Formaldehyde production from isoprene oxidation across NOx regimes

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Abstract

The chemical link between isoprene and formaldehyde (HCHO) is a strong, non-linear function of NOx (= NO + NO2). This relationship is a linchpin for top-down isoprene emission inventory verification from orbital HCHO column observations. It is also a benchmark for overall mechanism performance with regard to VOC oxidation. Using a comprehensive suite of airborne in situ observations over the Southeast U.S., we quantify HCHO production across the urban-rural spectrum. Analysis of isoprene and its major first-generation oxidation products allows us to define both a “prompt” yield of HCHO (molecules of HCHO produced per molecule of freshly-emitted isoprene) and the background HCHO mixing ratio (from oxidation of longer-lived hydrocarbons). Over the range of observed NOx values (roughly 0.1 – 2 ppbv), the prompt yield increases by a factor of 3 (from 0.3 to 0.9), while background HCHO increases by more than a factor of 2 (from 1.5 to 3.3 ppbv). We apply the same method to evaluate the performance of both a global chemical transport model (AM3) and a measurement-constrained 0-D chemical box model. Both models reproduce the NOx dependence of the prompt HCHO yield, illustrating that models with updated isoprene oxidation mechanisms can adequately capture the link between HCHO and recent isoprene emissions. On the other hand, both models under-estimate background HCHO mixing ratios, suggesting missing HCHO precursors, inadequate representation of later-generation isoprene degradation and/or under-estimated hydroxyl radical concentrations. Moreover, we find that the total organic peroxy radical production rate is essentially independent of NOx, as the increase in oxidizing capacity with NOx is largely balanced by a decrease in VOC reactivity. Thus, the observed NOx dependence of HCHO mainly reflects the changing fate of organic peroxy radicals.

1. Introduction

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

Globally, isoprene is the main precursor of near-surface HCHO. A highly reactive diene emitted by vegetation, isoprene comprises roughly one third of all non-methane VOC emissions (Guenther et al., 2012). Oxidation of isoprene in the presence of nitrogen oxides (NOₓ = NO + NO₂) stimulates the production of ozone (Trainer et al., 1987) and organic aerosol precursors (Xu et al., 2015), impacting air quality and climate in many continental regions. Despite the central role of isoprene, biogenic emission inventories struggle to accurately represent the spatiotemporal variability of isoprene emissions, with model-measurement discrepancies and differences among emission inventories approaching a factor of 2 or more (Carlton and Baker, 2011; Warneke et al., 2010). Such differences directly impact predicted ozone and aerosol distributions (Hogrefe et al., 2011).

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

Chemistry dictates the relationship between HCHO columns and underlying isoprene emissions. Many of the above-listed studies apply 0-D box model calculations to evaluate the yield of HCHO from isoprene as a function of oxidation time, NOₓ regime and chemical mechanism. In all cases, it is found that NOₓ enhances both the production rate and ultimate yield of HCHO. Slower production at lower NOₓ can lead to “smearing,” whereby HCHO production is displaced relative to the isoprene source. Palmer et al. (2003) define a characteristic smearing length scale, which can range from 10 to 100 km or more. Furthermore, accumulation of oxygenated VOC over multiple generations of isoprene
degradation can contribute to substantial background HCHO production, which is not directly linked with fresh isoprene emissions. Long-lived primary anthropogenic or biogenic emissions, like methane and methanol, can also contribute to this background. Background column concentrations are typically on the order of $5 \times 10^{15}$ cm$^{-2}$, equating to 20% or more of the isoprene-driven HCHO column enhancement (Barkley et al., 2013; Millet et al., 2006). A wave of recent theoretical (Peeters et al., 2014; Peeters and Müller, 2010; Peeters et al., 1999), laboratory (Crounse et al., 2012; Crounse et al., 2011; Paulot et al., 2009a; Paulot et al., 2009b) and field (Mao et al., 2012) research has highlighted shortcomings in low-NO$_x$ isoprene oxidation schemes. Such issues translate directly into top-down emission estimates; for example, Marais et al. (2012) report an uncertainty of 40% in OMI-derived African isoprene emissions at high-NO$_x$ and 40-90% at low-NO$_x$. Coarse resolution of averaged satellite observations and model simulations (typically 1° $\times$ 1° or more) has partly mitigated these problems in prior work, as variability in NO$_x$-dependent smearing and background production is averaged out. A more careful treatment will be needed to harness the enhanced resolution of near-future orbital observations (e.g., 8 $\times$ 4.5 km$^2$ for TEMPO), especially since these measurements will include diurnal variability.

