO (da Silva et al., 2010; Fuchs et al., 2013; Peeters et al., 2014;
 8 Peeters and Müller, 2010; Peeters et al., 2009). Regardless of the specific pathway, MVK or
 9 MACR are always co-produced with HCHO in the first generation. HCHO is also generated
 10 in subsequent chemistry, but on a longer timescale and from a much larger suite of precursors.
 11 For example, the OH lifetimes of MACR and MVK are respectively 3.5 and 5 times longer
 12 than that of isoprene. HCHO, MVK and MACR are also high-yield products of isoprene
 13 ozonolysis (Atkinson and Arey, 2003), but as noted above this reaction is relatively slow.
 14 Nighttime oxidation of isoprene by NO₃ radical is also likely a negligible source of these
 15 carbonyls (Brown et al., 2009). Yields are small (Atkinson and Arey, 2003; Kwok et al.,
 16 1996), and the lifetimes of MVK, MACR and HCHO are sufficiently short that any nighttime
 17 production should not influence the midday observations considered here.

18 Boundary layer composition reflects a mixture of emissions with various degrees of
 19 photochemical processing. To isolate the impact of “fresh” isoprene emissions, we exploit the
 20 relatively simple chemistry of MVK and MACR, which are produced via isoprene (ISOP)
 21 oxidation and lost primarily via reaction with OH.



25 Rate constants (k) are taken from the IUPAC database (Atkinson et al., 2006). These reactions
 26 form the basis for a photochemical clock of isoprene oxidation (de Gouw et al., 2005; Roberts
 27 et al., 2006; Stroud et al., 2001). Integration of the kinetic equations for this system shows
 28 that the product/parent ratios are a function of the rate constants, yield (y), reaction time (t)
 29 and mean OH concentration. In the case of MACR, for example:

30
$$\frac{[MACR]}{[ISOP]} = \frac{y_{MACR}k_1}{k_2 - k_1} (1 - \exp((k_1 - k_2)[OH]t)) \quad (1)$$

1 An analogous expression holds for MVK. As noted by Stroud et al. (2001), this “sequential
2 reaction model” is purely chemical and does not account for the effects of mixing and
3 transport. Indeed, this analysis relates daughter/parent ratios to an “average” photochemical
4 age, when in fact there is a broad distribution of ages in any mixed air mass. We also
5 implicitly assume that direct emissions (Fares et al., 2015) and deposition (Karl et al., 2010)
6 of MVK and MACR do not significantly influence the budget of these compounds.

7 Two potential issues arise when applying this model to the real atmosphere. First, the
8 yields of MVK and MACR are dependent on ISOPO₂ branching and are thus a non-linear
9 function of NO_x. Previous applications of this method (de Gouw et al., 2005; Roberts et al.,
10 2006; Stroud et al., 2001) have assumed lab-derived high-NO_x yields of 0.33 and 0.23 for
11 MVK and MACR, respectively (Atkinson and Arey, 2003), but this may not be appropriate in
12 the present case; furthermore, these yields are not fully consistent with current chemical
13 mechanisms. Given the wide range of conditions sampled, we explicitly account for NO_x-
14 dependent yields for MVK and MACR. For this purpose, we conducted a series of pseudo-
15 chamber simulations using a box model driven by the Master Chemical Mechanism (MCM)
16 v3.3.1 (Jenkin et al., 2015). As described in the SI, model setup mimics typical daytime
17 conditions in the Southeast U.S. (Fig. S3B), and yields are derived using a standard
18 procedure. Resulting yield curves (Fig. S3A) are then interpolated to observed NO mixing
19 ratios. Second, the photochemical age (*t*) implied by any observed daughter/parent ratio
20 depends on the concentration of OH, which was not measured and varies as an air mass ages.
21 Rather than assume a single “typical” value for OH, we express photochemical age in terms
22 of “exposure,” defined here as the product of OH concentration and reaction time averaged
23 over the photochemical lifetime of an air mass.

24 Figure 2 compares the observed relationship of iWAS MVK/isoprene and
25 MACR/isoprene ratios against theoretical trends predicted by the sequential reaction model.
26 Theoretical ratios are calculated at fixed exposures of 2, 4, 8, 12 and 16 × 10⁶ OH cm⁻³ h
27 using model derived yields for the 5th/95th percentiles of the observed NO distribution (NO =
28 20/200 pptv, $y_{\text{MVK}} = 0.18/0.38$, $y_{\text{MACR}} = 0.11/0.20$). Observed ratios of MVK/isoprene versus
29 MACR/isoprene exhibit a tight linear correlation. Higher ratios are often associated with
30 higher NO_x, likely reflecting enhanced OH and higher product yields in these air masses. Far
31 downwind from isoprene and NO_x source regions, we would expect to see higher
32 MVK/isoprene and MACR/isoprene ratios associated with lower NO_x due to removal of the

1 latter. The theoretical slope agrees well with observations, indicating exposures of $1 - 16 \times$
2 10^6 OH cm⁻³ h. For a typical daytime OH concentration of 4×10^6 cm⁻³, this corresponds to
3 processing times of 0.25 – 4 hours.

4 The assumed MVK and MACR yields dictate the correspondence between
5 daughter/parent ratios and exposure. For example, a MACR/isoprene ratio of 1 would be
6 consistent with an exposure of 7.9×10^6 OH cm⁻³ h at NO = 20 pptv versus 6.0×10^6 OH cm⁻³
7 h at NO = 200 pptv. Thus, for any given daughter/parent ratio, a higher assumed yield gives a
8 smaller derived exposure. The ratio of y_{MVK} to y_{MACR} determines the location of the
9 theoretical line, and the excellent agreement of this relationship with observations in Fig. 2
10 indicates that MCMv3.3.1 accurately represents the branching ratios for MVK and MACR
11 production within the sampled NO_x range.

