The role of OH production in interpreting the variability of CH$_2$O columns in the Southeast U.S.

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Main point #1: The formaldehyde column depends on the concentration of both OH and volatile organic compounds.

Main point #2: Top-down constraints of volatile organic compound emissions should consider variations of OH radical

Main point #3: The influence of nitrogen oxides on formaldehyde includes its feedback on OH radical concentrations
Abstract

Formaldehyde (CH₂O), a key atmospheric oxidation intermediate that is detectable from satellite-based UV/Visible spectrometers, is primarily formed when hydroxyl radical (OH) reacts with volatile organic compounds (VOC) and is removed by photolysis, reaction with OH or deposition. We investigate the influence of OH and VOC variability on the CH₂O column using a steady-state model and the WRF-Chem regional chemical transport model over the Southeast United States for the summer of 2012 (June - August).

The steady-state model indicates that the CH₂O column primarily depends on OH production rates (POH) at low concentrations of OH (< 3 × 10⁶ molecules cm⁻³), on both POH and VOC reactivity (VOCR: Σkᵢ[VOC]ᵢ) at moderate concentrations of OH (3 × 10⁶ - 7 × 10⁶ molecules cm⁻³) and on VOCR at high concentrations of OH (> 7 × 10⁶ molecules cm⁻³). When constrained with WRF-Chem values of boundary layer average POH and VOCR, the steady-state model of CH₂O explains most of the daily (r²=0.93) and average June – August (r²=0.97) spatial variance of the fully simulated cloud-free CH₂O column.

These findings imply that measurements of the CH₂O column offer the potential to better understand the processes affecting oxidation, particularly in remote regions, where OH concentrations are low. The findings also suggest that the inference of VOC emissions based on measurements of CH₂O, or any other intermediate oxidation species with a photolytic lifetime that is short relative to removal by reaction with OH (e.g., glyoxal), should carefully account for the influence of OH on the observed pattern, especially where OH concentrations are below 5 × 10⁶ molecules cm⁻³, as occurs in remote forests, where OH strongly varies, as occurs downwind of large nitrogen oxide (NOₓ: NO+NO₂) emission sources, or where OH sources are potentially biased.

1. Introduction

The hydroxyl radical (OH) is the most important oxidant in the troposphere, involved in the production of O₃ and particulate matter, and the removal of several greenhouse gases (e.g., CH₄, HCFCs). Some fraction of reactions between OH and volatile organic compounds (VOC) leads to the formation of formaldehyde (CH₂O). As the next generation of space-based UV/Visible sensors capable of observing CH₂O undergoes development (Chance et al., 2013; Fishman et al., 2012), there is a need and
opportunity to better understand the relationship of the CH$_2$O column with OH and its VOC precursors, such as methane and isoprene.

Remotely-sensed UV-visible measurements offer the potential to routinely measure the spatial distribution of CH$_2$O (e.g., De Smedt et al., 2012, Gonzalez Abad et al., 2015). Measurements from space-based spectrometers have provided extensive detail on the variability of the CH$_2$O column on daily (e.g., Palmer et al., 2006), seasonal (e.g., Martin et al., 2004; Palmer et al., 2006; Fu et al., 2007) and interannual time scales (e.g., Abbot et al., 2003; De Smedt et al., 2010) at global (e.g., Stavrakou et al., 2009a,b; Fortems-Cheiney et al., 2012), regional (e.g., Fu et al., 2007; Millet et al., 2008; Dufour et al., 2009; Marais et al., 2012; Barkley et al., 2013; Jin et al., 2015) and urban spatial scales (e.g., Duncan et al., 2010; Boeke et al., 2011; Witte et al., 2011; Zhu et al., 2014). The measurements of the CH$_2$O column have primarily been used to investigate the emissions of isoprene (E$_{ISOP}$) and other short-lived VOC that give rise to large, localized enhancements of CH$_2$O (e.g., Palmer et al., 2003; 2006; Fu et al., 2007; Barkley et al., 2008; 2013; Millet et al., 2008; Stavrakou et al., 2009a,b; Curci et al., 2010; Marais et al., 2012; 2014; Zhu et al., 2014). It is well known, however, that the concentration of CH$_2$O also depends on the concentration of OH, both in isoprene-rich regions (e.g., Sumner et al., 2001; Butler et al., 2008; Galloway et al., 2012) and in regions where CH$_4$ is the dominant VOC (e.g., Song et al., 2010). We thus hypothesize that variability in the CH$_2$O column systematically reflects variations of OH in addition to reflecting variations of VOC.

To investigate this hypothesis and quantify any implications for the inference of VOC emissions from CH$_2$O measurements, we first formulate a steady state equation for the CH$_2$O column (Section 2). We then test the assumptions underlying this steady state model using the WRF-Chem regional model (Section 3) before discussing the implications for inferring E$_{ISOP}$ from CH$_2$O column measurements (Section 4). We also explore the potential for daily CH$_2$O column measurements (Section 5) to provide constraints on the production of OH radicals (P$_{OH}$) and describe the necessary conditions for such constraints (Section 6) before concluding (Section 7).

2. A steady-state model for the CH$_2$O column: $f(P_{OH}, VOCR)$
The dominant source of CH$_2$O is the reaction of OH with VOC, primarily CH$_4$, isoprene or one of their products, with small contributions from ozonolysis and photolysis (Fortems-Cheney et al., 2012). In contrast, the CH$_2$O lifetime depends less on the concentration of OH as it is determined both by photolysis ($J_{CH2O} \approx 0.3$ h$^{-1}$; typical of summertime northern mid-latitudes) and by reaction with OH ($0.3$ h$^{-1}$ at [OH] = $1 \times 10^7$), with much slower loss to deposition. As a result, the concentration of CH$_2$O depends on the concentration of OH, both in ‘background’ conditions where most OH reacts with CH$_4$ or CO (e.g., Song et al., 2010) and in isoprene-rich conditions (e.g., Butler et al., 2008; Galloway et al., 2012).

To isolate the influence of OH production ($P_{OH}$) on the CH$_2$O column, we write CH$_2$O sources and sinks in terms of $P_{OH}$. $P_{OH}$ accounts for all primary (e.g., O$_1^D$+H$_2$O) and secondary (e.g., NO+HO$_2$) sources of OH. At steady state, OH production and OH loss are equal (i.e., $P_{OH} = \Sigma k_{Xi+OH}[Xi][OH]$). The rate of CH$_2$O production can be related to the rate of OH loss by incorporating the fractional yield of CH$_2$O ($\alpha_{Xi}$) from each reaction involving OH ($P_{CH2O} = \Sigma \alpha_{Xi} k_{Xi+OH}[Xi][OH]$). Instead of treating each species and its yield separately (e.g., $\alpha_{CH4} \leq 1$, $\alpha_{CO,NO2} = 0$; Sumner et al., 2001; Galloway et al., 2012), we define an effective yield, such that the rate of CH$_2$O production can be written as the rate of OH production ($P_{OH}$) multiplied by the effective yield of CH$_2$O ($\alpha_{eff}$: $P_{CH2O}$ $P_{OH}^{-1}$). We evaluate this approach by quantifying $\alpha_{eff}$ in WRF-Chem (Section 3.3) considering both the impacts of individual RO$_2$ radical pathways on $\alpha_{eff}$ (Section 3.3.1) and the impacts of VOC composition (Section 3.4). The CH$_2$O loss rate equals the rate of its loss by photolysis ($J_{CH2O}$) plus its loss by reaction with OH ($k_{CH2O+OH}[OH]$). The concentration of OH equals its source ($P_{OH}$) divided by its sink, which we assume is dominated by the reactivity weighted concentration of VOC ($VOCR: \Sigma k_i[VOC_i] + k_{CO+OH}[CO]$).