Here, we use a comprehensive set of in situ observations to quantify the impact of NO$_x$ on the isoprene-HCHO chemical link. Using isoprene and its unique first-generation products, we segregate HCHO into two categories. The first, defined as “prompt” HCHO, is produced from fresh isoprene emissions (on a timescale of less than a day) and retains the signature of isoprene emission source strength. The second category is “background” HCHO stemming from oxidation of longer-lived isoprene oxidation products and other VOC. We examine the NO$_x$ dependence of both quantities. Applying the same method to 0-D and global model simulations, we evaluate the ability of current chemical mechanisms to replicate the observed trends. Box model results are also used to elucidate the mechanistic underpinnings of the NO$_x$ influence on HCHO production.

### 2. SENEX Observations

The Southeast Nexus (SENEX) mission was an airborne campaign designed to examine the interaction of natural and anthropogenic emissions. During June and July of 2013, the NOAA WP-3D aircraft logged 114 flight hours over 18 research flights in a range of environments throughout the southeast United States, including urban centers, power plant plumes, natural gas extraction regions, agricultural areas...
and forests. The payload included a suite of gas- and particle-phase instrumentation (Warneke et al., in preparation, 2015); details and data are accessible on the SENEX website (http://www.esrl.noaa.gov/csd/projects/senex/). Here we utilize observations of HCHO, isoprene, methyl vinyl ketone (MVK), methacrolein (MACR), NO and NO₂. HCHO was measured at 1 Hz by the NASA In Situ Airborne Formaldehyde (ISAF) instrument, which relies on the laser-induced fluorescence technique and has an accuracy of ±10% (Cazorla et al., 2015). Isoprene, MVK and MACR were measured by both a quadrupole proton transfer reaction mass spectrometer (PTR-MS) and the NOAA improved whole-air sampler (iWAS) with offline gas chromatography. The PTR-MS (de Gouw and Warneke, 2007) has a stated accuracy of 20% and sequentially sampled masses for isoprene (m/z +69) and the sum of MVK and MACR (m/z +71) for 1 s each with a duty cycle of 14 s. The iWAS measurement uncertainty for speciated MVK and MACR is 20% (de Gouw et al., 2015). NO and NO₂ were measured at 1 Hz via chemiluminescence coupled with a photolytic NO₂ converter (Pollack et al., 2010; Ryerson et al., 1999) with an accuracy of 5%. Data are filtered to include only daytime boundary layer conditions (solar zenith angle < 60°, radar altitude < 1 km). Influence from biomass burning (acetonitrile > 210 pptv and CO > 300 ppbv) and very fresh power plant plumes (log(NOₓ) values exceeding a mean + 3σ threshold) are also removed. This procedure excludes 50% of all fast (1 Hz) data. After accounting for missing data, we retain 8435 1 Hz data points and 81 iWAS samples.

Measurements of MVK and MACR can 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). Theoretically, this mechanism could give rise to an analogous artifact in HCHO observations. ISOPOOH mixing ratios of roughly 0 to 2 ppbv were observed during SENEX (see supporting information (SI)). It is difficult to quantify the magnitude of any such interference from field observations alone. Based on a comparison to observations of other isoprene oxidation products and to 0-D box model results (SI), we argue that such artifacts are negligibly small in the PTR-MS and ISAF observations for SENEX. We cannot rule out a potential positive bias in the iWAS MVK measurement; nonetheless, as we show below, the correspondence between observed MVK and MACR mixing ratios is consistent with our current understanding of isoprene oxidation.