12 We can effectively reverse this photochemical clock to derive a proxy for the total
13 isoprene emissions that have been released into the sample air masses (de Gouw et al., 2005).
14 First, we calculate OH exposures from observed daughter/parent ratios by inverting Eqn. (1).
15 To perform this calculation with PTR-MS data (which has far greater coverage than the
16 iWAS), we partition the measured sum between MVK and MACR using MVK/MACR ratios
17 from steady-state box model calculations (Sect. 5). Modeled MVK/MACR ratios (with an
18 output interval of 1 minute) are linearly interpolated to the 14-second observational time base.
19 The MVK/MACR ratio does not vary dramatically (mean $\pm 1\sigma$: 2.3 ± 0.2), and using a
20 constant ratio instead alters exposures by less than 4%. Calculated exposures range from 1 to
21 20×10^6 OH cm⁻³ h (Fig. S4A). Exposures derived from MACR are 6% lower than those
22 from MVK on average, and we use the mean of these two values. Next, an “initial” isoprene
23 mixing ratio, $ISOP_0$, is estimated via reverse integration of isoprene’s first-order loss rate:

$$24 \quad [ISOP]_0 = [ISOP] \exp(k_1 [OH] t) \quad (2)$$

25 $ISOP_0$ represents the amount of isoprene that an air parcel would have to start with to generate
26 the amount of isoprene, MVK and MACR observed. Thus, it is an observationally-
27 constrained surrogate for isoprene emission strength (modulated to some degree by boundary
28 layer height, as it is a volume-based quantity). $ISOP_0$ mixing ratios are typically 2 – 20 times
29 higher than observed isoprene (Fig. S4B).

30

1 **4 The Yield of HCHO from Isoprene**

2 The definition of “yield” can vary with context and requires careful consideration when
3 quantifying chemical relationships. In a mechanistic sense, the “first generation yield” refers
4 to the amount of HCHO produced per unit isoprene consumed in the first stage of oxidation.
5 This is analogous to the yields of MVK and MACR used in the above calculation of initial
6 isoprene. The model-derived first-generation HCHO yield from isoprene varies by more than
7 a factor of 2 over the range of chemical environments encountered during SENEX (Fig. S3).
8 An alternative definition is that of the “total yield” (sometimes referred to as the “molar
9 yield,” e.g. Millet et al. (2006)), a time-dependent quantity that describes the total amount of
10 HCHO produced over multiple generations of oxidation. The total yield is typically derived
11 from model simulations and used to relate satellite HCHO column observations to isoprene
12 emissions (Marais et al., 2012; Millet et al., 2006). Early studies acknowledged the NO_x
13 dependence of the total yield (Millet et al., 2006; Palmer et al., 2003), and more recent work
14 has attempted to account for this dependence using NO_2 column observations (Marais et al.,
15 2012). Here, we define the “prompt yield” as the change in observed HCHO per unit change
16 in ISOP_0 ($\Delta\text{HCHO}/\Delta\text{ISOP}_0$). This is not the same as the first-generation yield, since the
17 prompt yield can include HCHO production and loss over several hours (depending on the
18 photochemical exposure of an air mass). Nor is it the same as the total yield, which inherently
19 does not account for HCHO loss as an air mass ages. The prompt yield is effectively a
20 quantity that relates isoprene emission strength to observed HCHO abundance. As we will
21 demonstrate, this quantity is well-suited for segregating the various drivers of HCHO and for
22 benchmarking model performance.

23 Figure 3A shows the relationship between calculated ISOP_0 and observed HCHO. The
24 overall correlation is linear with a striking NO_x gradient. To quantify this NO_x dependence,
25 we sort the data by $\log(\text{NO}_x)$, group it into 20 bins such that each bin contains the same
26 number of points ($N = 416$), and perform a major-axis linear fit of HCHO versus ISOP_0 for
27 each bin. Individual fits give r^2 values of 0.6-0.8, except for the highest NO_x bin ($r^2 = 0.48$)
28 that contains some heavily-polluted air masses, such as downwind from power plants. Very
29 fresh power plant plumes, defined as $\log(\text{NO}_x)$ values exceeding a mean + 3σ threshold, are
30 removed prior to this procedure to avoid skewing the highest NO_x bin. Results are
31 independent of the number of bins chosen or time resolution (e.g., 1-second versus 1-minute
32 data).

1 The HCHO-ISOP₀ slope (Fig. 3B) represents the prompt yield. This yield varies by a
2 factor of 3 over the range of observed NO_x, from 0.3 ppbv ppbv⁻¹ for NO_x mixing ratios of a
3 few hundred pptv to 0.9 ppbv ppbv⁻¹ at NO_x > 1 ppbv. At low NO_x, the prompt yield is
4 comparable to the MCM-predicted direct first-generation yield of HCHO (0.25-0.4 ppbv
5 ppbv⁻¹ at NO = 10-40 pptv, Fig. S3), while at high NO_x it is somewhat higher than the
6 predicted first-generation yield (0.75 ppbv ppbv⁻¹ at NO = 1000 pptv). This likely reflects the
7 inclusion of more than one generation of HCHO production at higher NO_x, where oxidation is
8 more rapid (median exposures increase by 38% over the range of observed NO_x values). Most
9 of this portion of the HCHO budget, however, stems from first-generation production.