At midday, CH$_2$O sources and sinks are both maximum and the CH$_2$O lifetime is sufficiently short to assume that the CH$_2$O concentration is in steady state. Assuming that alkene ozonolysis and photolysis are negligible sources of CH$_2$O, we write a steady state equation for the CH$_2$O concentration as

$$[CH_2O]_{steady-state} = \alpha_{eff} P_{OH} / (J_{CH2O} + k_{CH2O+OH} P_{OH} / VOCR)$$ (1)
The relationship of the CH$_2$O concentration to VOCR and P$_{OH}$ depends on the relative rates of CH$_2$O loss by photolysis and by reaction with OH ([OH] = P$_{OH}$/VOCR; Eqn. 1). At high OH concentrations (i.e., high P$_{OH}$ or low VOCR), loss by reaction with OH is dominant and the concentration of CH$_2$O depends on VOCR (~$\alpha_{eff}$ VOCR / $k_{CH2O+OH}$). At low OH concentrations (i.e., low P$_{OH}$ or high VOCR), loss by photolysis is dominant and the concentration of CH$_2$O depends on P$_{OH}$ (~$\alpha_{eff}$ P$_{OH}$ / $J_{CH2O}$). However, the feedback of P$_{OH}$ on VOCR must also be considered. For a given isoprene emission rate, VOCR decreases as P$_{OH}$ increases. The precise magnitude of this decrease is uncertain and mechanism-dependent (e.g., Karl et al., 2009, Fuchs et al. 2013; Nölscher et al., 2014). We quantify this effect in Section 3.3.2 using WRF-Chem and find that the combined feedbacks of P$_{OH}$ on CH$_2$O removal (i.e., via both P$_{OH}$ and VOCR; Eqn. 1, denominator) do not offset the impact of P$_{OH}$ on CH$_2$O production (Eqn. 1, numerator).

Figure 1 shows steady-state CH$_2$O columns (contours) computed as a function of P$_{OH}$ (x-axis) and VOCR (y-axis) where we specify values for the yield ($\alpha_{eff} = 0.30$ P$_{CH2O}$ P$_{OH}^{-1}$) and the loss rate constants ($J_{CH2O} = 0.3$ h$^{-1}$; $k_{CH2O+OH} = 0.3 \times 10^{-7}$ cm$^3$ molecule$^{-1}$ h$^{-1}$). To convert steady-state CH$_2$O concentrations to column values, we assume that VOCR and P$_{OH}$ are well mixed below 2 km. Above 2 km, CH$_2$O photolysis is fast, VOCR is low, and P$_{OH}$ is low, thus resulting in a small contribution to the total CH$_2$O column, which we assume here to be a constant value ($2 \times 10^{15}$ molecules cm$^{-2}$). Where the concentration of OH is low (P$_{OH}$ / VOCR < $3 \times 10^6$ molecules cm$^{-3}$; Fig. 1) and photolysis is dominant, the CH$_2$O column is more sensitive to changes of P$_{OH}$ and less sensitive changes in VOCR. The opposite is true when the OH concentration is high (P$_{OH}$ / VOCR > $7 \times 10^6$ molecules cm$^{-3}$ Fig. 1). At OH concentrations in between these end member cases, the CH$_2$O column is sensitive to both P$_{OH}$ and VOCR. For a constant OH concentration, the sensitivity (slope) of the CH$_2$O column to a perturbation of VOCR is steep for high OH concentrations (e.g., a steep increase of CH$_2$O column contours following along the [OH] = $7 \times 10^6$ molecules cm$^{-3}$ gray line; Fig. 1) and is shallow for low OH concentrations (e.g., a shallow increase along the [OH] = $3 \times 10^6$ molecules cm$^{-3}$ gray line; Fig. 1).

3. Testing the steady-state model with the regional WRF-Chem model

3.1 Model Configuration
We now investigate the relationship of $P_{OH}$ and VOCR to the CH$_2$O column using WRF-Chem, a state-of-the-art regional climate chemistry model (Grell et al., 2005). We simulate the chemistry over the southeast United States (27.7ºN – 43.8ºN; 74.7ºW – 101.3ºW) at 36 km horizontal grid resolution (50 N-S $\times$ 70 E-W) for 21 May 2012 – 31 August 2012. The model has 35 terrain-following hybrid pressure levels varying from $\sim$85 m thickness in the first model level to 300 m thickness 2.5 km above ground level and 3,000 m thickness at the model top ($z \approx 21$ km AGL). We only analyze model results from 1 June 2012 – 31 Aug 2012 and discard the five outermost grid rows of the domain to avoid excessive influence from the boundary conditions.

The chemical mechanism builds on the RACM2 photo-oxidation mechanism (Goliff et al., 2013) with recent updates to the isoprene oxidation pathways and extended monoterpene and monoterpene nitrate chemistry (Browne et al 2014). The updates to isoprene photochemistry follow those described by Paulot et al. (2009a,b), with further updates to peroxy radical isomerization rates (Crounse et al., 2011; 2012) and product yields (Peeters and Muller, 2010). In addition to standard model diagnostics, we track the rates of different classes of reactions within the mechanism to quantify the processes controlling the production and loss of OH, RO$_2$ and CH$_2$O.

We use ERA-interim reanalysis (Dee et al., 2011) as initial and boundary conditions for meteorological conditions (6-hourly), and MOZART-4/GEOS-5 output for chemical boundary conditions (6-hourly; Emmons et al., 2010; http://www.acd.ucar.edu/wrf-chem/mozart.shtml). For emissions, we use the US National Emission Inventory for 2005 (NEI2005, available online ftp://aftp.fsl.noaa.gov/divisions/taq/emissions_data_2005/). The anthropogenic nitrogen oxide (NO$_x$: NO+NO$_2$) emission rate ($E_{NOx}$) integrated over the domain is 3.65 Tg N y$^{-1}$. We also run a sensitivity simulation in which we uniformly decrease anthropogenic $E_{NOx}$ by a factor of ten. There are no biomass burning or lightning emission sources included in the simulation and any aircraft emissions included in the NEI2005 are allocated to the lower model layers. Biogenic emissions are driven by MEGAN v2.04 (Guenther et al., 2006) (http://www.acd.ucar.edu/wrf-chem/download.shtml). Domain total June-August 2012 biogenic $E_{NOx}$ is 0.31 Tg N y$^{-1}$ and $E_{ISOP}$ is 32 Tg C y$^{-1}$. The emission rate for
isoprene is in line with previous analyses (e.g., Millet et al., 2008) given differences in domain size and interannual variability.

3.2 Analysis of CH$_2$O column variability and its drivers

3.2.1 Diurnal variability of the CH$_2$O column and the isoprene columns

At a regional scale (32°N – 38°N; 75°W – 90°W), the CH$_2$O column is near steady state throughout the day (Fig. 2b), supporting our approach to understand CH$_2$O variability (Section 2). The column integrated sources and sinks of CH$_2$O are nearly identical except for a small production term through the nighttime due to O$_3$, NO$_3$ and OH oxidation of VOC, and a small offset in their rise through early morning and their fall in late afternoon (Fig. 2b). At a typical wind speed of 5 m s$^{-1}$, the lifetime of CH$_2$O at midday (~2 hours) corresponds to 36 km, or one model grid cell in our simulation. Thus, it is reasonable to assume that the CH$_2$O column at 1 PM reflects the balance of local sources and sinks.

While the steady state approximation for the CH$_2$O column is justified (Fig. 2b), column integrated isoprene, a major CH$_2$O precursor, is not in steady state with its emissions (Fig. 2a). The diurnal pattern of isoprene emissions is largest at midday and near zero at nighttime (Fig. 2a). The isoprene column increases through the daytime, as emissions exceed removal, and then decreases through the night with an e-folding timescale of 5.5 hours due to chemical loss (i.e., O$_3$, OH, NO$_3$) and transport out of the region, in agreement with previous results (Millet et al., 2008). The increase of the isoprene column through midday, at a rate of $2 \times 10^{15}$ atom C cm$^{-2}$ h$^{-1}$ or 8% of the emission rate at noon, indicates that POH is insufficient to oxidize all available isoprene, let alone its oxidation products to CH$_2$O. Thus, we conclude that isoprene is not in steady state with its emissions.