SENEX sampled a wide spectrum of chemical regimes (Figure 1). For the daytime boundary-layer observations presented here, maximum 1 Hz isoprene and NO mixing ratios respectively reach 8.1 and 95 ppbv, while minima are less than a few pptv. The distributions of both isoprene and NO observations are approximately log-normal (top and right panels of Fig. 1), peaking at 1.5 ppbv and 50 pptv,
respectively. Though these distributions may be biased towards areas of urban influence, the range of environments encountered during SENEX is representative of the Southeast U.S. summertime boundary layer. The long tail at the low end of the isoprene distribution is mostly associated with regions lacking significant tree cover, notably Illinois and Indiana, where isoprene emissions are generally lower. The NO distribution spans two orders of magnitude (10 – 1000 pptv), over which radical chemistry changes markedly. At NO mixing ratios of a few hundred pptv or more, organic peroxy radicals (RO\textsubscript{2}) react mostly with NO. At low NO (10’s of pptv or less), reaction with HO\textsubscript{2}, other RO\textsubscript{2} and isomerization dominate. The bulk of the NO\textsubscript{x} distribution lies in a transition region for radical chemistry, making this dataset ideal for probing the anthropogenic influence on biogenic VOC oxidation.

HCHO mixing ratios (color shading in Fig. 1) range from 0.8 to 14 ppbv with a mean value of 4.3 ppbv. HCHO is most abundant in regions where both isoprene and NO\textsubscript{x} are elevated. High NO\textsubscript{x} is often accompanied by increased concentrations of anthropogenic VOC; however, constrained box-model calculations demonstrate that isoprene is the dominant HCHO precursor even in these cases (Sect. 5). Thus, chemistry (and not co-variance of NO\textsubscript{x} and anthropogenic VOC) drives the observed NO\textsubscript{x} dependence of HCHO abundance.

3. Linking Observed and Emitted Isoprene

The isoprene photochemical cascade is a multi-step process. Isoprene oxidation is initiated by reaction with the hydroxyl radical (OH), ozone or the nitrate radical (NO\textsubscript{3}). In the Southeast U.S., typical daytime levels for OH, ozone and NO\textsubscript{3} are \(4 \times 10^6\) cm\(^{-3}\), 50 ppbv and 0.1 pptv, respectively (OH and NO\textsubscript{3} are estimated from median box model output, see Sect. 5). The corresponding isoprene lifetimes at 298K are 0.7 h, 17 h and 160 h, respectively. Thus, reaction with OH typically constitutes 95% or more of the total daytime isoprene sink in this environment. Addition of OH and reaction with O\textsubscript{2} generates one of several isoprene hydroxyperoxy radicals (ISOPO\textsubscript{2}). ISOPO\textsubscript{2} isomers interconvert rapidly due to reversible O\textsubscript{2} addition (Peeters et al., 2009) but are eventually destroyed via reaction with NO, hydroperoxy radical (HO\textsubscript{2}), other organic peroxy radicals (RO\textsubscript{2}) or isomerization. Most branches have the potential to produce HCHO, with varying yields. The laboratory-derived first-generation HCHO yield from the NO pathway is \(~0.6\) (Atkinson and Arey, 2003), though this value may be less representative of the real atmosphere due to the very high isoprene concentrations (and very short RO\textsubscript{2} lifetimes) in early chamber experiments. The first-generation yield from the HO\textsubscript{2} pathway is \(~0.06\) (Liu et al., 2013).
Isomerization chemistry is less well understood; the 1,5-H-shift is believed to produce HCHO with a unity yield, while the much faster 1,6-H-shift should not produce any HCHO (da Silva et al., 2010; Fuchs et al., 2013; Peeters et al., 2014; Peeters and Müller, 2010; Peeters et al., 2009). Regardless of the specific pathway, MVK or MACR are always co-produced with HCHO in the first generation. HCHO is also generated in subsequent chemistry, but on a longer timescale and from a much larger suite of precursors. For example, the OH lifetimes of MACR and MVK are respectively 3.5 and 5 times longer than that of isoprene.