10 The intercept (Fig. 3C) represents the abundance of “background” HCHO. This
11 portion of the HCHO budget stems mainly from air that either has not encountered strong
12 isoprene emissions or is so aged that most of the isoprene has reacted away and can no longer
13 be linked to a specific source region. Some of this background may also stem from oxidation
14 of long-lived primary emissions like methane or methanol. Box model calculations (Sect. 5)
15 indicate average HCHO budget contributions of 0.3 ± 0.2 ppbv and 0.2 ± 0.1 ppbv from
16 methane and methanol, respectively. Background HCHO also exhibits a marked NO_x
17 dependence, increasing from 1.6 to 3.3 ppbv over the observed NO_x range. As with the
18 prompt yield, we expect such behavior since NO_x regulates the fate of all organic peroxy
19 radicals (see Sect. 6). Assuming a 1 km mixed layer depth (Wagner et al., 2015), the
20 corresponding HCHO column density for this background is 4 – 8 x 10¹⁵ cm⁻². This is
21 comparable to the background reported by previous investigations of satellite-derived HCHO
22 columns (Barkley et al., 2013; Millet et al., 2006). None of these studies explicitly account for
23 the NO_x dependence of the background, though it can represent a substantial fraction of the
24 total HCHO column – maximum summertime HCHO columns over the southeast U.S. are
25 ~25 x 10¹⁵ cm⁻² (Millet et al., 2008). Given the strong NO_x dependence of both prompt and
26 background HCHO, grouping HCHO column observations by NO_x (e.g. using simultaneous
27 observations of NO₂ columns (Marais et al., 2012) or model-derived NO_x) and performing an
28 analysis similar to that described here could provide a robust means of accounting for these
29 influences.

30

1 **5 Model Evaluation**

2 Next, we compare the observed HCHO-ISOP₀ relationship to results from a global chemical-
3 transport model and a 0-D box model. Our goals are to both illustrate the utility of this
4 analysis and evaluate model performance. By going beyond a simple comparison of modeled
5 and measured mixing ratios, we can more accurately pinpoint potential shortcomings in
6 model chemistry.

7 The GFDL AM3 model is an atmospheric general circulation model with interactive
8 chemistry (Donner et al., 2011), including recent updates to the representation of isoprene
9 degradation (Mao et al., 2013; Naik et al., 2013). Model simulations were carried out at 50 ×
10 50 km² resolution with horizontal winds nudged to NCEP GFS analyses and sampled along
11 the SENEX flight tracks at a time resolution of 1 minute. Further details are available
12 elsewhere (Li et al., 2016).

13 The University of Washington Chemical Box Model (UWCM v2.2) is a versatile 0-
14 dimensional framework for simulating various chemical systems, including lab chamber
15 experiments (Wolfe et al., 2012) and observations from ground (Kim et al., 2015; Kim et al.,
16 2013; Wolfe et al., 2014) and airborne (Marvin et al., 2015) platforms. Multiple chemical
17 mechanisms are available within UWCM; here we used the latest version of the Master
18 Chemical Mechanism (MCM v3.3.1, Jenkin et al. (2015)). UWCM was constrained with 1-
19 minute average observations of isoprene, NO₂, ozone, CO, PAN, methane, methanol and
20 meteorology and assumed clear-sky conditions for photolysis frequencies. The chemical
21 system was integrated forward in time to diel steady state (total integration time of 3 days) for
22 each set of measurements. This setup inherently assumes that the atmosphere is in chemical
23 steady state – that is, that production and loss of HCHO, MVK, MACR and other species are
24 roughly balanced. This assumption is rarely strictly true and may fail for highly-aged air
25 masses (where isoprene is depleted) or when close to strong local emissions. Nonetheless, it is
26 a fair approximation for the daytime well-mixed boundary layer observations that prevailed
27 during SENEX. Monoterpenes and anthropogenic VOC are excluded from the simulation
28 since observations of these species (from the iWAS) are relatively sparse. Separate sensitivity
29 simulations utilizing the iWAS data suggest that observed monoterpenes and anthropogenic
30 VOC (a subset of alkanes, alkenes and aromatics) increase modeled HCHO by 1 ± 2% and 2
31 ± 3%, respectively. A more detailed evaluation of box model performance is forthcoming
32 (Marvin et al., 2015).

1 Output from both models is filtered for daytime, boundary-layer, non-biomass burning
2 points using the same criteria as that for observations (Sect. 2). Both models adequately
3 reproduce observed HCHO mixing ratios (Fig. S5). We perform the same analyses as
4 described above to derive model prompt yield and background HCHO. Because of the
5 reduced time resolution, we group results into 10 NO_x bins, instead of 20, before fitting. For
6 AM3, this results in 172 points per bin and typical r² values of 0.4 – 0.8. For UWCM, there
7 are 134 points per bin and all r² values are > 0.86.

8 Both AM3 and UWCM reproduce the observed NO_x dependence of the prompt yield
9 (Fig. 4A). AM3 agrees well with observations in both magnitude and trend, though with some
10 scatter at mid-NO_x levels. UWCM tends to be slightly low throughout most of the NO_x range,
11 which may reflect an issue with the mechanism (discussed below) or an inherent shortcoming
12 of the steady-state assumption. Regardless of minor differences, these results suggest that
13 both models provide excellent representation of early generation isoprene oxidation across
14 NO_x regimes.

