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Chemical Feedback From Decreasing Carbon Monoxide Emissions

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Abstract

Understanding changes in the burden and growth rate of atmospheric methane (CH_4) has been the focus of several recent studies but still lacks scientific consensus. Here we investigate the role of decreasing anthropogenic carbon monoxide (CO) emissions since 2002 on hydroxyl radical (OH)

sinks and tropospheric CH_4 loss. We quantify this impact by contrasting two model simulations for 2002–2013: (1) a Measurement of the Pollution in the Troposphere (MOPITT) CO reanalysis and (2) a Control-Run without CO assimilation. These simulations are performed with the Community Atmosphere Model with Chemistry of the Community Earth System Model fully coupled chemistry climate model with prescribed CH_4 surface concentrations. The assimilation of MOPITT observations constrains the global CO burden, which significantly decreased over this period by ~20%. We find that this decrease results to (a) increase in CO chemical production, (b) higher CH_4 oxidation by OH, and (c) ~8% shorter CH_4 lifetime. We elucidate this coupling by a surrogate mechanism for CO-OH-CH_4 that is quantified from the full chemistry simulations.

1 Introduction

The tropospheric burden and lifetime of carbon monoxide (CO), methane (CH_4), and ozone (O_3) are tightly and nonlinearly coupled (Crutzen et al., 1973; Guthrie, 1989; Lin et al., 1988). Central to this coupling is the chemical oxidation process that is catalyzed by the hydroxyl radical (OH) and related oxidants (e.g., Lelieveld et al., 2016). Attribution of the changes in tropospheric burden of these species hinges upon proper representation of the sources and sinks of OH. At the global scale, CO is the major sink of OH, followed by CH_4 (Levy, 1971). CO is hence a key constituent in understanding global tropospheric chemistry and studies related to atmospheric composition.

Before 2000, measurements from the global surface network from the National Oceanic and Atmospheric Administration (NOAA) had shown a long-term decline in CO abundance (especially in the Northern Hemisphere or NH) due to reductions in fossil fuel emissions (e.g., Novelli et al., 2003). About half of the CO burden in the troposphere is due to chemical oxidation of CH_4 and volatile organic compounds (VOCs) (e.g., Duncan et al., 2007; Stein et al., 2014). Observational constraints on the CO burden have been largely complemented by spaceborne instruments such as from Measurement of the Pollution in the Troposphere (MOPITT), Atmospheric Infrared Sounder (AIRS), Tropospheric Emission Spectrometer (TES), and Infrared Atmospheric Sounding Interferometer (IASI) instruments (Beer et al., 2006; Clerbaux et al., 2009; Drummond & Mand, 1996; Warner et al., 2007).

Recently, Worden et al. (2013) showed good consistency in CO column retrievals from those four instruments showing decreasing trends for both the NH and the Southern Hemisphere (SH). Statistically significant CO trends at 1-sigma have been reported only for MOPITT and AIRS products, which have longest data records. These long-term trends are well correlated with the trends in bottom-up emissions especially over the eastern United States and Europe, where CO emissions from anthropogenic sources have decreased (Granier et al., 2011; He et al., 2013;

Kuenen et al., 2014). Worden et al. (2013) reported overall decreasing trends, which is supported by results from several studies suggesting improvement in combustion efficiency in China (Li & Liu, 2011; Tohjima et al., 2014; Wang et al., 2010) within the context of increasing NO_x emissions and CO_2 emissions (Liu, Guan, et al., 2015; Liu, Zhang, et al., 2015; Miyazaki et al., 2017). However, several forward modeling studies with the same emissions failed to reproduce these observed trends over China (Strode et al., 2016; Warner et al., 2013; Yoon & Pozzer, 2014). Along with large uncertainties in CO emissions inventories, it appears that dry deposition, convective transport, [OH] and tropospheric chemistry in general are also significant sources of model error and impact inverse modeling results (Arellano et al., 2007; Barré et al., 2015; Gaubert et al., 2016; Jiang et al., 2013, 2015; Miyazaki et al., 2015; Stein et al., 2014; Strode et al., 2015; Yin et al., 2015). As a consequence of the decrease in direct CO emissions, the significance of chemistry and secondary sources of CO in the global CO budget has also increased. This has been corroborated by isotope measurements (e.g., Park et al., 2015) and aircraft observations (Hudman et al., 2008).