3.2.2 Spatial variability of the CH$_2$O column

We next explore the spatial patterns of summer average $E_{ISOP}$, VOCR, POH and the steady-state estimate of the CH$_2$O column at 1 PM CST (Fig. 3; left column). Unless otherwise stated, we compute the steady-state value of the CH$_2$O column using simulated PBL-average (<2.5 km) values for POH and VOCR as inputs to Equation 1, and we specify the yield of CH$_2$O per OH consumed ($\alpha_{eff} = 0.30 \ P_{CH2O} \ P_{OH}^{-1}$) and loss rate constants ($J_{\text{CH2O}} = 0.3$ h$^{-1}$; $k_{\text{CH2O-OH}} = 0.3 \times 10^{-7}$ molecules$^{-1}$ cm$^{-3}$ h$^{-1}$). We convert the
PBL steady-state value to a column value in all grid cells using the slope \((3.1 \times 10^5 \text{ cm})\)
and y-intercept \((2 \times 10^{15} \text{ molecules cm}^{-2})\) derived from the reduced major axis linear
regression of the fully simulated \(\text{CH}_2\text{O}\) column to the PBL average \(\text{CH}_2\text{O}\) concentration
for all daily 1 PM CST cloud-free WRF-Chem grid cells over land \((r^2=0.98; N = 106,320)\). The strong correlation supports our assumption that \(\text{CH}_2\text{O}\) concentrations
below 2.5 km drive the overall variability of the column, with a smaller and more
uniform contribution above 2.5 km.

The June – August 2012 average spatial pattern of isoprene emissions is highly
variable, with a maximum over the Ozarks \((35^{\circ}\text{N} – 38^{\circ}\text{N}; 91^{\circ}\text{W} – 95^{\circ}\text{W})\) where
emissions exceed all other high-emitting regions by 50\% - 100\% \((\text{Fig. 3a}; \text{e.g.,}
Wiedinmyer et al., 2005; Carlton et al., 2011)\). The spatial pattern of \(\text{VOCR}\) closely
resembles the pattern of \(E_{\text{ISOP}}\) with slight smoothing due to transport \((r^2 = 0.90; \text{Fig. 3a}
vs. 3d)\), indicating the importance of isoprene emission to total \(\text{VOCR}\) during summer in
the region \((\text{e.g., Millet et al., 2008})\). On average, \(P_{\text{OH}}\) is relatively uniform at a regional
scale except for local maxima over large \(\text{NO}_x\) emission sources where \(\text{NO} + \text{HO}_2\) reactions
strongly enhance \(P_{\text{OH}}\) \((\text{Fig. 3g})\). According to Figure 1, at \(P_{\text{OH}}\) of \(2.5 \times 10^7 \text{ molecules cm}^{-3}\)
s\(^{-1}\) \((\text{i.e., the regional background value}; \text{Fig. 3g})\), the \(\text{CH}_2\text{O}\) column will linearly respond
to \(\text{VOCR}\), and by extension to \(E_{\text{ISOP}}\), for \(\text{VOCR}\) less than \(~5 \text{ s}^{-1}\) but will saturate at larger
values of \(\text{VOCR}\) \((\text{i.e., } P_{\text{OH}}/\text{VOCR} \leq 5 \times 10^6 \text{ molecules cm}^{-3})\). The corresponding
threshold where the \(\text{CH}_2\text{O}\) column will saturate with respect to increases in \(E_{\text{ISOP}}\) is
\(~1 \times 10^{13} \text{ atom C cm}^{-2} \text{ s}^{-1}\) \((\text{Fig. 3a,d})\). Approximately 25\% of the grid cells over land are
above this threshold and contribute 54\% of the total \(E_{\text{ISOP}}\).

As expected based on the steady state model \((\text{Fig. 1})\), the spatial pattern of the
June-August average \(\text{CH}_2\text{O}\) column is described well by a reduced major axis linear
regression to \(E_{\text{ISOP}}\) \((\text{Fig. 3a. vs. 3m}, r^2 = 0.62)\) and \(\text{VOCR}\) \((\text{Fig. 3d vs. 3m}, r^2 = 0.69)\)
where \(E_{\text{ISOP}}\) is less than \(1 \times 10^{13} \text{ atom C cm}^{-2} \text{ s}^{-1}\) \((N = 1569 \text{ grid cells})\) but saturates at \(~2.5 \times 10^{16} \text{ molecules cm}^{-2}\) for larger values of \(E_{\text{ISOP}}\) \((\text{Fig. 3a vs. 3m})\). As a result, \(E_{\text{ISOP}}\) and
\(\text{VOCR}\) explain less spatial variance of the \(\text{CH}_2\text{O}\) column where \(E_{\text{ISOP}}\) values are greater
than \(1 \times 10^{13} \text{ atom C cm}^{-2} \text{ s}^{-1}\) \((N=577 \text{ grid cells}; r^2 = 0.40, 0.34, \text{respectively})\). The steady-
state model, which accounts for these saturating effects by considering variations of \(P_{\text{OH}}\)
\((\text{Fig. 1})\), explains nearly all of the spatial variance in the \(\text{CH}_2\text{O}\) columns \((r^2=0.97; \text{Fig. 3j})\).
vs. 3m), including where \( E_{\text{ISOP}} \) is large (> \( 1 \times 10^{13} \) atom C cm\(^{-2}\) s\(^{-1}\); \( r^2 = 0.93 \)). The threshold at which the CH\(_2\)O column saturates with respect to increases of VOCR, or to \( E_{\text{ISOP}} \) by extension, depends on the background average \( P_{\text{OH}} \) (Fig. 1). Thus, biases of \( P_{\text{OH}} \) (e.g., Lelieveld et al., 2008; Butler et al., 2008) or failure to accurately segregate isoprene from OH sources (e.g., Butler et al., 2008) will impact the simulated relationship of the CH\(_2\)O column to \( E_{\text{ISOP}} \), especially in high-VOC, low-\( P_{\text{OH}} \) conditions (Fig. 1; lower right corner).

3.3 The sensitivity of the CH\(_2\)O column to \( E_{\text{NOx}} \)

Due to the implementation of successful and ongoing NO\(_x\) emission control strategies, NO\(_2\) columns decreased by ~30% over U.S. cities from 2005 to 2011 (Russell et al., 2012) and by 30 – 40% over the East U.S. from 2005 – 2013 (Lamsal et al., 2015). NO\(_x\) is a major source of OH (i.e., NO-HO\(_2\) reactions, O\(_3\) production) and thus we expect variations of \( E_{\text{NOx}} \) to affect the CH\(_2\)O column. The concentration of NO\(_x\) also affects the rates of the high-yield RO\(_2\)-NO reactions relative to the lower-yield RO\(_2\)-HO\(_2\) reactions and thus should affect \( \alpha_{\text{eff}} \) (e.g., Palmer et al., 2003; Millet et al., 2008; Marais et al., 2012). To disentangle the influences of NO\(_x\) on \( \alpha_{\text{eff}} \) (Section 3.3.1) and \( P_{\text{OH}} \) (Section 3.3.2), we perform a WRF-Chem simulation identical to our base case except we decrease anthropogenic \( E_{\text{NOx}} \) by a factor of ten. We evaluate the role of individual reaction pathways (i.e., \( \alpha_{\text{eff}} \)) leading to CH\(_2\)O production in both simulations (Figs. 4-7, Table 1).

