

Effects of Interactive Hydroxyl Chemistry on Decadal Methane Emissions Estimates

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The rise of atmospheric methane experienced a brief pause between 2000 and 2007 with a subsequent resumption in growth continuing to the present day. Questions on both the commencement and termination of this stabilization remain open due to uncertainty in methane sources and its main sink, reaction with the hydroxyl radical (OH). In the atmosphere, methane undergoes oxidation reactions and thus, its lifetime depends on the concentration of hydroxyl radicals. Methyl Chloroform has been used to constrain global hydroxyl concentrations and infer methane lifetimes. Here, we report on results using a two-hemispheres box model that includes dynamic chemistry of methane, carbon monoxide, and the hydroxyl radical. We will discuss the impact of critical assumptions on methane flux inversions: 1) Constant OH concentrations and 2) Constant OH sources with interactive chemistry assuming constant or variable CO, 3) variable OH sources, 4) variations in OH inter-hemispheric gradients. Hemispheric sources are calculated from a nonlinear, stochastic Bayesian inversion constrained by data from methane (NOAA), carbon monoxide (NOAA), and Methyl chloroform (NOAA, GAGE/AGAGE) observations. We perform sensitivity experiments by calculating the impact that including each aspect of the chemical system has on the emissions estimates. Based on our results, we find that when ignoring interactive OH chemistry, methane emissions have a negative bias at the beginning of the 21st century, during negative OH anomalies. How-

ever, when CO emissions are accounted for, the reduction in CO emissions beginning in the 1990s results in increasing methane emissions but relatively higher OH concentrations; this is due to CO emissions decreasing during this period. We also find that when account for a variable OH source, our results agree with those found in [Turner et al., 2017, @].

1. Introduction

The steady rise of methane concentrations in the Earth's atmosphere was interrupted by a brief stabilization from 2000 to 2007 with a subsequent resumption in growth; the causes of the onset and renewed growth remain ambiguous. Overall, methane concentrations have tripled from 750 ppb in 1850 to 1850 ppb in the present day [IPCC, 2014, @]. Methane is not only the second most important anthropogenic greenhouse gas but also a precursor to tropospheric ozone, itself a greenhouse gas and air pollutant [Fiore et al., 2006, @; Shindell et al., 2012, @; IPCC, 2014, @]. Its sources are spatially and temporally heterogeneous and its sinks can also be variable, resulting in major uncertainties in determining the cause of the stabilization.

Changes in methane sources have been proposed as possible explanations for the cause of the renewed growth. Major sources include microbial production in wetlands, permafrost melting in the high latitudes, biomass burning, rice cultivation, solid and liquid waste, and activities related to fossil fuel extraction. A shift in global $\delta^{13}\text{C}$ towards more depleted carbon indicates that the end of the stabilization could have been driven by a change in methane sources [Bousquet et al., 2006, @; Kai et al., 2011, @].

Biogenic sources favor lighter C and a shift towards more depleted $\delta^{13}\text{C}$ can indicate either an increase in isotopically lighter, e.g. biogenic, sources or a decrease in heavier, e.g. pyrogenic and thermogenic, sources [Nisbet et al., , @; Schaefer et al., 2016, @]. An analysis by [Nisbet et al., , @] concludes that a shift towards lighter isotopes demonstrate an increase in wetland emissions, while [Schaefer et al., 2016, @] conclude that the isotopic shift is due to increased emissions from agricultural production. Yet, the change in the isotopic composition can also have been caused by a decrease in biomass burning sources, which are isotopically heavy, alongside an increase in fossil fuel sources, which are generally lighter than biomass burning sources and heavier than biogenic sources; [Worden et al., 2017, @] concludes this. These studies came to different conclusions with the same constraints indicating that the problem may be undetermined.

Other studies have focused on a change in the methane sink. Methane loss is primarily driven by oxidation via OH radicals but also transport to the stratosphere, consumption by methanotrophic microbes in soils, and oxidation by chlorine radicals. The Hydroxyl Radical accounts for about 90% of methane loss and thus is the main mechanism of methane loss in the troposphere. [Turner et al., 2017, @] and [Rigby et al., 2017, @], using Methyl Chloroform (MCF) as a proxy

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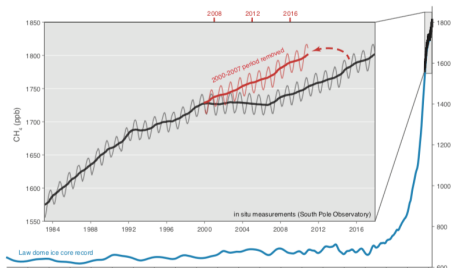


Fig. 1. Observations of atmospheric methane over the past 2000 years. Low dome ice core record (blue; 4) and direct atmospheric observations from the South Pole (black; de-seasonalized in gray; 6). Red line illustrates if the 7-year stabilization period is removed.