This CO decrease needs to be placed in the context of its strong coupling with CH_4 and O_3. In fact, there is an ongoing scientific debate on the causes of the factors governing the CH_4 budget, for which the atmospheric growth is well constrained, but it is still challenging to robustly quantify the sources and sinks of CH_4 (Kirschke et al., 2013; Saunois, Bousquet, et al., 2016). Within a context of large interannual variability, atmospheric growth rate of CH_4 decreased between 2000 and 2006, which is followed by higher growth rate starting in 2007 (e.g., Saunois, Bousquet, et al., 2016). This "renewed atmospheric growth" of CH_4 since 2006 suggests an increase of the sources rather than a decreasing sink, but there is no consensus scenario (Rigby et al., 2008; Saunois, Jackson, et al., 2016). First, emissions from China have increased and contributed significantly to the CH_4 growth despite a lower growth than initially suggested by prior emission inventories (Thompson et al., 2015; Patra et al., 2016). Second, the increase in the U.S. CH_4 emissions, in particular, from oil and gas production is contributing to the global atmospheric growth (Franco et al., 2016; Turner et al., 2016). Finally, the examination of CH_4 isotopes (e.g., Monteil et al., 2011) are characterized by a biogenic signature supporting an increase from wetlands and rice cultivation, following increased precipitation during La Niña conditions (Schaefer et al., 2016; Nisbet et al., 2016).

Although CH_4 isotopes help us understand the sources of CH_4, they only bring limited information on CH_4 sinks (Schaefer et al., 2016). Despite its importance, the determination of the main CH_4 sink (i.e., chemical reaction with OH) is challenging because of the very short lifetime of OH, hence making it even more difficult to measure and to represent from limited

measurements alone (Stone et al., 2012). Analysis of methyl chloroform, as a proxy of OH, showed that OH concentrations are well buffered against perturbations, resulting in a stable global mean OH concentration with very small interannual variability (Montzka et al., 2011). This has been corroborated with modeling results, suggesting that [OH] is stable because of its catalytic recycling (e.g., Lelieveld et al., 2016; Taraborrelli et al., 2012).

Recent studies pointed out that attributing trends of the CH_4 sources and sinks is an underdetermined problem (Prather & Holmes, 2017; Rigby et al., 2017; Turner et al., 2017), and it suggests that changes in OH could explain recent CH_4 atmospheric growth rate variations. They acknowledge the need for a better understanding of the mechanism responsible for the changes of [OH]. It is important to recall that a change in OH sources and sinks does not necessarily mean a change in the global tropospheric [OH]. For instance, as shown in Gaubert et al. (2016), an increase in the OH sink due to higher CO from MOPITT assimilation is compensated by an increase in O_3 formation that increases both [OH] and the OH source (Lelieveld et al., 2002, 2016). Forward model simulations and comparisons with observations suggest that NO_x and CO emissions mostly account for the interannual variability and long-term trends in the CH_4 sink (Dalsøren & Isaksen, 2006; Holmes et al., 2013). These simulations suggest a decreasing CH_4 lifetime relative to an increasing oxidizing capacity, as characterized by changes in the sources (e.g., NO_x) and sinks (e.g., CO) of OH (Dalsøren et al., 2016; McNorton et al., 2016). Finally, the recent study looking at the factors governing the CH_4 lifetime with several models confirm the important role of CO (Naik et al., 2013; Nicely et al., 2017).

There is an opportunity to further investigate the trend in CH_4 sinks from the perspective of CH_4-OH-CO interactions given that the burden of CH_4 and CO can be well constrained with current observations. Some of the inversion studies use CH_4, methyl chloroform, and CO observations to solve for the chemical sources of CO but with limited chemical interactions because of a prescribed OH (e.g., Pison et al., 2009; Yin et al., 2015). Miyazaki et al. (2015) and Gaubert et al. (2016) use an ensemble of model forecasts that determines [OH] explicitly but with a prescribed CH_4. In addition to the full chemistry, biases can be reduced by assimilation of satellite observations in reanalyses exercises (Flemming et al., 2017; Gaubert et al., 2016; Inness et al., 2013; Miyazaki et al., 2015).

We elucidate in this study the potential contribution of the chemical feedback of decreasing CO emissions to CH_4 loss. We look at this problem from the model-simulated trends in the chemical oxidation of CH_4 and subsequent chemical source of CO when the abundance of CH_4 is forced and CO is observationally constrained in the atmosphere but when OH is calculated explicitly. This is facilitated by a reanalysis of MOPITT CO retrievals in a full chemistry climate model

(CAM-Chem) for the period starting from 2002 to 2013 with spatiotemporal prescriptions of CH_4 (Gaubert et al., 2016). This reanalysis is contrasted with a Control-Run scenario where MOPITT CO is not assimilated and running a Control-Run with 4-D CO fields replaced by CO fields from our MOPITT-Reanalysis (hereafter called Control-SCO, where SCO stands for Specified CO), briefly presented in section 2. These comparisons were designed to decouple the effect of meteorology and chemistry on the indirect impact of decreasing CO on CH_4 loss. We then present our results in section 3, starting with annual global production and loss rates within the context of a surrogate mechanism and followed by decomposition of the trends exhibited by these rates. We discuss in section 4 the implication of this work on the observed CH_4 growth rate.