15 Background HCHO mixing ratios are under-predicted by 0.5 – 1 ppbv by both models
16 (Fig. 4B). The range of under-prediction is consistent with the offsets between observed and
17 modeled total HCHO abundances (Fig. S5 fit x-intercepts: 0.3 ppbv (AM3) and 1.1 ppbv
18 (UWCM)). It is possible that both models are missing some HCHO precursors (e.g. from
19 multi-generation isoprene oxidation or other VOC not related to isoprene). This is especially
20 plausible for the UWCM simulation, which only includes isoprene, methane and methanol as
21 primary VOC and does not account for horizontal transport. Under-estimated OH
22 concentrations might also explain part of this discrepancy, though we cannot easily evaluate
23 this possibility. AM3 performs somewhat better than UWCM in terms of overall magnitude
24 but exhibits a less clear NO_x trend, which may reflect dilution over fairly large grid scales
25 (note that the range of binned NO_x values is smaller for AM3 than both observations and the
26 UWCM). This result again highlights the need to consider this background before using a
27 model to interpret observed HCHO columns that effectively average HCHO sources over
28 space and time.

29 The agreement between AM3 and UWCM-MCMv3.3.1 is consistent with how these
30 mechanisms treat first-generation ISOPO₂ radicals (Figs. S6 and S7). Both models use the
31 same rate constants for reactions of ISOPO₂ with NO and HO₂, which comprise the bulk of
32 ISOPO₂ sink. The AM3 mechanism assigns a 12% yield of HCHO to the reaction of ISOPO₂

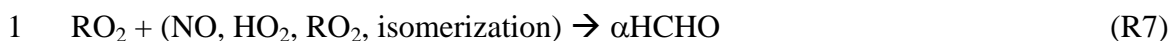
1 with HO₂ (Paulot et al., 2009b), while the MCM assumes 100% production of peroxides for
2 this channel. This may explain some of the discrepancy in the prompt yield at low NO_x (Fig.
3 4A), though neither mechanism is consistent with the current experimental HCHO yield of
4 ~6% HCHO (Liu et al., 2013). There are also two key differences in the minor reaction
5 channels. First, the rate constant for reaction of ISOPO₂ with other RO₂ is an order of
6 magnitude lower in AM3 compared to MCMv3.3.1 (1.54 vs. 12 – 16 × 10⁻¹³ cm³ s⁻¹, the latter
7 depending on the ISOPO₂ isomer distribution). This reaction produces HCHO with yields
8 comparable to that of ISOPO₂ + NO and may be an important source in very-low NO_x
9 regimes. Second, AM3 assumes a constant ISOPO₂ isomer distribution and thus under-
10 predicts the isomerization rate relative to MCMv3.3.1, especially at mid to high NO_x (Fig.
11 S7D). AM3 also includes HCHO and other small oxidized VOC as direct products of
12 isomerization rather than producing hydroperoxyaldehydes and other large products, which
13 influences the timescale of HCHO production and thus the partitioning between prompt and
14 background HCHO. The impact of the RO₂ reaction and isomerization channels on HCHO
15 yields is likely minor but depends significantly on the RO₂/HO₂ ratio (at low NO_x) and on the
16 overall ISOPO₂ lifetime, which affects the ISOPO₂ isomer distribution. For the particular
17 model conditions in Fig. S3B, ISOPO₂ lifetimes for the two mechanisms can differ by as
18 much as 25% at the lowest NO_x values (Fig. S7E). Regardless of these differences, the results
19 shown in Fig. 4 confirm that both the condensed AM3 and explicit MCMv3.3.1 mechanisms
20 perform similarly with regard to overall HCHO production.

21

22 **6 Mechanistic Drivers of the NO_x – HCHO Relationship**

23 Despite the complexity of gas-phase organic chemistry, the impact of NO_x on HCHO
24 production essentially reduces to two factors: radical cycling and RO₂ branching. Increasing
25 NO enhances the conversion of HO₂ to OH (R4) and thus accelerates VOC oxidation (R5).
26 RO₂ is also produced, to a lesser extent, by VOC ozonolysis and photolysis (R6). Subsequent
27 production of HCHO depends on the structure and fate of RO₂ intermediates, which can react
28 with NO, HO₂, other RO₂, or isomerize (R7).





2 Here, α represents a bulk branching ratio for HCHO production weighted over all RO_2
3 reactions. The RO_2 lifetime is typically less than 100 s during the day, so (R5) is the rate-
4 limiting step in HCHO formation. The HCHO production rate is then equal to the product of
5 the total RO_2 production rate and the bulk branching ratio:

6 $P(\text{HCHO}) = \alpha P(\text{RO}_2)$ (3)

7 Though total RO_2 losses include reactions that do not make HCHO, α is still a useful metric
8 for the relationship between HCHO production and overall VOC oxidation.

9 To disentangle these factors, we extract chemical rates from the diel steady-state
10 UWCM simulations discussed in Sect. 5. Figure 5A shows the gross production rates for total
11 peroxy radicals and HCHO as a function of NO_x . Consistent with our earlier discussion,
12 HCHO production increases by a factor of 3 from low to high NO_x . Total RO_2 production
13 increases by a factor of 2 over this same range, driven primarily by increasing OH. The bulk
14 branching ratio α , calculated as the ratio of HCHO and RO_2 production rates, increases from
15 0.43 to 0.62 (Fig. 5B). This trend is consistent with NO_x -dependent branching ratios of
16 several major HCHO precursors, including isoprene hydroxyperoxy radicals (ISOPO_2) and
17 methyl peroxy radical (Fig. 5B). Based on this analysis, we conclude that enhanced OH
18 production is the main driver for the NO_x dependence of HCHO production, with variations in
19 RO_2 branching playing a lesser (but still important) role.