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

\[
\text{ISOP} + \text{OH} \rightarrow y_{\text{MACR}} \text{MACR} + y_{\text{MVK}} \text{MVK} \\
k_1 = 2.7 \times 10^{-11} \text{e}^{390/T} \\
\text{(R1)}
\]

\[
\text{MACR} + \text{OH} \rightarrow \text{products} \\
k_2 = 8.0 \times 10^{-12} \text{e}^{380/T} \\
\text{(R2)}
\]

\[
\text{MVK} + \text{OH} \rightarrow \text{products} \\
k_3 = 2.6 \times 10^{-12} \text{e}^{610/T} \\
\text{(R3)}
\]

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

\[
\frac{[\text{MACR}]}{[\text{ISOP}]} = \frac{y_{\text{MACR}} k_1}{k_2 - k_1} \left(1 - e^{(k_1 - k_2)[OH]t}\right) \\
\text{(1)}
\]

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

Two potential issues arise when applying this model to the real atmosphere. First, the yields of MVK and MACR are dependent on ISOPO\(_2\) branching and are thus a non-linear function of NO\(_x\). Previous
applications of this method (de Gouw et al., 2005; Roberts et al., 2006; Stroud et al., 2001) have assumed lab-derived high-NO\textsubscript{x} yields of 0.33 and 0.23 for MVK and MACR, respectively (Atkinson and Arey, 2003), but this may not be appropriate in the present case; furthermore, these yields are not fully consistent with current chemical mechanisms (Fig. S4). We explicitly examine the effects of NO\textsubscript{x}-varying yields below using yield curves derived from box model simulations (see SI for details). Second, the photochemical age (t) implied by any observed daughter/parent ratio depends on the concentration of OH, which was not measured and varies as an air mass ages. Rather than assume a single “typical” value for OH, we express photochemical age in terms of “exposure,” defined here as the product of OH concentration and reaction time integrated over the photochemical lifetime of an air mass.

Figure 2 compares the observed relationship of MVK/isoprene and MACR/isoprene ratios against theoretical trends predicted by the sequential reaction model. Theoretical ratios are calculated at fixed exposures of 2, 4, 8, 12 and 16×10\textsuperscript{6} OH cm\textsuperscript{-3} h using two sets of yields: high NO (NO = 1000 pptv, \(\gamma_{\text{MVK}} = 0.41, \gamma_{\text{MACR}} = 0.28\)) and low NO (NO = 50 pptv, \(\gamma_{\text{MVK}} = 0.21, \gamma_{\text{MACR}} = 0.19\)). Observed ratios of MVK/isoprene versus MACR/isoprene exhibit a tight linear correlation (Fig. 2). Higher ratios are often associated with higher NO\textsubscript{x}, likely reflecting enhanced OH and higher HCHO yields in these air masses. Far downwind from isoprene and NO\textsubscript{x} source regions, we would expect to see higher MVK/isoprene and MACR/isoprene ratios associated with lower NO\textsubscript{x} due to removal of the latter. The theoretical slope agrees well with observations, indicating exposures of 1 – 16×10\textsuperscript{6} OH cm\textsuperscript{-3} h. For a typical daytime OH concentration of 4×10\textsuperscript{6} cm\textsuperscript{-3}, this corresponds to processing times of 15 minutes to 4 hours.

The ratio of \(\gamma_{\text{MVK}}\) to \(\gamma_{\text{MACR}}\) dictates the location of the theoretical line and thus the correspondence between daughter/parent ratios and exposure. For example, a MACR/isoprene ratio of 1 would be consistent with an exposure of 4.9 × 10\textsuperscript{6} OH cm\textsuperscript{-3} h at high-NO\textsubscript{x} conditions (NO = 1000 pptv) versus 6.1 × 10\textsuperscript{6} OH cm\textsuperscript{-3} h at low-NO\textsubscript{x} (NO = 50 pptv). Thus, for any given daughter/parent ratio, a higher assumed yield gives a smaller derived exposure. Observations in Fig. 2 fall above the high-NO\textsubscript{x} theoretical relationship. As discussed in the SI, however, iWAS MVK measurement may contain a positive artifact on the order of 50%. This potential systematic error (thick black line in Fig. 2) overlaps both the high and low-NO\textsubscript{x} theoretical relationships. Given the wide range of conditions sampled, it is most appropriate to use a NO\textsubscript{x}-dependent yield for MVK and MACR. For this purpose, model-derived yields (Fig. S4 and SI) are interpolated to observed NO mixing ratios.
We can effectively reverse this photochemical clock to derive a proxy for the total isoprene emissions that had been released into the sample air masses (de Gouw et al., 2005). First, we calculate OH exposures from observed daughter/parent ratios by inverting Eqn. (1). To perform this calculation with PTR-MS data (which has far greater coverage), we partition the measured sum between MVK and MACR using MVK/MACR ratios from box model calculations (Sect. 5). Modeled MVK/MACR ratios (with an output interval of 1 minute) are linearly interpolated to the 14-second observational time base. The MVK/MACR ratio does not vary dramatically (mean ± 1σ: 1.3 ± 0.2), and using a constant ratio instead alters results by less than 4%. Calculated exposures range from 0.5 to $18 \times 10^6$ OH cm$^{-3}$ h (Fig. S5A). Exposures derived from MACR are 6% higher than those from MVK on average, and we use the mean of these two values. Next, an “initial” isoprene mixing ratio, $ISOP_0$, is estimated via reverse integration of isoprene’s first-order loss rate:

$$[ISOP]_0 = [ISOP]e^{k_1[OH]t}$$

$ISOP_0$ represents the amount of isoprene that an air parcel would have to start with to generate the amount of isoprene, MVK and MACR observed. Thus, it is an observationally-constrained surrogate for isoprene emission strength (modulated to some degree by boundary layer height, as it is a volume-based quantity). $ISOP_0$ mixing ratios are typically 2 – 10 times higher than observed isoprene (Fig. S5B).

4. The Yield of HCHO from Isoprene

The definition of “yield” can vary with context and requires careful consideration when quantifying the isoprene-HCHO relationship. In a mechanistic sense, the “first generation yield” refers to the amount of HCHO produced per unit isoprene consumed in the first stage of oxidation. This is analogous to the yields of MVK and MACR used in the above calculation of initial isoprene. The model-derived first-generation HCHO yield from isoprene varies by more than a factor of 2 over the range of chemical environments encountered during SENEX (Fig. S4). An alternative definition is that of the “total yield” (sometimes referred to as the “molar yield,” e.g. Millet et al. (2006)), a time-dependent quantity that describes the total amount of HCHO produced over multiple generations of oxidation. The total yield is typically derived from model simulations and used to relate satellite HCHO column observations to isoprene emissions (Marais et al., 2012; Millet et al., 2006). Early studies acknowledged the NO$_x$ dependence of the total yield (Millet et al., 2006; Palmer et al., 2003) and more recent work has
attempted to account for the dependence using NO\textsubscript{2} column observations (Marais et al., 2012). Here, we define the "prompt yield" as the change in observed HCHO per unit change in ISOP\textsubscript{0} ($y_p = \Delta \text{HCHO}/\Delta \text{ISOP}_0$). This is not the same as the first-generation yield, since $y_p$ can include HCHO production and loss over several hours (depending on the photochemical exposure of an air mass). Nor is it the same as the total yield, which inherently does not account for HCHO loss as an air mass ages. The prompt yield is effectively a quantity that relates isoprene emission strength to observed HCHO abundance. As we will demonstrate, $y_p$ is well-suited for segregating the various drivers of HCHO and for benchmarking model performance.

Figure 3A shows the relationship between calculated ISOP\textsubscript{0} and observed HCHO. The overall correlation is linear with a striking NO\textsubscript{x} gradient. To quantify this NO\textsubscript{x} dependence, we sort the data by log(NO\textsubscript{x}), group it into 20 bins such that each bin contains the same number of points (N = 416), and perform a major-axis linear fit of HCHO versus ISOP\textsubscript{0} for each bin. Individual fits give $r^2$ values of 0.6-0.8, except for the highest NO\textsubscript{x} bin ($r^2 = 0.48$) that contains some heavily-polluted air masses, such as downwind from power plants. Results are independent of the number of bins chosen or time resolution (e.g., 1-second versus 1-minute data).

The HCHO-ISOP\textsubscript{0} slope (Fig. 3B) represents the prompt yield. This yield varies by a factor of 3 over the range of observed NO\textsubscript{x}, from 0.3 for NO\textsubscript{x} mixing ratios of a few hundred pptv to 0.9 at NO\textsubscript{x} > 1 ppbv. At low NO\textsubscript{x}, $y_p$ is comparable to the MCM-predicted direct first-generation yield of HCHO (0.3-0.4 at NO = 10-40 pptv, Fig. S4), while at high NO\textsubscript{x} it is somewhat higher than the predicted first-generation yield (0.74 at NO = 1000 pptv). This likely reflects the inclusion of more than one generation of HCHO production at higher NO\textsubscript{x}, where oxidation is more rapid (median exposures increase by 38% over the range of observed NO\textsubscript{x} values). Most of this portion of the HCHO budget, however, stems from first-generation production.