2 Methods

As described in Gaubert et al. (2016), our reanalysis of MOPITT CO uses the Community Atmosphere Model with Chemistry of the Community Earth System Model (CESM/CAM-Chem) (Tilmes et al., 2015) and the ensemble-based Data Assimilation Research Testbed (DART) (Anderson et al., 2009). Both conventional meteorological observations and MOPITT V5J (MOPITT-CO) multispectral retrievals of CO partial columns (Deeter et al., 2013; Worden et al., 2010) are assimilated every 6 h as described in Barré et al. (2015). The assimilation is used to optimize initial conditions (i.e., CO concentration at each analysis step). The Control-Run is a deterministic CAM-Chem simulation with meteorology nudged to the Modern-Era Retrospective Analysis for Research and Applications (MERRA) reanalysis (Rienecker et al., 2011). This simulation uses the same chemistry configuration as the MOPITT-Reanalysis and same emission inventories; however, NO sources from lightning and biogenic Non Methane Volatile Organic Compounds (NMVOC's) can differ because of meteorology. In addition, differences are expected because of different transport, vertical grid, water vapor, radiation, and temperature fields. Those differences are more than likely to affect the sources and sinks of OH. In order to isolate the effect of CO on CH_4 lifetime, we conducted another Control-Run for which the CO fields are replaced by the MOPITT-Reanalysis forecast every day at 00 h UTC during the course of the full simulation (April 2002 to April 2013). This new simulation (Control-SCO) is thus exactly the same as the Control-Run, except for the CO fields. Because of the long lifetime of CO, the Control-SCO has [CO] close to the MOPITT-Reanalysis but is slightly underestimated since it is forced every 24 h instead of 6 h. A more detailed discussion of the methodology can be found in the supporting information (Anderson, 2001; Emmons et al., 2010; Eyring et al., 2013; Guenther et al., 2012; Lamarque et al., 2012; Lawrence et al., 2011; Meinshausen et al., 2011; Raeder et al., 2012; Val Martin et al., 2014; Wiedinmyer et al., 2011).

3 Results

3.1 Annual-Mean Global Tropospheric Rates

We focus on the CO-OH-CH$_4$ coupled chemical system to investigate the mechanism in which the time variation of the CO burden (as constrained by assimilation) impacts CH$_4$lifetime. As an example, following Prather ([1994](#), [2007](#)), this coupling can be represented into the following surrogate mechanism:

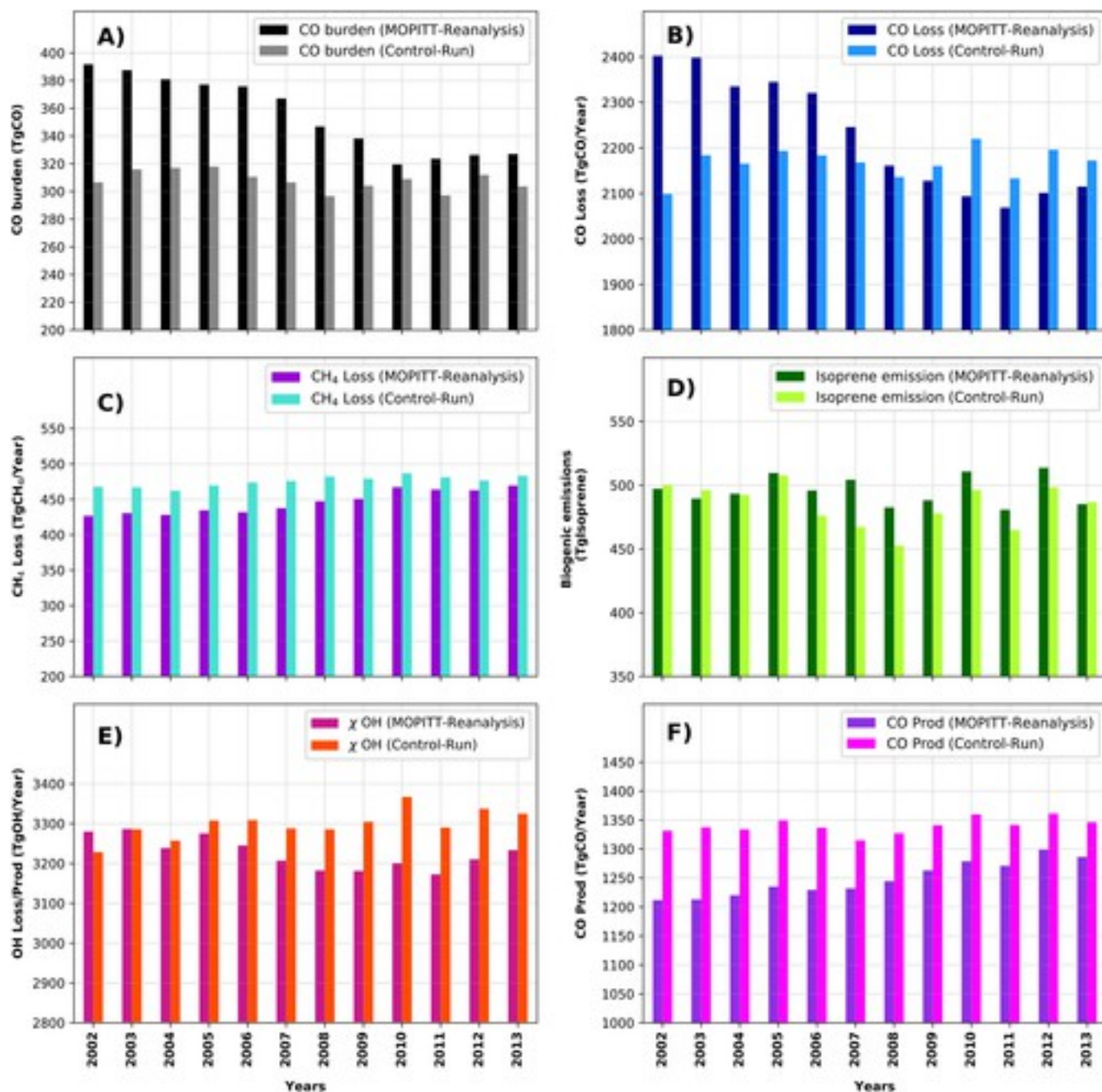$$\frac{d[CH_4]}{dt} = S_{CH_4} - R1; R1 = k_1[CH_4][OH] \tag{1}$$