3.3.1 Dependence of the CH\(_2\)O yield from RO\(_2\) chemistry on \( E_{\text{NOx}} \)

Until now we have assumed that \( \alpha_{\text{eff}} \) (0.3 P\(_{\text{CH2O}}\) P\(_{\text{OH}}\)^{-1}) and J\(_{\text{CH2O}}\) (0.3 h\(^{-1}\)) are constant. The production of CH\(_2\)O from RO\(_2\) radicals (i.e., \( \alpha_{\text{eff}} \)), however, is expected to depend on the relative concentrations of HO\(_2\), RO\(_2\) and NO and on the identity of the parent VOC (e.g., CH\(_4\) or isoprene). Our initial findings suggest that in the southeast U.S. these effects are small; the quality of the linear fit of the fully simulated CH\(_2\)O column to the steady-state model (Fig. 3) suggests that any variability in \( \alpha_{\text{eff}} \) resulting from the details of the RO\(_2\) radical chemistry is small relative to the variability driven by \( P_{\text{OH}} \) or VOCR. Furthermore, for a ten-fold decrease of anthropogenic \( E_{\text{NOx}} \), we find that there is little change in the slope of the fully simulated CH\(_2\)O column to the steady-state estimate of the column assuming the same \( \alpha_{\text{eff}} \) in both regressions (Fig. 4a vs. 4b).
The initial finding that $\alpha_{\text{eff}}$ does not depend strongly on $E_{\text{NOx}}$ motivates us to investigate the parameters affecting $\alpha_{\text{eff}}$ in more detail. Table 1 reports all known processes affecting $\alpha_{\text{eff}}$ in WRF-Chem. Instantaneous rates and yields are calculated explicitly at 1 PM CST in WRF-Chem for three locations, each with different photochemical characteristics: a high-isoprene, low-NO$_x$ regime (the Ozarks; 37°N 92°W); a high-isoprene, high-NO$_x$ regime (Atlanta; 34°N 84°W); and a low-isoprene, low-NO$_x$ regime (central Illinois; 40°N 89°W).

The results presented in Table 1 confirm previous findings: RO$_2$-NO reactions are high-yield, RO$_2$-HO$_2$ reactions are low-yield and these reactions together determine the fate of ~75 – 95% of all RO$_2$ (e.g., Archibald et al., 2010, and references therein; Marais et al., 2012; Mao et al., 2013). Thus, we expect that $\alpha_{\text{eff}}$ should be larger in the high $E_{\text{NOx}}$ simulation. However, ~5 – 25% of all RO$_2$ react with RO$_2$, a high-yield reaction, or, in the case of isoprene peroxy radical, undergo isomerization to form hydroperoxyenals (HPALDs; Peeters and Muller, 2010; Crounse et al., 2011; Wolfe et al., 2012) before yielding CH$_2$O. These high-yield RO$_2$ channels increase in importance as NO concentrations decrease (Table 1), and thus buffer $\alpha_{\text{eff}}$ to the 10-fold decrease of anthropogenic $E_{\text{NOx}}$ in background regions (e.g., Ozarks: 0.38 vs. 0.39 P$_{\text{CH}_2\text{O P}_{\text{OH}}^{-1}}$; Central Illinois: 0.21 vs. 0.24 P$_{\text{CH}_2\text{O P}_{\text{OH}}^{-1}}$). In cities (e.g., Atlanta: 0.23 vs. 0.33 P$_{\text{CH}_2\text{O P}_{\text{OH}}^{-1}}$), $\alpha_{\text{eff}}$ actually increases ~50% for the 10-fold reduction of $E_{\text{NOx}}$, in part due to the buffering effects of high-yield RO$_2$ channels discussed above, but also due to a large increase in the yield per RO$_2$-NO reaction at lower $E_{\text{NOx}}$ (0.42 vs. 0.52 for high versus low $E_{\text{NOx}}$ scenarios, respectively; Table 1). The latter effect is likely due to differences of CH$_2$O yields in the earlier generations versus later generations of VOC oxidation that result from the nearly 3-fold decrease of $P_{\text{OH}}$ (Table 1). Thus, we conclude that CH$_2$O yield from RO$_2$ chemistry is buffered to the effects of NO$_x$ by high-yield RO$_2$ channels (Table 1).

More than 90% of the photolytic source of CH$_2$O over the Ozarks, and thus a large fraction of total CH$_2$O production in the region (up to 25%; Table 1) is due to the rapid photolysis of HPALDs ($\tau_{\text{HPALD-photolysis}}$ ~ 30 minutes). Due to the short lifetime of HPALDs, we attribute its contribution to CH$_2$O to its source, the reaction of OH with
isoprene, thus maintaining our assumption that OVOC photolysis and ozonolysis are relatively small sources of CH$_2$O in comparison to OH-VOC reactions (Table 1).

3.3.2 Dependence of P$_{OH}$ and VOCR on E$_{NOx}$

Assuming that $\alpha_{eff}$ does not depend on E$_{NOx}$ (see Section 3.3.1), we quantify the response of VOCR and P$_{OH}$ to the decrease of anthropogenic E$_{NOx}$, and then attribute the response of the CH$_2$O column to each of those two factors (Figs. 5-6). In response to the 10-fold reduction of E$_{NOx}$, boundary layer NO$_x$ concentrations decrease 61% and P$_{OH}$ decreases 37%, from 2.7 $\times$ 10$^7$ molecules cm$^{-3}$ s$^{-1}$ (Fig. 5a) to 1.7 $\times$ 10$^7$ molecules cm$^{-3}$ s$^{-1}$ (Fig. 4b). As a result of the decreased P$_{OH}$, VOC lifetimes increase and the boundary layer average VOCR increases from 3.1 s$^{-1}$ (Fig. 5a) to 4.6 s$^{-1}$ (Fig. 5b), much of it due to an increase of isoprene, which increases from a column concentration of 1.2 $\times$ 10$^{16}$ atoms C cm$^{-2}$ to 3.0 $\times$ 10$^{16}$ atoms C cm$^{-2}$.

The decrease of P$_{OH}$ has both a direct and indirect effect on the CH$_2$O removal rate due to its feedback on VOCR ($J_{CH2O} + k_{CH2O+OH} P_{OH} / VOCR$; Eqn. 1). In regions where E$_{ISOP}$ is high (> 1$\times$10$^{13}$ molecules cm$^{-2}$ s$^{-1}$), we find that P$_{OH}$ decreases 40% and VOCR increases 60% for a combined 62% decrease of the OH concentration (i.e., $\Delta$[OH] $\sim$ $\Delta$P$_{OH}$ / $\Delta$VOCR; $\sim$ 0.6 / 1.6). However, the net effect on the CH$_2$O lifetime is much smaller (21% increase) because photolysis does not change (2% difference). Thus, the ~40% reduction in CH$_2$O production ($\alpha_{eff}$P$_{OH}$) is offset by a ~ 20% increase in the CH$_2$O lifetime, half due to the direct impact of declining E$_{NOx}$ on P$_{OH}$ and half due to the indirect feedback on VOCR, resulting in a net 20% decrease of the CH$_2$O column (Fig. 6c). In regions where E$_{ISOP}$ is low, the feedbacks of P$_{OH}$ on the CH$_2$O lifetime more fully offset its effects on CH$_2$O production, such that the net effect on the CH$_2$O column is closer to zero (compare Figures 3a and 6c).