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

5. Model Evaluation

To illustrate the utility of this analysis, we compare the observed HCHO-ISOP$_0$ relationship to results from a global chemical-transport model and a 0-D box model. Goals?

The GFDL AM3 model is an atmospheric general circulation model with interactive chemistry (Donner et al., 2011), including recent updates to the representation of isoprene degradation (Mao et al., 2013; Naik et al., 2013). Model simulations were carried out at $50 \times 50$ km$^2$ resolution with horizontal winds nudged to NCEP GFS analyses and sampled along the SENEX flight tracks at a time resolution of 1 minute. Further details are available elsewhere (Li et al., 2015).

The University of Washington Chemical Box Model (UWCM v2.2) is a versatile 0-dimensional framework for simulating various chemical systems, including lab chamber experiments (Wolfe et al., 2012) and observations from ground (Kim et al., 2015; Kim et al., 2013; Wolfe et al., 2014) and airborne (Marvin et al., 2015) platforms. Multiple chemical mechanisms are available within UWCM; here we use the latest version of the Master Chemical Mechanism (MCM v3.3, Jenkin et al. (2015)). UWCM is constrained with 1-minute average observations of isoprene, NO$_2$, ozone, CO, PAN, methane, methanol and meteorology and assumes clear-sky conditions for photolysis frequencies. The chemical system is integrated forward in time to diel steady state (total integration time of 3 days) for each set of measurements. This setup inherently assumes that the atmosphere is in chemical steady state – that is, that production and loss of HCHO, MVK, MACR and other species are roughly balanced. This assumption is rarely strictly true and may fail for highly-aged air masses (where isoprene is depleted) or close to...
strong local emissions. Nonetheless, it is a fair approximation for the daytime well-mixed boundary layer observations that prevailed during SENEX. Monoterpenes and anthropogenic VOC are excluded from the simulation since observations of these species (from the iWAS) are relatively sparse. Separate sensitivity simulations utilizing the iWAS data suggest that observed monoterpenes and anthropogenic VOC (a subset of alkanes, alkenes and aromatics) increase modeled HCHO by $1 \pm 2\%$ and $2 \pm 3\%$, respectively. A more detailed evaluation of box model performance is forthcoming (Marvin et al., 2015).

Output from both models is filtered for daytime, boundary-layer, non-biomass burning points using the same criteria as that for observations (Sect. 2). Both models adequately reproduce observed HCHO mixing ratios (Fig. S6). We perform the same analyses as described above to derive model $y_p$ and background HCHO. Because of the reduced time resolution, we group results into 10 NO$_x$ bins, instead of 20, before fitting. For AM3, this results in 172 points per bin and typical $r^2$ values of $0.5 - 0.8$. For UWCM, there are 157 points per bin and all $r^2$ values are $>0.9$.

Both AM3 and UWCM reproduce the observed NO$_x$ dependence of the prompt yield (Fig. 4A). AM3 agrees well with observations in both magnitude and trend, though with some scatter at mid-NO$_x$ levels. UWCM tends be slightly high throughout the whole NO$_x$ range, which may reflect an over-estimation of first-generation HCHO production due to holding isoprene constant throughout the model step and/or assuming diel steady state. Regardless, these results suggest that both models provide excellent representation of early generation isoprene oxidation across NO$_x$ regimes.

Background HCHO mixing ratios are under-predicted by $0.5 - 1$ ppbv by both models (Fig. 4B). The range of under-prediction is consistent with the offsets between observed and modeled total HCHO abundances (Fig. S6 fit x-intercepts: 0.3 ppbv (AM3) and 0.9 ppbv (UWCM)). It is possible that both models are missing some HCHO precursors (e.g. from multi-generation isoprene oxidation or other VOC not related to isoprene). This is especially plausible for the UWCM simulation, which only includes isoprene, methane and methanol as primary VOC and does not account for horizontal transport. Under-estimated OH concentrations might also explain part of this discrepancy, though we cannot easily evaluate this possibility. AM3 performs somewhat better than UWCM in terms of overall magnitude but exhibits a less clear NO$_x$ trend, which may reflect dilution over fairly large grid scales (note that the range of binned NO$_x$ values is smaller for AM3 than both observations and the UWCM). This result again highlights the need to consider this background before using a model to interpret observed HCHO columns that effectively integrate HCHO sources over space and time.
6. Mechanistic Drivers of the NO\textsubscript{x} – HCHO Relationship