$$\frac{d[CO]}{dt} = S_{CO} + R1 - R2; R2 = k_2[CO][OH] \tag{2}$$

$$\frac{d[OH]}{dt} = S_{OH} - R1 - R2 - R3; R3 = k_3[X][OH] \tag{3}$$

Although a more comprehensive reaction mechanism is represented in the full chemistry model, the key reactions of this coupling are the loss of CO and CH$_4$ due to OH reaction ($R2$ and $R1$). $R2$ representS the main sink of OH followed by $R1$. As mentioned, the surface [CH$_4$] for each year is prescribed in both simulations; therefore, the S$_{CH4}$ and $\frac{d[CH_4]}{dt}$ are forced. The surface emissions of CO (S_{CO}) are also the same in both simulations. Since [CO] is adjusted in MOPITT-Reanalysis through MOPITT assimilation, its time evolution of [CO] is not correlated with prescribed anthropogenic emissions ($R = -0.17$) and model-derived biogenic emissions ($R = -0.29$) as in the Control-Run ($R = 0.55$ and $R = 0.64$, respectively). The assimilation controls the CO burden in MOPITT-Reanalysis. The low correlation suggests that there needs to be adjustments in $S_{CO,}$ which is consistent with Strode et al.'s ([2016](#)) suggestion that model simulations using Representative Concentration Pathway (RCP)-based emissions fail to capture the observed trends in MOPITT CO over China. Observational constraints in [CO] also allow us to glean upon $R2$ and [OH], for which biases can feedback both to the time evolution of [CO] and [CH$_4$] (e.g., Strode et al., [2015](#)). Since evolution of [OH] is a fast process (in seconds), it can be easily buffered from perturbations in CO (e.g., Montzka et al., [2011](#); Lelieveld et al., [2016](#)), which has relatively moderate lifetime (in months) and CH$_4$, which has longer lifetime (in years). A change in $R2$ is usually compensated by a change in $R1$ and $R3$. Note that the full chemical system includes a large number of chemical species X, but isoprene is the most important one. The chemical response of a perturbation in OH sinks ($R1$, $R2$, and $R3$) can be nonlinear and can result to changes in S_{OH} in equation [3](#) (e.g., change of chemical regime).