Thus, in response to lower E$_{NOx}$, the simulated CH$_2$O column decreases everywhere (Fig. 6). The decreases are largest (-23%, Fig. 6c) where E$_{ISOP}$ is large (> 10 $\times$ 10$^{12}$ atoms C cm$^{-2}$ s$^{-1}$) and near zero (-5%) where E$_{ISOP}$ is small (< 1 $\times$ 10$^{12}$ atoms C cm$^{-2}$ s$^{-1}$), a pattern consistent with a decrease in regional background P$_{OH}$ (Fig. 1) and the feedbacks of P$_{OH}$ on CH$_2$O production and loss described above. Due to larger decreases of the CH$_2$O column where E$_{ISOP}$ is large, the spatial correlation simulated between the
CH$_2$O column and E$_{ISOP}$ weakens ($r^2 = 0.59$; Figs. 3a, 6b all grid cells; $r^2 = 0.76$, Figs. 3a, 6a all grid cells).

We perform the same WRF-Chem simulation with low E$_{NOx}$ (0.1×NEI2005; Fig. 6b) but also decrease E$_{ISOP}$ by 20% over the Ozarks (89.4 – 94.9°W; 35.3 – 39.1°N). As expected for low-P$_{OH}$, high-VOCR conditions (Fig. 1), the CH$_2$O column over the same region is not very sensitive to changes of E$_{ISOP}$ and decreases by only 5.2%. Thus, in this high-VOC regime, a 40% perturbation or bias of P$_{OH}$ can have a 2-fold larger effect on the CH$_2$O column (~20%; Fig. 6) than does a 20% perturbation of E$_{ISOP}$ (~5%), assuming a linear scaling to compare the perturbations.

**Section 3.4: $\alpha_{eff}$ dependence on ambient VOC mixture.**

Figure 7 shows the spatial variability of $\alpha_{eff}$ in both the standard and reduced E$_{NOx}$ simulations. The value for $\alpha_{eff}$ (P$_{CH2O}$ P$_{OH}^{-1}$) is calculated explicitly from 1PM CST June – August 2012 average values for P$_{CH2O}$ and P$_{OH}$. The spatial pattern and magnitude of $\alpha_{eff}$ does not depend strongly on the 10-fold decrease of E$_{NOx}$ (Fig. 7a vs 7b), again demonstrating that $\alpha_{eff}$ is relatively buffered to variations of E$_{NOx}$ (see Section 3.3.1). The spatial pattern of $\alpha_{eff}$ in both scenarios reflects differences in the regionally relevant VOC mixture (i.e., isoprene vs. background CH$_4$). In general, $\alpha_{eff}$ is near 0.25 P$_{CH2O}$ P$_{OH}^{-1}$ in the regional background and is between 0.3 – 0.4 P$_{CH2O}$ P$_{OH}^{-1}$ in the high-VOCR regions. Because $\alpha_{eff}$ tends to be large where CH$_2$O columns are largest, and small where CH$_2$O columns are smallest, the steady-state calculation of CH$_2$O is systematically biased (slope > 1; Fig. 4) because it assumes that $\alpha_{eff}$ is spatially constant ($\alpha_{eff}$=0.30 P$_{CH2O}$ P$_{OH}^{-1}$). In background regions, CH$_4$ ($\alpha_{CH4} \leq 1$) and CO ($\alpha_{CO} = 0$) are the most important sinks of OH. Thus $\alpha_{eff}$,background depends on their relative concentration and may change as their abundances change in the future. On the other hand, in isoprene-rich regions, almost every OH radical reacts with isoprene or one of its products, so $\alpha_{eff}$ in these regions will be buffered to any changes in background CO or CH$_4$ concentrations. Thus, in isoprene-rich regions, long-term trends of the CH$_2$O column should primarily reflect changing P$_{OH}$ and VOCR assuming that $\alpha_{eff}$ is buffered (see also Section 3.3.1).

**4. Implications for VOC emission inversions from OVOC measurements**
To investigate the implications of our findings for retrieving $E_{ISOP}$ from measurements of the CH$_2$O column, we evaluate the relationship of the CH$_2$O column to $E_{ISOP}$ in the WRF-Chem simulation (Fig. 8a), and discuss our findings in the context of VOCR (Fig. 8b) and the steady-state estimate of the CH$_2$O column (Fig. 8c). We average model results (36 km $\times$ 36 km) to a coarser spatial scale (216 km $\times$ 216 km) similar to the model resolution used in previous analyses (e.g., Palmer et al., 2003; 2006; Millet et al., 2008; Barkley et al., 2008; Marais et al., 2012). We have highlighted values from individual grid cells over the Missouri Ozarks (37°N 92.5°W; cyan), Alabama (33.5°N 85.5°W; yellow) and SW Arkansas (33.5°N 92.5°W; magenta), to illustrate the regional differences among the domain-wide relationships (Fig. 8).

As shown previously (e.g., Palmer et al., 2003; 2006; Millet et al., 2008), there is a strong relationship between the CH$_2$O column and $E_{ISOP}$ when considering all daily values from individual grid cells as a single statistical ensemble ($r^2=0.69$; Fig. 8a). As expected for lower POH conditions, this relationship is weaker in the lower ENOx simulation ($r^2 = 0.49$). The relationship is varied locally, with inferred slopes varying by more than a factor of two between some locations (Fig. 8a, colors), confounding the retrieval of $E_{ISOP}$ for a given value of the CH$_2$O column (e.g., magenta-Ozarks, vs. cyan-SW Arkansas), a finding also noted in previous studies (e.g., Millet et al., 2008; Marais et al., 2012).

One hypothesis for the regional differences in slopes of CH$_2$O to $E_{ISOP}$ is that the transport of isoprene and its products from high-emission grid cells to downwind grid cells diminishes the sensitivity of CH$_2$O to $E_{ISOP}$ in the high-emission grid cells and inflates it downwind (Millet et al., 2008). However, VOCR accounts for transport, yet its relationship with the CH$_2$O column is equally varied across the regions (Fig. 8a vs. 8b; e.g., magenta-Ozarks, vs. cyan-SW Arkansas), thus excluding transport as the primary cause. The steady state model on the other hand is able to explain the regional differences in slopes to within 5% of one another in each location (Fig. 8c, colors), suggesting that the regional differences in the relationship of CH$_2$O to $E_{ISOP}$ or VOCR are due to differences of POH (Fig. 8a,b vs. 8c).

Despite regional variability, the local relationships of CH$_2$O to $E_{ISOP}$ or VOCR are remarkably strong, with correlation coefficients ranging from 0.73 to 0.91 for $E_{ISOP}$ (Fig.
The strong linear relationship between VOCR and CH$_2$O requires that the other driving variable, P$_{OH}$, be positively correlated with VOCR such that the day-to-day variation of the OH concentration is small (i.e., daily values of VOCR and P$_{OH}$ lie on a line of constant slope in Figure 1). Positive correlation of VOCR and P$_{OH}$ suggests that the conditions that result in higher E$_{ISOP}$ and VOCR in a region tend to result in higher P$_{OH}$: high temperatures and clear skies are associated with larger E$_{ISOP}$ (Guenther et al., 2006), high concentrations of water vapor and ozone, both of which are important precursors of OH radicals. Assuming that the day-to-day variation of OH is small in any given location, the sensitivity (i.e., slope) of the CH$_2$O column to a perturbation of VOCR in that location is directly proportional to its OH concentration: the slope is steep where the OH concentration is high (e.g., the rise of CH$_2$O contours following the gray line with [OH] = 7×10$^6$ molecules cm$^{-3}$ in Figure 1) and is shallow where the OH concentration is low (e.g., the same for the gray line with [OH] = 3×10$^6$ molecules cm$^{-3}$ in Figure 1). This same effect will be weaker for E$_{ISOP}$ due to the feedbacks of P$_{OH}$ on VOCR, but should follow the same general trend (Section 3.3.2).