20 Using a combination of regional modeling and satellite observations, a recent study by
21 Valin et al. (2016) also examines the drivers of HCHO production. They concur that OH
22 production exerts a controlling influence on HCHO throughout the Southeast U.S. In contrast
23 to our study, however, they assert that changes in RO_2 branching have a negligible effect on
24 the HCHO- NO_x dependence. There are several potential explanations for this discrepancy.
25 First, Valin et al. (2016) derive an “effective branching ratio” that is analogous to the bulk
26 branching ratio in Eqn. (3) but calculated with reference to production of OH rather than RO_2 .
27 Many OH sinks do not form RO_2 radicals (e.g. reaction with CO, HCHO, methanol and NO_2)
28 and thus will not make HCHO. The fractional contribution of such reactants to total modeled
29 OH reactivity increases from 36% to 60% over our NO_x range; thus, using $P(\text{OH})$ instead of
30 $P(\text{RO}_2)$ to calculate α from Eqn. (3) would effectively normalize out the NO_x dependence of
31 RO_2 branching (Fig. 5B). Second, these two studies use very different photochemical

1 mechanisms. Valin et al. (2016) use a modified version of the lumped Regional Atmospheric
2 Chemistry Mechanism 2 (RACM2) (Browne et al., 2014; Goliff et al., 2013), while our box
3 model uses the explicit MCMv3.3.1 (Jenkin et al., 2015). In Valin et al. (2016), it is stated
4 that decreasing HCHO production from the $\text{RO}_2 + \text{NO}$ channel is compensated for by
5 increasing production from $\text{RO}_2 + \text{RO}_2$ – an effect that we do not observe. Deeper
6 investigation reveals that the rate constant for reaction of ISOPO_2 with HO_2 in RACM2,
7 which is based on work by Paulot et al. (2009b), is a factor of 2 lower than those used in both
8 MCMv3.3.1 and the AM3 mechanism. Thus, our model predicts a significantly larger
9 contribution of $\text{RO}_2 + \text{HO}_2$ (which produces negligible HCHO) to the total RO_2 sink. These
10 differences highlight the importance of carefully evaluating chemical mechanisms before
11 using models to interpret *in situ* and satellite observations.

12 Increased OH also reduces the lifetime of HCHO, which may affect the HCHO budget
13 if this reaction becomes competitive with photolysis. UWCM predicts an average HCHO
14 photolysis lifetime of 4 hours and OH reaction lifetimes that range from 3 hours at high NO_x
15 to 12 hours at low NO_x . Thus, photolysis is typically the dominant loss process and the
16 scaling of HCHO lifetime with OH is typically weak. The net chemical tendency of HCHO
17 (production minus loss) is positive and increasing throughout the range of model NO_x
18 conditions. Faster loss due to reaction with OH therefore only slightly dampens the
19 enhancement in HCHO production.

20

21 **7 Conclusions**

22 Using SENEX aircraft observations, we have quantified the NO_x dependence of the
23 relationship between isoprene emission strength and HCHO mixing ratios. Simultaneous
24 measurements of isoprene, MVK and MACR define a photochemical clock for isoprene
25 oxidation, allowing separation of prompt HCHO production (which retains the isoprene
26 source signature) and background HCHO from late-generation isoprene oxidation products,
27 methane and other long-lived VOC. The prompt HCHO yield increases by a factor of 3 (0.3 to
28 $0.9 \text{ ppbv ppbv}^{-1}$) and the average background HCHO mixing ratio doubles (1.6 to 3.3 ppbv)
29 over the range of NO_x values encountered in the southeast U.S. (0.1 – 2 ppbv). This analytical
30 method is applied to evaluate the performance of a global chemical transport model and a 0-D
31 steady-state box model. Both models accurately reproduce the observed NO_x trend of the
32 prompt HCHO yield, indicating that both chemical mechanisms accurately capture early-stage

1 isoprene oxidation. On the other hand, both models also under-predict background HCHO
2 abundance by 0.5 – 1 ppbv, which is a significant fraction of total HCHO in some cases. This
3 suggests insufficient build-up of isoprene-derived long-lived precursors in the models,
4 missing VOC not related to isoprene, or insufficient OH. Box model results also provide
5 insight into the mechanistic drivers of the observed NO_x trends. Over the NO_x range studied
6 here, a 100% increase in total RO₂ production and a 40% increase in the HCHO production
7 branching ratio give rise to a 3-fold increase in total HCHO production.

8 To our knowledge, there are no direct laboratory measurements of HCHO yields from
9 low-NO_x isoprene chemistry; thus, the results presented here constitute the first measurement-
10 constrained evaluation of the isoprene-HCHO link across NO_x regimes. The AM3 and
11 MCMv3.3.1 mechanisms differ substantially (the former is highly condensed while the latter
12 is explicit), but both contain recent updates to isoprene degradation. We expect that other
13 mechanisms will also perform well if they accurately reflect our current best understanding.
14 The observations presented here do not include the extremely-low NO_x regime (NO_x < 0.1
15 ppbv) typical of remote regions like the Amazon and equatorial Africa. In such pristine
16 regions, smearing of HCHO production is expected to be more severe (Barkley et al., 2013),
17 and total HCHO production may be significantly lower if the RO₂ fate favors
18 functionalization over fragmentation (e.g. isomerization). More work is needed to map out
19 this area of the urban-rural spectrum. It may also be possible to apply the methods developed
20 here to evaluate the chemistry of glyoxal, another key tracer of VOC oxidation that is also
21 amenable to orbital observations (Kaiser et al., 2015b; Li et al., 2016) and is believed to be an
22 important precursor for SOA (McNeill et al., 2012).