Figure 1 shows a time series of annual global tropospheric CO burden and chemical production and loss rates from MOPITT-Reanalysis and Control-Run simulations. The assimilation led to an increase in total CO burden relative to the Control-Run (Figure 1a). Also, we find a larger average rate of decrease with time (−1.4% per year) for the global CO burden in the MOPITT-Reanalysis during this period (2002–2013) compared to the Control-Run (−0.01% per year). The steeper decline during this period (from ~380 TgCO to ~310 TgCO) is consistent with the observed trends in MOPITT (Worden et al., 2013). The two simulations converge during the last 4 years (2009–2013) to a small difference of ~10–20 TgCO since there is no long-term trend in the Control-Run. As has been suggested, the large difference in early 2000 is attributed to a likely underestimation of anthropogenic emissions for this period, while the small difference in later years is likely due to the decrease in CO emissions over East Asia and US (e.g., Jiang et al., 2017; Yin et al., 2015). As shown in Figure 1b, we find that $R2$ is highly controlled by [CO] in MOPITT-Reanalysis (with a time correlation of $r = 0.99$) which is more than in the Control-Run ($r = 0.65$). Higher [CO] leads to a larger CO loss ($R2 = 2400$ TgCO/yr) that is reduced following the temporal trend of [CO]. The loss of [OH] in $R2$ is the main pathway for a change in CO to impact the other species. The air mass-weighted tropospheric mean [OH] in MOPITT-Reanalysis across the time period is lower by 19% relative to Control-Run. This is reflected as lower magnitude of $R3$ and higher CH_4 lifetime ($\tau_{CH_4} = 1/k_1[OH]$) in MOPITT-Reanalysis (Figure 2) since [CH_4] is the same for both simulations. However, given that d[CH_4]/dt is prescribed, the steeper rate of increase with time in $R3$ and correspondingly a steeper rate of decrease in τ_{CH_4} (from 9.3 to 8.6 years) in MOPITT-Reanalysis strongly suggest that the rate of change in [CO] affects the rate of change in [OH] at shorter time scales. The Pearson's correlation coefficient between the annual global tropospheric decrease of [CO] and τ_{CH_4} is 0.99. In order to verify this hypothesis, we look at the time evolution of isoprene emissions (Figure 1d), the other main potential OH sink (X in $R3$). It shows no specific long-term change with an average rate of around −0.15%/yr. This result is consistent for both simulation despite the fact that isoprene emissions are obtained from the Community Land Model/Model of Emissions of Gases and Aerosols from Nature (CLM/MEGAN) model driven by two different meteorological fields. The sources of OH for a given year are equal to the sinks of OH which allows us to further analyze the impact of changes in CO and CH_4. From 2002 to 2009, Figure 1e shows a decreasing chemical flux of OH in MOPITT-Reanalysis, which could correspond to the tendency of having a lower OH sink, due to a slower rate of $R2$ that is not totally compensated by an increase in $R3$. Because of the small direct effect of increasing CH_4 and larger effects due to the chemical feedback resulting from decreasing [CO], the faster rate of increase in CH_4 oxidation leads to a faster rate of increase in CO chemical production over time (Figure 1f).

Figure 1

Global, annual, and tropospheric integrated (a, TgCO) CO burden, (b, TgCO yr^{-1}) CO chemical loss, (c, TgCH4 yr^{-1}) CH$_4$ loss, (d, TgIsoprene yr^{-1}) isoprene emissions, (e, TgOH yr^{-1}) OH chemical loss/production, denoted as χ, and (f, TgCO yr^{-1}) CO chemical production. The CH$_4$ lifetime (with regard to OH) is shown in Figure 1d and the air mass-weighted tropospheric mean OH is also plotted in Figure 1f.
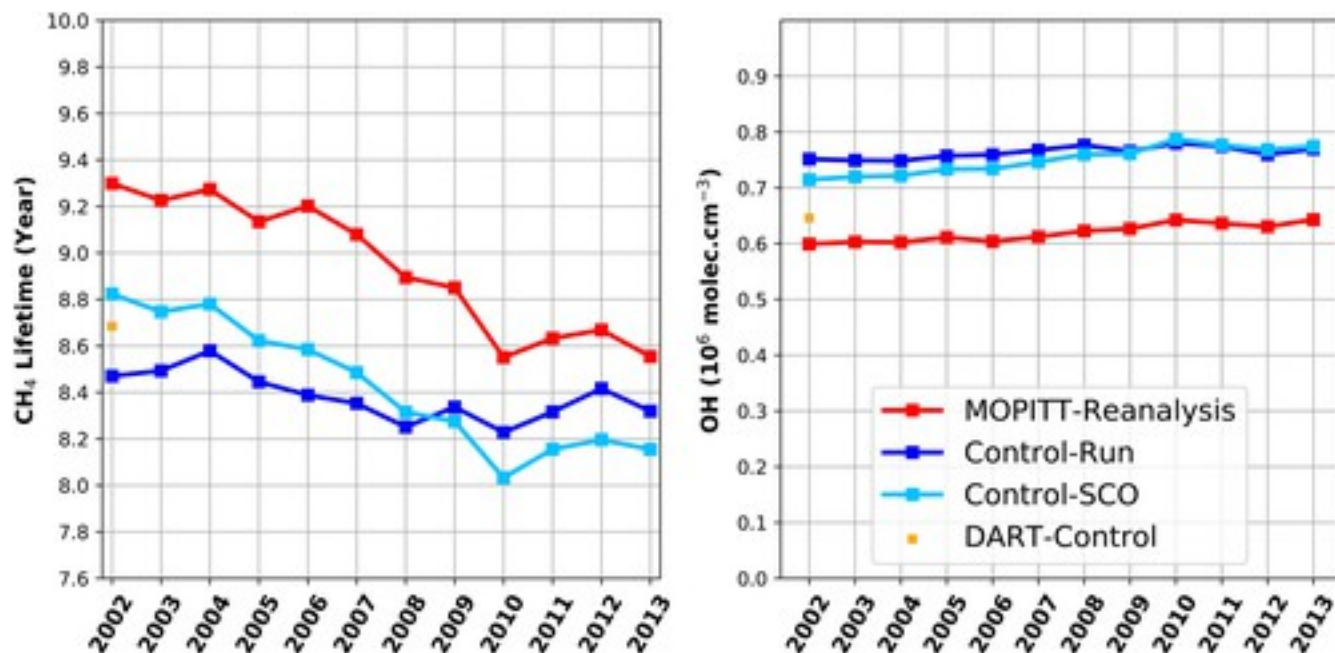
Figure 2
Open in figure viewerPowerPoint
(left) Yearly global integrated tropospheric CH$_4$ lifetime with respect to OH and (right) yearly global integrated tropospheric air mass-weighted OH calculated for all simulation experiments (MOPITT-Reanalysis, Control-Run, Control-SCO, and DART-Control) of this work.