To evaluate this hypothesis, we compare the simulated cloud-free June – August 1 PM CST average OH concentration (Fig. 9c) to the CH$_2$O column sensitivity to VOCR (Fig. 9b) and E$_{ISOP}$ (Fig. 9a) at the native model resolution (36 × 36 km$^2$). As expected based on Figure 1, the concentration of OH explains much of the spatial variance of the CH$_2$O column sensitivity to VOCR ($r^2 = 0.64$; Fig 9b vs. 9c). The CH$_2$O lifetime at 1 PM is too short (~2 h) for its direct transport from source regions to strongly influence its relationship with VOCR downwind, and any transport will similarly affect VOCR, thus not disturbing their ratio.

Performing the same analysis for E$_{ISOP}$ instead of VOCR, we find that the quantitative agreement is not as strong ($r^2 = 0.26$; Fig 9a vs. 9c), but qualitatively, the results are similar. Previous analyses found anomalously high sensitivities in grid cells where summer average E$_{ISOP}$ was low, attributing the enhancement to transport from larger upwind sources (< 2 × 10$^{12}$ atom C cm$^{-2}$ s$^{-1}$; Millet et al., 2008). We restrict our analysis to grid cells where average E$_{ISOP}$ is greater than 5 × 10$^{12}$ atom C cm$^{-2}$ s$^{-1}$.

Transport of isoprene and its oxidation products does affect the sensitivity (slope) of
CH$_2$O to E$_{ISOP}$ at the edge of large isoprene sources (e.g., Fig 9a, downwind edge of the Ozarks; e.g., Millet et al., 2008), but the spatial pattern of OH concentrations also plays a role (Fig. 9c). CH$_2$O columns are most sensitive to E$_{ISOP}$ over cities where OH concentrations are highest, and are less sensitive in regions where E$_{ISOP}$ is largest and OH concentrations are lowest (Fig. 3a, 9). We would not expect the relationship between OH concentrations and the CH$_2$O-to-E$_{ISOP}$ slopes (Fig. 9a vs. 9c) to be as strong as that for VOCR (Fig. 9b vs. 9c) because of VOC transport (e.g., Millet et al., 2008), particularly at this finer spatial scale, and in light of feedbacks of OH concentrations on VOCR (e.g., Karl et al., 2009; Section 3.3.2).

The slopes and y-intercepts inferred for regressions of the CH$_2$O column to variations of E$_{ISOP}$ depend on the temporal and spatial scale over which they are derived, and thus should not be applied to other temporal and spatial scales (Figs. 3, 6, 8, 9). For example, the slope retrieved for the entire ensemble of grid cells is smaller than the slope derived in every individual grid cell (Fig. 8a), a gross bias due to combining very high-E$_{ISOP}$, low-OH locations (i.e., the Ozarks) with lower-E$_{ISOP}$, higher-OH locations. The range of the locally derived y-intercepts in the same example is also large (Fig. 8a; $\mu \pm \sigma$; 0.1$x10^{15} \pm 3.0x10^{15}$ molecules cm$^{-2}$), and is much smaller than that derived for the entire ensemble of grid cells (Fig. 8a; 8.8$x10^{15}$ molecules cm$^{-2}$). This finding suggests that the y-intercept does not simply represent the background CH$_2$O column due to methane oxidation in the absence of isoprene emission (e.g., Palmer et al., 2006), but also reflects nonlinearities in the OH and VOC chemistry that drive CH$_2$O variability (Fig. 1, 5). As such, the y-intercept should be treated as a free variable along with the scaling parameter (slope).

Based on our findings, we recommend a full formal inversion to derive E$_{ISOP}$ from measurements of the CH$_2$O column that accounts for nonlinearities of the OH and VOC chemistry. However, as long as the day-to-day variability of OH concentrations under cloud free conditions is small (Fig. 1; lines of constant slope), our results provide a basis (Fig. 9) for performing inversions using locally-derived linear formulations, originally introduced by Millet et al. (2008) and improved by Marais et al. (2012). These inversions should account for spatial variations of the OH concentration and recognize the limitations of inferring variations of E$_{ISOP}$ in low-P$_{OH}$ environments (e.g., Fig. 6b). Marais
et al., (2012) incorporated information on the variability of the NO$_2$ column, an adaptation that implicitly accounts for some, but not all of the variability of OH concentrations, and is uncertain in regions where NO$_2$ columns are near their detection limit. We recommend that a first test of any linear inversion is the comparison of a second iteration of the forward model with updated E$_{ISOP}$ to the CH$_2$O column measurements.

The influence of OH on the variability of CH$_2$O is due to the short photolytic lifetime of CH$_2$O relative to that of reaction with OH (see Equation 1). Thus the findings that we present here, that variations of the OH radical influence the variability of CH$_2$O, also apply to other oxidized VOC intermediates with short lifetimes against photolysis (e.g., glyoxal; $\tau_{\text{photolysis}} \sim 2$ h; $\tau_{\text{OH+glyoxal}} \sim 2.8$ h at $[\text{OH}] = 1 \times 10^7$ molecules cm$^{-2}$).

5. Daily variations of the CH$_2$O column

The daily variability of CH$_2$O column has been used to infer daily variability of E$_{ISOP}$ (e.g., Palmer et al., 2003). However, the factors affecting POH, and thus its influence on the CH$_2$O column, also vary daily. From 25 June 2012 to 27 June 2012 (Fig. 3, center and right column), boundary layer average POH over Arkansas and Missouri, two U.S. states in the center west of the domain, decreases from $4.2 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ to $2.4 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$. The decrease of POH is due primarily to a decrease of water vapor in the region (i.e., less O$^1$D+H$_2$O $\rightarrow$ 2 OH). The MODIS near infrared retrieval of the water vapor column indicates that WRF is accurately simulating the regional-scale patterns of the observed water vapor distribution (not shown). On these same days, there is little change in E$_{ISOP}$ ($\sim 3\%$, $1.13 \times 10^{13}$ to $1.10 \times 10^{13}$ atoms C cm$^{-2}$ s$^{-1}$), VOCR ($\sim 5\%$, 5.8 s$^{-1}$ vs. 5.5 s$^{-1}$) or ground-level temperature (33.5°C vs. 32.5°C) over the region. Due to the low-POH, high-VOCR conditions, the CH$_2$O column in the region is sensitive to the decrease of POH (Fig. 1) and the statewide average over Missouri and Arkansas decreases from $2.6 \times 10^{16}$ molecules cm$^{-2}$ on 25 June 2012 to $1.9 \times 10^{16}$ molecules cm$^{-2}$ on 27 June 2012, a decrease that is well explained by the steady-state model (Figs. 3k, l, n, o). This result again highlights the need to use the appropriate time and space domains for any inversion of E$_{ISOP}$ from measurements of the CH$_2$O column, as the sensitivity of the CH$_2$O column to E$_{ISOP}$ depends on daily variations of POH.
To demonstrate that these daily variations of the CH$_2$O column are observable, Figure 10 shows the CH$_2$O columns measured by the Ozone Monitoring Instrument (OMI) from the most recent NASA/SAO product (Version 3, González Abad et al., 2015) and again shows those simulated by WRF-Chem (see also Fig. 3), zoomed in over the south-central U.S. on 25 and 27 June 2012. The spatial pattern of the simulated CH$_2$O column matches the observations at a regional scale (Fig. 10). On 25 June 2012, the CH$_2$O columns are minimum in the northeast corner of the domain but larger throughout the rest of the domain, even exceeding $4 \times 10^{16}$ molecules cm$^{-2}$ in North Central Arkansas, likely indicating that boundary layer average P$_{OH}$ (>4x10$^7$ molecules cm$^{-3}$ s$^{-1}$) and VOCR (>7.5 s$^{-1}$) are both high (i.e., towards the upper right corner of Fig. 1). On 27 June 2012, the columns are much lower throughout the domain with a local minimum in the center of the image and in the far northeast corner, indicating that either P$_{OH}$ or VOCR is lower than it was on 25 June 2012. Canopy-scale isoprene flux measurements in the region increased from 25 June to 27 June 2012 (Seco et al., 2015; 38.74°N, 92.20°W) suggesting that VOCR is unlikely to be lower on 27 June. Consequently the observed decrease in the CH$_2$O columns is likely due to the decrease of P$_{OH}$ in the region (Fig. 3h,i), primarily driven by the decrease of water vapor.