Despite the complexity of gas-phase organic chemistry, the impact of NO\textsubscript{x} on HCHO production essentially reduces to two factors: radical cycling and RO\textsubscript{2} branching. Increasing NO enhances the conversion of HO\textsubscript{2} to OH (R4) and thus accelerates VOC oxidation (R5) and HCHO loss. Subsequent production of HCHO depends on the structure and fate of RO\textsubscript{2} intermediates, which can react with NO, HO\textsubscript{2}, other RO\textsubscript{2}, or isomerize (R6).

\begin{align*}
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \quad \text{(R4)} \\
\text{VOC} + \text{OH} & \rightarrow \text{RO}_2 \quad \text{(R5)} \\
\text{RO}_2 + (\text{NO, HO}_2, \text{RO}_2, \text{isomerization}) & \rightarrow \alpha\text{HCHO} \quad \text{(R6)}
\end{align*}

Here, \(\alpha\) represents a bulk branching ratio for HCHO production weighted over all RO\textsubscript{2} reactions. The RO\textsubscript{2} lifetime is typically less than 100 s during the day, so (R5) is the rate-limiting step in HCHO formation. The HCHO production rate is then equal to the product of the total RO\textsubscript{2} production rate and the bulk branching ratio.

To disentangle these factors, we extract chemical rates from the diel steady-state UWCM simulations discussed in Sect. 5. Figure 5 shows the gross production rates of total peroxy radicals and HCHO as a function of NO\textsubscript{x}. Consistent with our earlier discussion, total HCHO production increases by more than a factor of 3 from low to high NO\textsubscript{x}. In contrast, RO\textsubscript{2} production is effectively constant within model variability. Closer investigation (results not shown) reveals that a factor of 3 – 4 increase in OH concentrations between low and high NO\textsubscript{x} is more than offset by a similar reduction in isoprene. The ratio of HCHO to RO\textsubscript{2} production rates gives an estimate for \(\alpha\), which increases from 0.14 to 0.39 across this NO\textsubscript{x} range (Fig. 5). Though the total RO\textsubscript{2} production rate includes reactions that do not make HCHO, \(\alpha\) is still a useful metric for the relationship between HCHO production and overall VOC oxidation. Based on this analysis, we conclude that changes in RO\textsubscript{2} branching are the dominant factor driving the NO\textsubscript{x} dependence of HCHO production and abundance.

Increased OH also reduces the lifetime of HCHO, which may affect the HCHO budget if this reaction becomes competitive with photolysis. UWCM predicts an average HCHO photolysis lifetime of 4 hours and OH reaction lifetimes that range from 3 hours at high NO\textsubscript{x} to 12 hours at low NO\textsubscript{x}. Thus,
photolysis is typically the dominant loss process and the scaling of HCHO lifetime with OH is typically weak. As a result, the net chemical tendency of HCHO (production minus loss, not shown) is positive and increasing throughout the range of model NO\textsubscript{x} conditions. Faster loss due to reaction with OH therefore only slightly dampens the enhancement in HCHO production.