We summarize in Figure 2 the resulting CH$_4$ lifetime and OH burden from simulations with DART meteorology with (MOPITT-Reanalysis) and without MOPITT assimilation (DART-Control). We contrast these patterns with simulations using MERRA meteorology with original CO (Control-Run) or forced CO (Control-SCO) from MOPITT assimilation. Note that the OH levels are higher in the CAM-Chem simulations forced by MERRA. We speculate that this is due to larger sources of OH (e.g., lightning NO$_x$ sources, water vapor, and radiation) but this would require further study. For both meteorological prescriptions in year 2002 (DART and MERRA), the increase in CO (MOPITT-Reanalysis and Control-SCO) leads to lower OH levels and an increased CH$_4$ lifetime. The time variation of those quantities strongly supports the hypothesis that the CH$_4$ lifetime is sensitive to the changes in CO. We find that the correlation of the CH$_4$ lifetime (CH$_4$ loss) between the MOPITT-Reanalysis and the initial Control-Run increases from 0.74 to 0.98 (0.86 to 0.98) when compared to the Control-SCO simulation. In the same manner, the correlation of OH changes from 0.81 to 0.98 while the correlation between the Control-Run and the Control-SCO is 0.88. The small change in [OH] with time and low interannual variability confirms that global [OH] is well buffered within the chemical system driven mostly by larger sets of sources and sinks (Figure 2, right) and because of the local nature of chemical perturbations (Montzka et al., 2011; Prather, 2007; Voulgarakis et al., 2013). We note however that [OH] shows a small positive trend with an average rate of 0.6%/yr for the

MOPITT-Reanalysis and 0.2%/yr for the Control-Run. This result is consistent with a negative trend of $R2$ and no particular temporal increase in isoprene. It means that the chemical scheme does not respond to the rate of decrease with time of $R2$ by only decreasing τ_{CH_4} but also suggests a local increase in [OH]. This positive trend in [OH] is consistent with other studies (Gratz et al., 2015; Dalsøren et al., 2016; McNorton et al., 2016). However, we consider that quantifying and explaining the OH trends is beyond the scope of this study since other relevant parameters such as air temperature, water vapor, ozone column, biomass burning emissions, and lightning NO_x emissions have not been analyzed in detail (e.g., Holmes et al., 2013). In the next section, we describe a more detailed analysis of the trends on the associated chemical fluxes of CO and CH_4.3.2 Trends over the tropics.

In all simulations, the tropics (between 30°S and 30°N) contributes to between 60 (summer) and 80% (winter) of both the global tropospheric CH_4 oxidation and the global CO chemical production (Figure S1 in the supporting information). There is also a large contribution to the CO chemical production from isoprene oxidation. In order to separate the long-term trends to the seasonal variations, we employ the Seasonal Trend decomposition using Loess (locally weighted scatterplot smoothing), or STL (Cleveland et al., 1990; Stephens et al., 2013). We apply this curve fitting algorithm to the tropospheric and tropical column of abundance of CO, the CO chemical production, the CH_4 chemical loss, as well as surface isoprene emissions estimated from CLM/MEGAN. This method presents the advantage of separating the trend and seasonal component from the original time series. Pickers and Manning (2015) evaluated three different curve fitting algorithms and showed that the STL is an efficient method with regard to the long-term trends and recommended to test the sensitivity of the input parameters. We compare a set of eight different combination of input parameters (Table S2, Figures S2, S3, and S4) and results presented in Figure 3 are the mean of the experiments, the linear trends were significant at a 95% interval for all experiments. We show in Figure 3 the long-term trend component of the tropical tropospheric CO abundance, CH_4 lifetime, CO chemical production, and CH_4 chemical loss. These chemical fluxes are integrated across the tropics for each month. Overall, these trends are consistent with the global statistics presented in the previous section. The [CO] between the MOPITT-Reanalysis and Control-SCO is almost identical, as expected since the CO fields are replaced every 24 h. The higher [OH] in the specified dynamic simulations (Control-Run and Control-SCO) leads to higher CH_4 chemical loss, increased CO chemical production, and a shorter CH_4 lifetime. However, we find that the trends in [CO], CH_4 lifetime, CO chemical production, and CH_4 loss are almost identical in the MOPITT-Reanalysis and Control-SCO runs. The reduction of [CO] across the period is remarkably well correlated with the CH_4 lifetime, supporting the surrogate mechanism presented above. The correlation coefficient between the