The simulated CH$_2$O columns are biased high relative to the measurements on both days (Fig. 10), suggesting that the simulated P$_{OH}$ or VOCR is biased high, though it is also possible that the measurements are systematically biased. If the air mass factor (AMF) from version 2 of the retrieval were applied to the version 3 slant columns, the vertical columns would be approximately 33% larger, and in better agreement with the simulated values. We are not suggesting that the AMF from one version is better than the other, but are rather highlighting the systematic uncertainty of the measurements due to retrieval inputs (e.g., Palmer et al., 2001; Russell et al., 2011; Barkley et al., 2012).

Section 6: Variability of the CH$_2$O column: a constraint on P$_{OH}$?

Despite these potential biases, the observed variability suggests that in addition to reflecting variations of isoprene emissions due to temperature (e.g., Palmer et al., 2003), the CH$_2$O column reflects variation of OH sources, such as ozone, NO$_x$, water vapor and of particular interest, the magnitude of a potentially large hypothesized source of OH in high-VOC, low NO$_x$ environments (Lelieveld et al., 2008; Hofzumahaus et al., 2009;
Whalley et al., 2010; Mao et al., 2012; Fuchs et al., 2013; Nölscher et al., 2014; Rohrer et al., 2014). Measurement-based studies suggest that our conventional understanding of OH sources grossly underestimates $P_{\text{OH}}$ in high-isoprene, low-$\text{NO}_x$ conditions (e.g., $1 \times – 3 \times$ conventional sources; Lelieveld et al. 2008; Fuchs et al., 2013), However, there is also evidence from quantitative, detailed laboratory studies (Paulot et al., 2009a,b; Crounse et al., 2011; 2012) and the field (e.g., Mao et al., 2012) that suggests that the magnitude of the postulated OH sources is not much larger than conventionally understood. If the postulated source of OH were much larger than what is conventionally understood ($1 \times – 3 \times$ conventional sources; e.g., Lelieveld et al. 2008; Fuchs et al., 2013), then the CH$_2$O column should be less sensitive to variations of $P_{\text{OH}}$ and more sensitive to variations of VOCLR (i.e., towards the top of Figure 1; $[\text{OH}] \approx 5 \times 10^6$ molecules cm$^{-3}$).

However, the observations show that the CH$_2$O column is sensitive to the variability of conventional sources of OH (i.e., water vapor). The observed variability (Fig. 10) is in line with that simulated in WRF-Chem, which we estimate regenerates approximately 33% of conventional OH sources in isoprene-rich conditions (e.g., Paulot et al., 2009a,b; Crounse et al., 2011; 2012), approximately an order of magnitude less than that postulated based on recent OH measurements (~3-fold increase; e.g., Lelieveld et al., 2008). To make this estimate, we classify OH production in to five classes and assume that all production via photolysis, RO$_2$-HO$_2$ and VOC-OH reactions are unconventional while that due to inorganic reactions and ozonolysis is conventional, and is thus an upper bound on the estimated rate. We isolate the effect of low-$\text{NO}_x$ isoprene chemistry by making the estimate for 27 June 2012 over the Ozarks ($37.4^\circ \text{N}, 91.1^\circ \text{W}$), where surface level isoprene concentrations are high (18 ppb) and NO concentrations are low (47 ppt).

Thus, the observed variability is consistent with an OH source with a magnitude that is closer to that of conventional sources (i.e., towards the bottom of Figure 1). The large uncertainty of any single column measurement (e.g., González Abad et al., 2015) limits the strength with which we can make this conclusion from only two overpasses (25 and 27 June 2012; Fig. 10). However, in situ measurements of CH$_2$O also indicate that a source of OH far larger than conventionally understood is not consistent with the observed abundance of CH$_2$O.
7. Conclusions

We describe the variability of the fully simulated daily June – August 1PM CST CH$_2$O column in WRF-Chem (Figs. 2-9) using a steady-state framework (Eqn. 1, Figs. 1, 6) with simulated POH and VOCR as the only variables. We find that the CH$_2$O column depends on POH most strongly where the midday OH concentration is low and depends on VOCR where the midday OH concentration is high (Fig. 1). We find that the spatial pattern of E$_{ISOP}$ in the East U.S. drives the pattern of VOCR (Fig. 3). Thus, based on the spatial pattern of OH concentration in WRF-Chem (~ POH / VOCR; Fig. 9c), we conclude that the CH$_2$O column is most sensitive to E$_{ISOP}$ where E$_{ISOP}$ is small or where NO$_x$ emissions (i.e., POH) are large and is least sensitive to E$_{ISOP}$ where E$_{ISOP}$ is large (Fig. 9a vs. 9c). The opposite is true for the relationship of POH to the CH$_2$O column.

Our findings indicate that variability of the OH concentration should be considered when using measurements of the CH$_2$O column to understand the variability of E$_{ISOP}$ and other VOC emissions. Our finding has been alluded to in previous work (e.g., Marais et al., 2012), but was not attributed to the variability of POH. The prior attribution to NO$_x$ (Marais et al., 2012) is consistent with our findings in that NO$_x$ is a large source of OH radicals, but neglects the impacts of other OH sources such as water vapor, ozone, or possible isoprene-dependent OH production pathways recently discovered (Crounse et al., 2011; 2012) or hypothesized (e.g., Lelieveld et al., 2008; Hofzumahaus et al., 2009). We examine the influence of NO$_x$ on RO$_2$ chemistry by tracking the CH$_2$O yield from individual radical reaction pathways, and find that the yield of CH$_2$O at low NO$_x$ concentrations is buffered by high-yield RO$_2$-RO$_2$ reactions (Table 1). Thus, we conclude that in isoprene-rich regions, the influence of NO$_x$ on CH$_2$O production is primarily due to its feedback on POH, which controls the rate of RO$_2$ formation, and less so through its effect on the fate of individual RO$_2$.

Our findings suggest that measurements of the CH$_2$O column have the potential to improve our understanding of OH chemistry. For example, our framework (Fig. 1) implies that measurements of the CH$_2$O column in regions where VOCR is known to be high (e.g., Lelieveld et al., 2008; ~10 s$^{-1}$; Hofzumahaus et al., 2009; ~ 20 s$^{-1}$) can be used to test hypothesized OH sources, insofar as the assumption of a relatively insensitive CH$_2$O yield per POH ($\alpha_{eff}$) is valid for any changes to the oxidation mechanism. While this
assumption would not hold for all possible isoprene oxidation mechanisms or VOC environments, we show here that the yield of CH₂O per POH ($\alpha_{\text{eff}}$) in a state-of-the science chemical mechanism is insensitive to a broad range of photochemical conditions in a isoprene-rich environment (Fig. 7; Table 1). Regardless of these details, any proposed isoprene oxidation mechanism must reconcile itself with CH₂O measurements (as well as those of other oxidized VOC), a task which has proven difficult in previous modeling analyses (e.g., Butler et al., 2008; Galloway et al., 2012).