23 These results also carry implications for top-down isoprene emission estimates.
24 Uncertainties in low-NO_x chemistry are often cited as the largest source of potential error in
25 derived emissions (Marais et al., 2012; Palmer et al., 2006). Based on our analysis, current
26 mechanisms appear to capture low-NO_x production of HCHO, MVK and MACR, thus such
27 errors are likely less severe than commonly asserted. Recent work has acknowledged the
28 impact of NO_x on the prompt yield of HCHO from isoprene (Marais et al., 2012). We
29 advocate considering the NO_x dependence of background HCHO as well, since this can
30 constitute a significant fraction of the total HCHO column. For scale, the derived background
31 HCHO mixing ratio of 1.6 – 3.3 ppbv is 37 – 77% of the campaign-mean observed HCHO
32 mixing ratio of 4.3 ppbv. Forthcoming geostationary observations will resolve local gradients

1 in chemical regime, and smearing and background HCHO production will become
2 problematic even in high-NO_x regions. Indeed, even current-generation orbital instruments are
3 capable of resolving some urban-rural gradients in HCHO columns (Boeke et al., 2011).
4 When applying advanced statistical techniques like inversion, model results will only be as
5 accurate as the chemical mechanisms driving them. Continued field observations are crucial
6 for providing confidence in our ability to link HCHO to its sources. In this regard, recent
7 work has highlighted the potential of airborne eddy covariance fluxes to quantify both
8 surface-atmosphere exchange and *in situ* chemical processes (Karl et al., 2013; Kaser et al.,
9 2015; Misztal et al., 2014; Wolfe et al., 2015). With such tools, it should be possible to
10 simultaneously measure both isoprene emissions and HCHO columns, thereby obtaining a
11 direct experimental constraint on the link between these two quantities.

12

13 **Data Availability**

14 All data used in this study are publicly accessible on the SENEX website
15 (<http://www.esrl.noaa.gov/csd/projects/senex/>).