7. Conclusions

Using SENEX aircraft observations, we have quantified the NO\textsubscript{x} dependence of the relationship between isoprene emission strength and HCHO mixing ratios. Simultaneous measurements of isoprene, MVK and MACR define a photochemical clock for isoprene oxidation, allowing separation of prompt HCHO production (which retains the isoprene source signature) and background HCHO from late-generation isoprene oxidation products, methane and other long-lived VOC. The prompt HCHO yield increases by a factor of 3 (0.3 to 0.9 mol/mol) and the average background HCHO mixing ratio more than doubles (1.6 to 3.3 ppbv) over the range of NO\textsubscript{x} values encountered in the southeast U.S. This analytical method is applied to evaluate the performance of a global chemical transport model and a 0-D box model. Both models accurately reproduce the observed NO\textsubscript{x} trend of the prompt HCHO yield, indicating that both chemical mechanisms accurately capture early-stage isoprene oxidation. On the other hand, both models also under-predict background HCHO abundance by 0.5 – 1 ppbv, which may be a significant fraction of total HCHO in some cases. This may suggest insufficient build-up of isoprene-derived long-lived precursors in the models, missing VOC not related to isoprene, or insufficient OH. Box model results also provide insight into the mechanistic drivers of the observed NO\textsubscript{x} trends. We find that increasing NO\textsubscript{x} does not significantly affect total RO\textsubscript{2} production due to the cancelling effects of higher OH and lower VOC, and thus the positive correlation between NO\textsubscript{x} and HCHO primarily reflects the changing fate of RO\textsubscript{2} radicals.

To our knowledge, there are no direct laboratory measurements of HCHO yields from low-NO\textsubscript{x} isoprene chemistry; thus, the results presented here constitute the first measurement-constrained evaluation of the isoprene-HCHO link across NO\textsubscript{x} regimes. The AM3 and MCMv3.3 mechanisms differ substantially (the former is highly condensed while the latter is explicit), but both contain recent updates to isoprene degradation. We expect that other mechanisms will also perform well if they accurately reflect our current best understanding. The observations presented here do not include the extremely-low NO\textsubscript{x} regime (NO\textsubscript{x} < 0.1 ppbv) typical of remote regions like the Amazon and equatorial
Africa. In such pristine regions, smearing of HCHO production is expected to be more severe (Barkley et al., 2013), and total HCHO production may be significantly lower if the RO$_2$ fate favors functionalization over fragmentation (e.g. isomerization). More work is needed to map out this area of the urban-rural spectrum. It may also be possible to apply the methods developed here to evaluate the chemistry of glyoxal, another key tracer of VOC oxidation that is also amenable to orbital observations (Kaiser et al., 2015b; Li et al., 2015) and is believed to be an important precursor for SOA (McNeill et al., 2012).

These results also carry implications for top-down isoprene emission estimates. Uncertainties in low-NO$_x$ chemistry are often cited as the largest source of potential error in derived emissions (Marais et al., 2012; Palmer et al., 2006). Based on our analysis, current mechanisms appear to capture low-NO$_x$ production of HCHO, MVK and MACR, thus such errors are likely less severe than commonly asserted. Recent work has acknowledged the impact of NO$_x$ on the prompt yield of HCHO from isoprene (Marais et al., 2012). We advocate considering the NO$_x$ dependence of background HCHO as well, since this can constitute a significant fraction of the total HCHO column. For scale, the derived background HCHO mixing ratio of 1.6 – 3.3 ppbv is 37 – 77% of the campaign-mean observed HCHO mixing ratio of 4.3 ppbv. Forthcoming geostationary observations will deliver sufficient resolution to delineate local gradients in chemical regime, and smearing and background HCHO production will become problematic even in high-NO$_x$ regions. Indeed, even current-generation orbital instruments are capable of resolving urban-rural gradients in HCHO columns (Boeke et al., 2011). When applying advanced statistical techniques like inversion, model results will only be as accurate as the chemical mechanisms driving them. Continued field observations are crucial for providing confidence in our ability to link HCHO to its sources.

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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 sampled NO and isoprene distributions.
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 50 pptv (triangles) and 1000 pptv (squares). The thick black line denotes the systematic error due to a potential 50% positive artifact in MVK observations (see SI).
Figure 3. (A) NO$_x$ modulates the relationship between observed HCHO and calculated initial isoprene mixing ratios. Symbols denote all 1-second data points. 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.
Figure 4. Comparison of observed and model-derived relationship 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.
Figure 5. NO\textsubscript{x} dependence of chemical properties related to HCHO production, extracted from the UWCM simulation of SENEX observations. Production rates for HCHO (blue) and total RO\textsubscript{2} (orange) are averaged over NO\textsubscript{x} using 10 bins with equal numbers of points. Solid lines show the mean, shading is 1\sigma variability. Note that RO\textsubscript{2} production is scaled down by a factor of 10. The ratio of HCHO to RO\textsubscript{2} production gives the bulk HCHO branching ratio (dashed line).