two times series is 0.99 for the MOPITT-Reanalysis (and Control-SCO) and 0.25 for the Control-Run. The correlation between CO chemical production and CH_4 loss ($R1$) is much higher in the MOPITT-Reanalysis and Control-SCO ($R = 0.99$) than in the Control-Run ($R = 0.61$) even though both simulations have the same CH_4 burden suggesting that the trend in CO chemical production is due to trend in CH_4 loss. We also find that globally the isoprene emission from MEGAN does exhibit a small and negative long-term trend in either simulation (Figure S3). We exclude the possibility of a positive trend from NMVOC emissions from biogenic sources. Our results confirm that the assimilation of CO measurements, which by forcing OH to be higher, is increasing the CH_4 loss. These long-term trends provide strong evidence of a positive trend of 0.27 $TgCH_4$/yr for the CH_4 chemical loss and 0.38 TgCO/yr for CO chemical production in the MOPITT-Reanalysis and Control-SCO. In contrast, the trends in CH_4 loss obtained by the prescribed fields of the Control-Run are 0.11 $TgCH_4$/yr. This means that the reduction of CO induced a twice faster rate of increase in CH_4 loss. This has obvious implications with regard to inferring S_{CH4} from dCH_4/dt in equation 1.
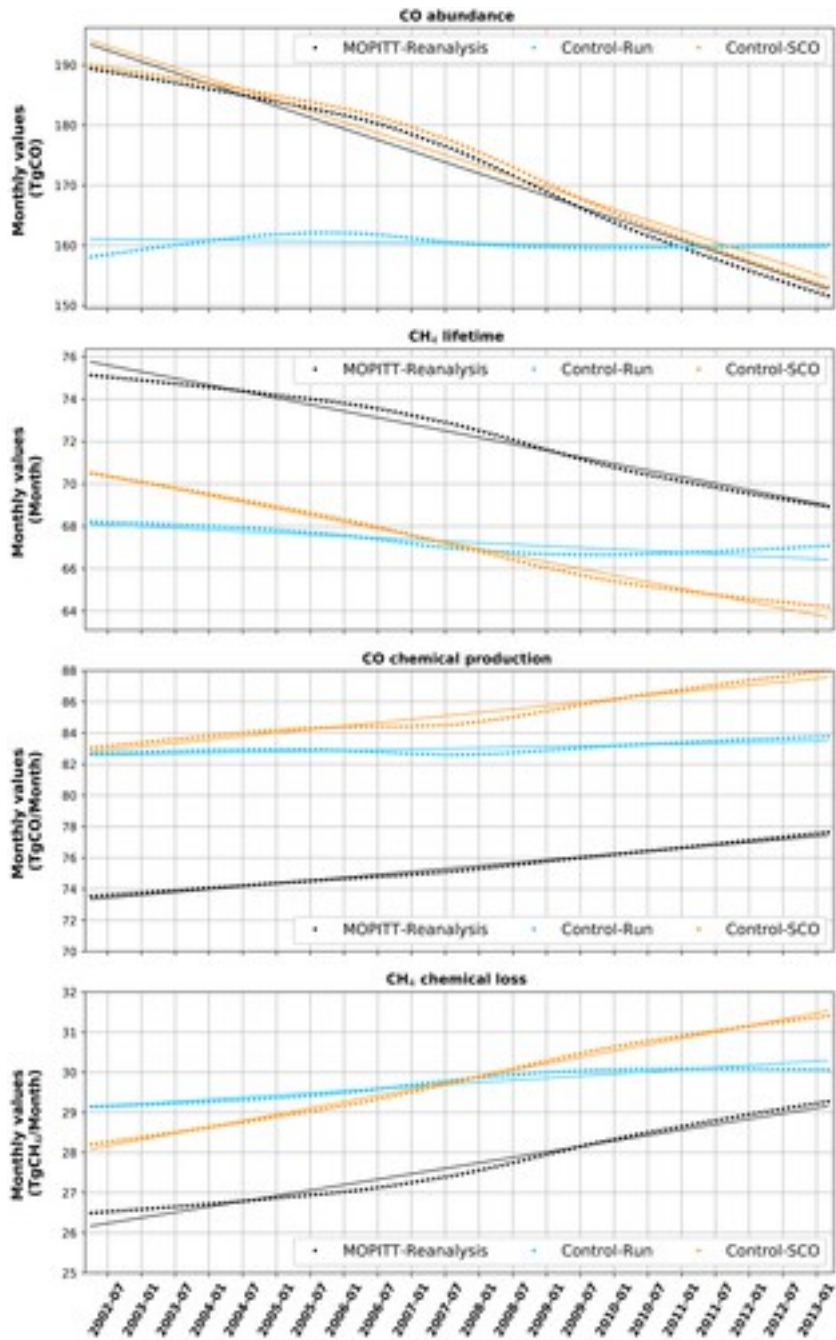
Figure 3
Trend component of the tropical and tropospheric column integrated column of CO burden (TgCO yr^{-1}), CH$_4$ lifetime (months), CO chemical production (TgCO yr^{-1}), and CH$_4$ chemical loss (TgCH$_4$ yr^{-1}) from three simulation experiments.