16

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27

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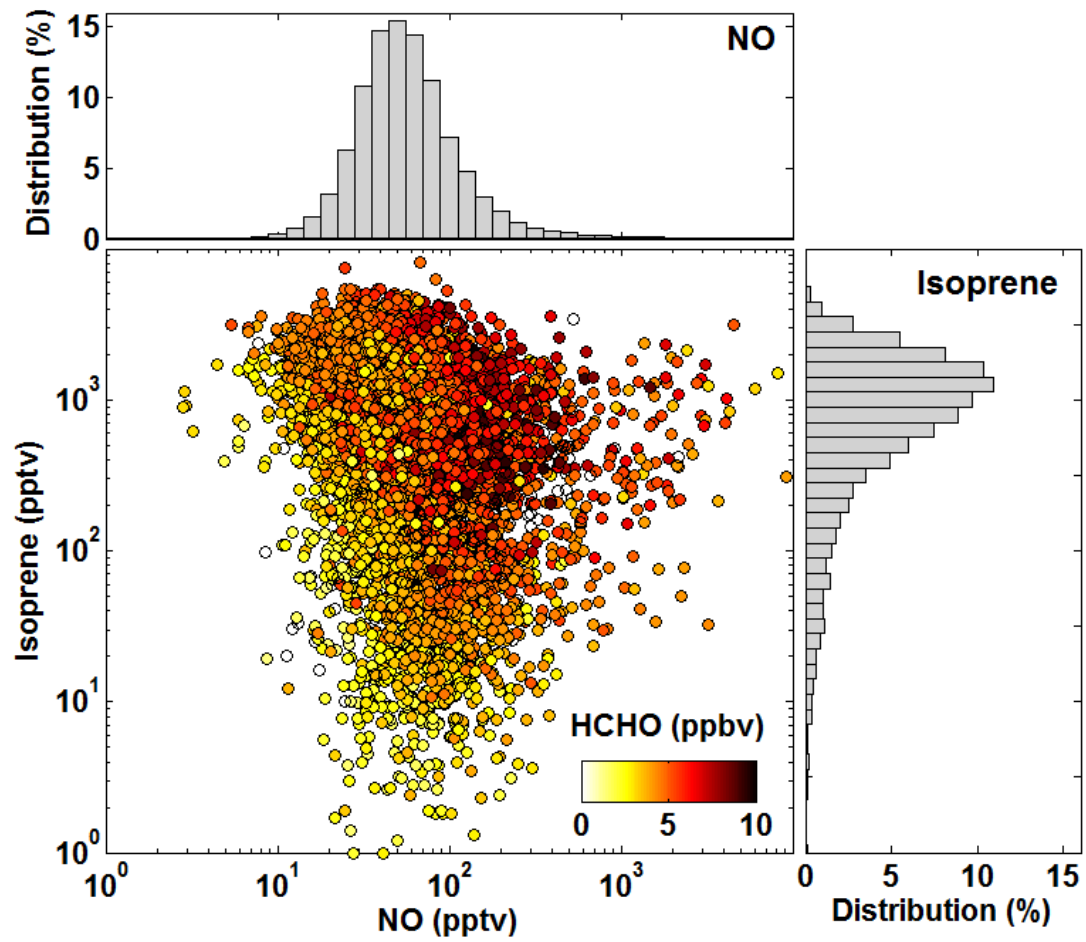
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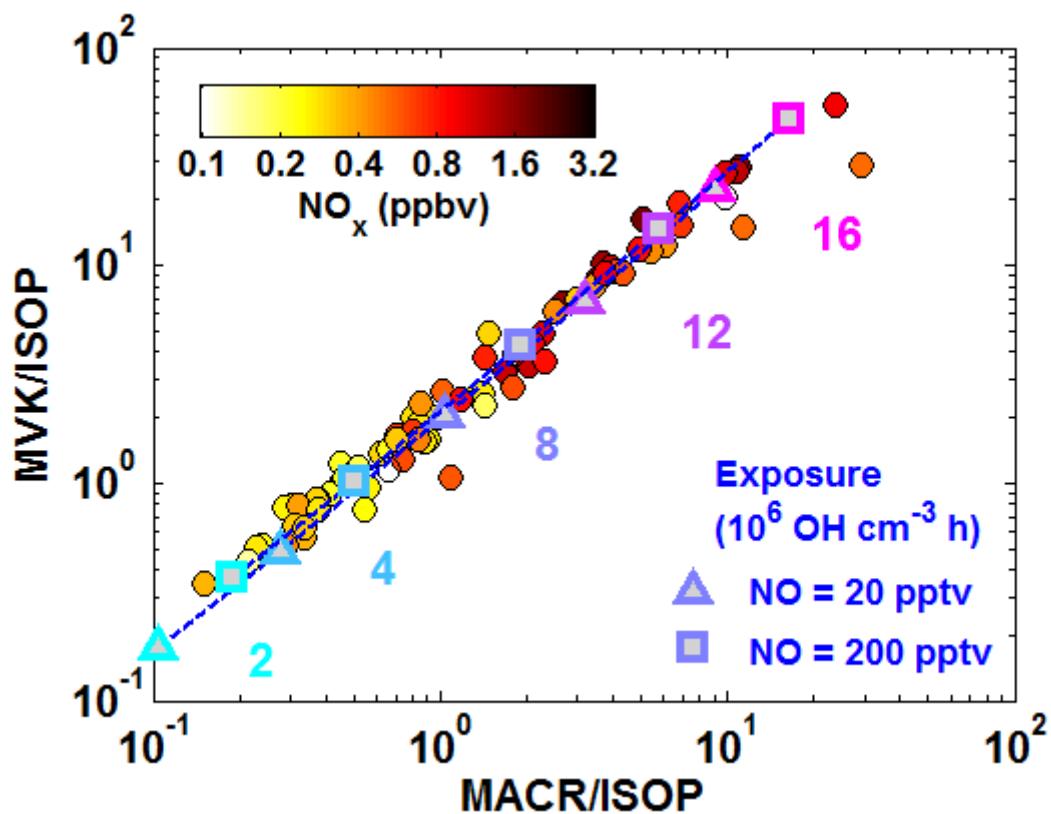
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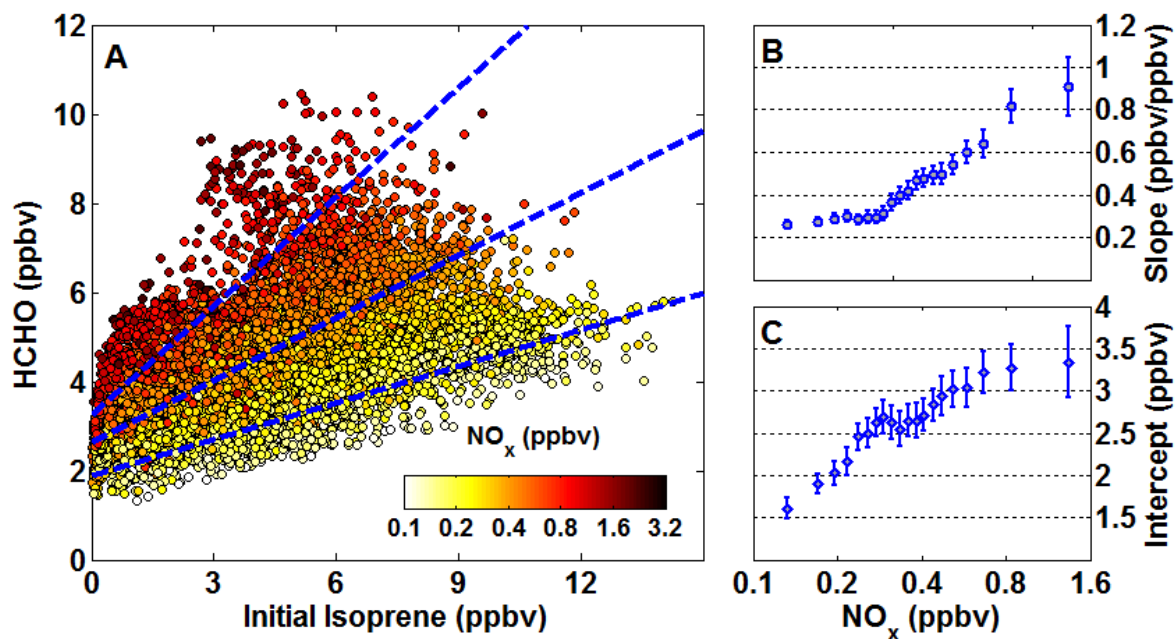
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Figure 1. Co-variation of isoprene, NO and HCHO mixing ratios in the summertime Southeast U.S. Data are limited to daytime boundary layer observations. Histograms show the corresponding NO and isoprene distributions.