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Table 1. Chemistry affecting α<sub>eff</sub> calculated instantaneously at 1 PM CST for June – Aug 2012 at high (1×) and low (0.1×) ENOx

<table>
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<th>High VOCR, Low NO&lt;sub&gt;x&lt;/sub&gt;</th>
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<th>Low VOCR, Low NO&lt;sub&gt;x&lt;/sub&gt;</th>
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<tr>
<td>P&lt;sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O Total&lt;/sub&gt; (x10&lt;sup&gt;6&lt;/sup&gt; molecules cm&lt;sup&gt;-3&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>9.6, 6.7</td>
<td>13.4, 6.6</td>
<td>5.8, 4.0</td>
</tr>
<tr>
<td>P&lt;sub&gt;OH&lt;/sub&gt; (x10&lt;sup&gt;6&lt;/sup&gt; molecules cm&lt;sup&gt;-3&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>25.2, 17.0</td>
<td>57.5, 19.8</td>
<td>27.3, 16.6</td>
</tr>
<tr>
<td>α&lt;sub&gt;eff&lt;/sub&gt; (P&lt;sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O&lt;/sub&gt;/P&lt;sub&gt;OH&lt;/sub&gt;)</td>
<td>0.38, 0.39</td>
<td>0.23, 0.33</td>
<td>0.21, 0.24</td>
</tr>
<tr>
<td>% P&lt;sub&gt;OH&lt;/sub&gt; that reacts with VOC or CO</td>
<td>92.8, 93.4</td>
<td>83.7, 92.3</td>
<td>80.2, 84.8</td>
</tr>
</tbody>
</table>
Figure 1. The steady-state CH₂O column (colored curves; molecules cm⁻²) as a function of VOC reactivity (x-axis; VOCR; s⁻¹) and OH production (y-axis; POH; molecules cm⁻³ s⁻¹). The column is computed using Equation 1 ($\alpha_{\text{eff}} = 0.3 \ P_{\text{CH}_2\text{O}} P_{\text{OH}}^{-1}, J_{\text{CH}_2\text{O}} = 0.30 \ h^{-1}, k_{\text{CH}_2\text{O} + \text{OH}}[\text{OH}] = 0.03 \ h^{-1}$ at $[\text{OH}] = 1 \times 10^6$ molecules cm⁻³) assuming that POH and VOCR are uniformly mixed from 0 – 2 km above ground level and are zero above 2 km. Values of constant OH concentration are indicated on the plot (gray-dashed lines) under the assumption that VOCR is the only sink of OH radicals.
Figure 2. The diurnal profile of (a) isoprene emissions (atom C cm\(^{-2}\) h\(^{-1}\)) and the isoprene column (atom C cm\(^{-2}\)) and (b) the CH\(_2\)O vertical column (atom C cm\(^{-2}\)) and the column integrated production rate (atom C cm\(^{-2}\) h\(^{-1}\)), loss rate (atom C cm\(^{-2}\) h\(^{-1}\)) and lifetime of CH\(_2\)O (h) for June – August 2012 over the Southeast U.S. (32°N – 38°N; 75°W – 90°W), following the approach of Millet et al. (2008; see Figure 3 of their paper for comparison with our results).
Figure 3. WRF-Chem 19 UTC (1 PM Central Standard Time; CST) E_{\text{ISOP}} (a-c; atoms C cm$^{-2}$ s$^{-1}$), PBL VOCR ($z=0-2.5$ km; d-f; s$^{-1}$), P_{OH} ($z=0-2.5$ km; g-i; molecules cm$^{-3}$ s$^{-1}$) and the steady-state CH$_2$O column (molecules cm$^{-2}$; Eqn. 1; see text; j-l), and the fully simulated CH$_2$O column (m-o; molecules cm$^{-2}$) for the June – August 2012 average (left column), 25 June (middle column) and 27 June 2012 (right column). Only values from cloud-free grid cells over land are included in the results.
Figure 4. The daily 1 PM CST June – August 2012 CH$_2$O column (y-axis; molecules cm$^{-2}$) versus the steady-state CH$_2$O column (x-axis; molecules cm$^{-2}$; Eqn. 1; see text) for all cloud-free grid cells over land in the standard simulation (a, ENO$_x$ = 1 $\times$ NEI2005) and in a simulation with ENO$_x$ reduced 10-fold (b; ENO$_x$ = 0.1 $\times$ NEI2005). The reduced major axis regression (dashed) and one-to-one (solid) line are included.
Figure 5. Daily June – August 2012 1PM CST CH$_2$O column (colors; molecules cm$^{-2}$) for boundary layer ($\leq$ 2.5 km) average P$_{OH}$ (y-axis; molecules cm$^{-3}$ s$^{-1}$) and VOCR (x-axis; s$^{-1}$) in WRF-Chem grid cells over land (36 km $\times$ 36 km) that have been averaged to a spatial scale of 216 km $\times$ 216 km for (a) the standard simulation and for (b) the sensitivity simulation in which anthropogenic E$_{NOx}$ is decreased by a factor of ten. The magnitude of E$_{ISOP}$ in each grid cell is indicated by the size of the marker. E$_{ISOP}$ is identical in the two simulations, but on average, there is 51% more VOCR per unit of E$_{ISOP}$ in the lower E$_{NOx}$ scenario due to the decrease of P$_{OH}$. We include only values where fewer than 20% of the native 36km $\times$ 36 km grid cells in the spatial average had clouds. Contours from Figure 1 are included for reference.
Figure 6. The June – August 2012 average CH$_2$O column simulated with WRF-Chem at 19 UTC (1 PM Central Standard Time; CST) including only cloud-free grid cells over land in (a) the standard simulation, (b) the sensitivity simulation in which anthropogenic E$_{NOx}$ is decreased by a factor of ten and (c) the percent difference between the two simulations.
Figure 7. The June – August 2012 1 PM CST average of $\alpha_{\text{eff}}$ (colors; $P_{\text{CH2O}} P_{\text{OH}^{-1}}$) in the lower troposphere ($\leq 2.5$ km) calculated explicitly with WRF-Chem for cloud free grid cells over land in both the standard simulation (a, $E_{\text{NOx}} = 1 \times \text{NEI2005}$) and in a simulation with $E_{\text{NOx}}$ reduced 10-fold (b; $E_{\text{NOx}} = 0.1 \times \text{NEI2005}$).
Figure 8. Daily 1 PM CH$_2$O column versus (a) isoprene emissions, (b) VOCR and (c) the CH$_2$O column derived by assuming steady-state (Eqn. 1; $\alpha_{\text{eff}} = 0.3$ P$_{\text{CH}_2\text{O}}$ P$_{\text{OH}}^{-1}$) for June – August 2012 over the Southeast U.S. (29° - 39°N, 78°-100°W) in the WRF-Chem model. Values are averaged from the native WRF-Chem grid to a coarser grid of 216 km $\times$ 216 km. Columns over the Missouri Ozarks (37°N 92.5°W; cyan), Alabama (33.5°N 85.5°W; yellow) and SW Arkansas (33.5°N 92.5°W; magenta) are highlighted to illustrate nonlinear effects. Values with cloud fraction above 0.2 are excluded. Reduced major axis least square regression fits are reported in the lower right corner.
Figure 9. The scaling factor relating CH$_2$O columns to a) $E_{\text{ISOP}}$ (seconds) and b) VOCR (molecule cm$^{-2}$ s$^{-1}$) derived as the slope from reduced major axis linear regression within each individual WRF-Chem grid cell over land where Jun – Aug 2012 average $E_{\text{ISOP}} > 5 \times 10^{12}$ atom C cm$^{-2}$ s$^{-1}$, screened for cloud-free conditions. Also shown is c) the Jun – Aug 2012 boundary layer average OH concentration (molecules cm$^{-3}$) in grid cells meeting these criteria.
Figure 10. Simulated (a-b) and observed (c-d) CH$_2$O column at 1PM CST on a day when POH is high (25 June 2012; left column) and on a day when POH is low (27 June 2012; right column). E$_{ISOP}$ varied little between these two days over the central U.S (~3% decrease simulated using WRF-Chem/MEGANv2.04). The OMI view geometry is similar on both days (~200 km further east on 27 June 2012). MODIS true color composite images recorded ~15 minutes prior to the OMI measurements indicate areas of vegetation and the cloud distribution (e-f).