4 Discussion and Implication for CH$_4$ Studies

CH$_4$, CO, and OH are in a tight chemical coupling, and numerous efforts have been made to model these species in an integrated framework (e.g., Elshorbany et al., 2016), including using

data assimilation (e.g., Pison et al., 2009). It is frequent in CH_4 inversions that the chemical feedback from CO to CH_4 is neglected, mostly because of the use of archived OH fields (Houweling et al., 2016). Our results indicate that chemical feedbacks have to be considered in forward and inverse modeling of CH_4. The explicit modeling of all of those parameters is challenging and some fields are usually prescribed, which is also the case in this study for CH_4. While our results point to the role of OH in identifying the contribution of chemical feedbacks in CH_4 burden (i.e., chemical oxidation of CH_4), explicitly quantifying this role is very challenging given the strong nonlinear coupling of OH with tropospheric constituents at multiple scales. We have elucidated this effect by presenting the relative response of CH_4 loss to changes in the sinks of OH. This is facilitated by contrasting a simulation where CO and CH_4 burden are constrained (MOPITT-Reanalysis/Control-SCO) with a simulation where only CH_4 is constrained (Control-Run). In addition to those constraints, [OH] is explicitly calculated using a full gas-phase chemistry scheme with online coupling of physics and dynamics. These explicit calculations are important in representing short-term variations in OH and associated chemical regimes which can occur at multiple scales, allowing us to understand CO and CH_4 losses as well as CO chemical production.

Anthropogenic emissions of CO have been shown to be drastically reduced drastically in recent decades since the launch of MOPITT (Jiang et al., 2017; Yin et al., 2015), while the CH_4abundance has increased at a faster rate since 2006 (Nisbet et al., 2016). Although the annual-average OH burden is lower in the MOPITT-Reanalysis/Control-SCO relative to Control-Run (as an effective response to higher CO burden after data assimilation), there is very little difference in the rate of change of OH burden with time in both simulations at this time scale. Since [OH] is in steady state on time scales relevant to CO (and CH_4) oxidation and is well buffered among the numerous perturbations, it is found that annual-average [OH] does not exhibit a significant long-term increase or large interannual variability across the period considered here. However, perturbations and/or variations in the OH sources and sinks have cascading net effects on the integrated fluxes of CH_4 loss (and lifetime). Representing [OH] variations is crucial to understanding the CH_4 budget and consequently the CO budget. Hence, the increase in CO chemical production and CH_4 loss with time in the MOPITT-Reanalysis reflects this cascading net effect. This feedback of increased CO chemical production (of around 7%) due to a reduction in CO emissions is shown here for the first time. Future work will aim to improve estimation of [OH] sources and sinks using a more detailed chemical scheme, and the simultaneous assimilation of multiple relevant species (O_3, NO_2, CH_2O, and CO) (e.g., Miyazaki et al., 2015). Using global and tropospheric statistics, we demonstrate that the decrease in CO abundance of about 20% (at the global scale) in 12 years has a significant impact on overall CO-

OH-CH$_4$ coupled system. The decreases in CO anthropogenic emissions in recent decades (around 20%) results in enhanced CH$_4$ loss (almost 10%) and shorter lifetime (8% or 9 months) and also implies that the observed growth rate in CH$_4$ (equation 1) is influenced by the decrease in CO emissions (S_{CO}). We infer from our analysis that the growth rate in CH$_4$ would be most likely higher if CO had not decreased over the past decade and assessments of CH$_4$ emissions need to account for this effect. This has broad implications for the ongoing scientific debate on the causes of observed CH$_4$ growth.

Acknowledgments