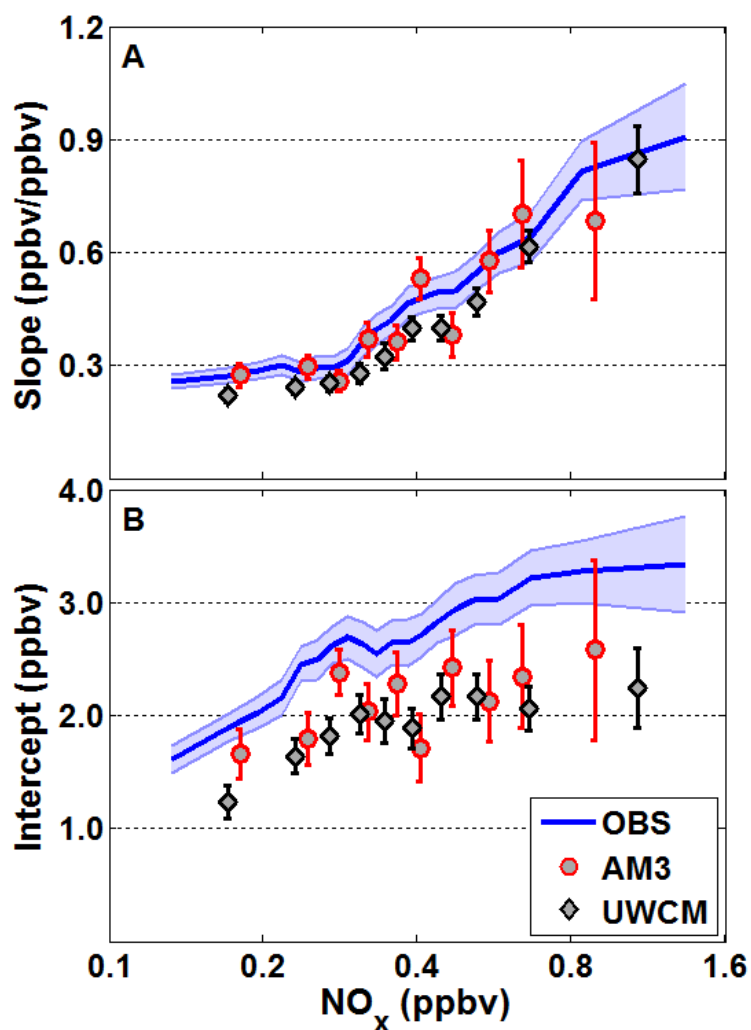
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Figure 2. A photochemical clock of isoprene oxidation defined by the progression of daughter/parent ratios. Solid circles show the observed ratios calculated from iWAS observations, colored by NO_x . Blue/purple symbols, dashed lines, and text indicate the theoretical exposures (the product of OH concentration and time) corresponding to any given daughter/parent relationship. Theoretical values are calculated at 298K using MVK and MACR yields for NO values of 20 pptv (triangles) and 200 pptv (squares).



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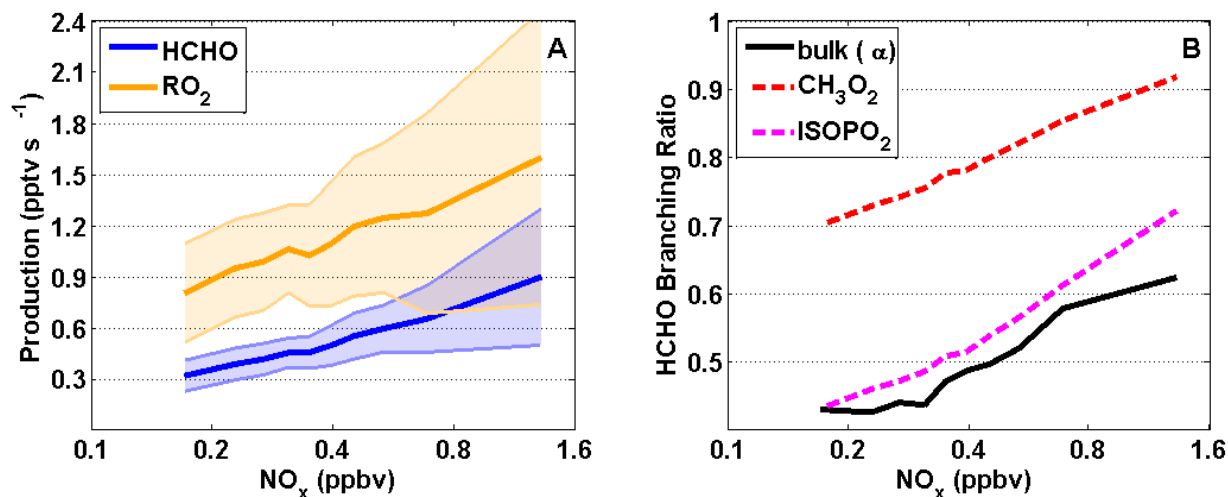
Figure 3. (A) NO_x modulates the relationship between observed HCHO and calculated initial isoprene mixing ratios. Symbols denote all 1-second data. Dashed lines illustrate representative major-axis fits of NO_x-grouped subsets at mean NO_x values of 170, 380 and 810 pptv (see text for details of fitting procedure). The slope (B) and intercept (C) of these fits are the prompt HCHO yield and background HCHO mixing ratio, respectively. Error bars in (B) and (C) are 3σ fitting uncertainties.



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Figure 4. Comparison of observed and model-derived relationships between HCHO and initial isoprene versus NO_x . Slopes (A) and intercepts (B) are calculated as described in the text. The observed values (blue line with shading) are the same as those shown in Figs. 3B-C. Symbols represent fit results for the global AM3 model (red circles) and the 0-D UWCM box model (black diamonds). Error bars denote 3σ fitting uncertainties.

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4 **Figure 5.** NO_x dependence of chemical properties related to HCHO production, extracted
5 from the UWCM simulation of SENEX observations. (A) Production rates for HCHO (blue)
6 and total RO_2 (orange). (B) Branching ratios for HCHO production weighted over all RO_2
7 (solid black line) and for several individual RO_2 , including methyl peroxy radical (red) and
8 total isoprene hydroxyperoxy radicals (magenta). All quantities are averaged over NO_x using
9 10 bins with equal numbers of points. In (A), solid lines show the mean and shading is 1 σ
10 variability.