Figure 1. Plotted is a timeseries of methane concentrations collected through ice core measurements from the last 2,000 years. On the right, decadal scale concentrations are shown with focus on the Methane Stabilization.

for Hydroxyl Radical concentrations, conclude that changes in hydroxyl concentrations occurred during the stabilization period. Yet, their conclusions differ. [Rigby et al., 2017, @] conclude that a decline in Hydroxyl concentrations accompanied by a slow-down in the methane growth rate was implicated in the renewed growth, while [Turner et al., 2017, @] find that the renewed growth was caused by a decline in Hydroxyl radicals with a decrease in methane emissions. Yet, a causal mechanism for a decrease in hydroxyl concentrations has not been found. Quantifying the effect of dynamical Hydroxyl concentrations on methane emissions estimates provides a useful constraint on the methane stability problem.

The relationship between methane concentrations and emissions is nonlinear; this increases the complexity of the system and makes emissions estimates more difficult. Methane is a short lived greenhouse gas with a lifetime of approximately a decade. However, its lifetime primarily depends on the concentration of the Hydroxyl Radical, e.g. higher concentrations of OH results in a shorter methane lifetime. In addition, the oxidation of methane yields carbon monoxide which also consumes hydroxyl radicals [Prather, 2007, @]. Previous studies use MCF to constrain methane lifetime [Rigby et al., 2017, @; Turner et al., 2017, @]. We instead account for variable methane lifetime by including dynamic CH₄, CO, and OH chemistry in our model. The objective of the present study is to quantify the systematic biases when including (excluding) variable methane lifetimes and thus interactive chemistry in the estimation of emissions.

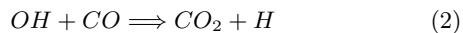
Here, we include interactive methane chemistry in our inversions by using a two hemispheres box model with CH₄, CO, and OH chemistry. We will discuss the impact of critical assumptions on methane flux inversions: 1) Constant OH concentrations and 2) Constant OH sources with interactive chemistry assuming constant or variable CO, 3) variable OH sources, 4) variations in OH inter-hemispheric gradients. Section 2 provides the theoretical background for the variability of methane lifetimes, Section 3 describes the model and data employed in the current study, and in Section 4, we discuss the conclusions of the study and provide recommendations for future work in methane emissions estimates over the decadal timescale.

2. Theoretical Background and Forward Model

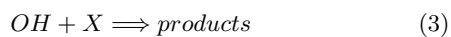
We use the model developed by [Prather, 1996, @; Prather, 1994, @] in the development of our forward model. In the atmosphere, the hydroxyl radical is the primary mechanism of methane loss.



CO is the largest sink of OH in the troposphere and thus, the concentration of OH depends on both the concentrations of CH₄ and CO.



In addition, the hydroxyl radical also reacts with other compounds in the atmosphere such as ethane, propane, and other non methane hydrocarbons in addition to being recycled with the emission of NO_x. Therefore, we create another OH loss reaction that abstracts this complexity with an arbitrary group of molecules X [Prather, 1996, @; Prather, 1994, @].



These reactions form the OH loss terms in our box model. From these reactions and their kinetics, we can form a set of coupled differential equations:

$$R_1 = k_1[OH][CH_4] \quad (4)$$

$$R_2 = k_2[OH][CO] \quad (5)$$

$$R_3 = k_3[OH][X] \quad (6)$$

$$\frac{d[CH_4]}{dt} = S_{CH_4} - R_1 - \frac{\Delta[CH_4]}{\tau} \quad (7)$$

$$\frac{d[CO]}{dt} = S_{CO} + R_1 - R_2 - \frac{\Delta[CO]}{\tau} \quad (8)$$

$$\frac{d[OH]}{dt} = S_{OH} - R_1 - R_2 - R_3 - \frac{\Delta[OH]}{\tau} \quad (9)$$

Above, $\Delta[c]$ is the difference in the concentration of species c between the Northern and Southern Hemispheres, τ is the inter hemispheric exchange timescale, 1 yr, and hence, $\Delta[c]/\tau$ is the inter hemispheric transport term. Finally, S_c is the source term which represents the emission of the species c and in the case of OH, represents the production rate. These equations are computed in our forward model.

As a test of our forward model, we run the model with prescribed emissions. We then add a 50

3. Methods

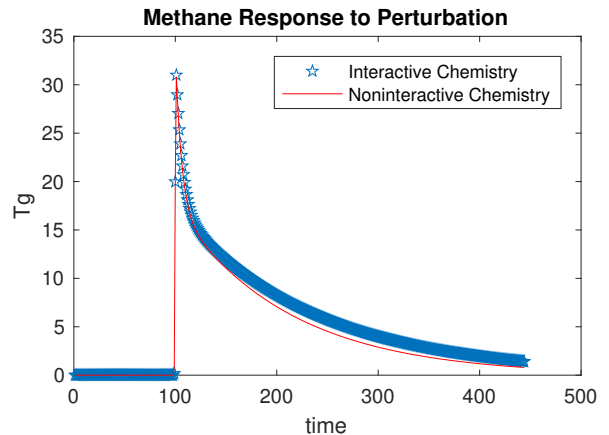
3.1. Data and Inversion

Our box model (section 2) maps emissions to concentrations and thus, by inverting our model, we map concentrations to emissions. Emissions are estimated using a non-linear bayesian inversion method, the Levenberg-Marquardt algorithm. We use observations of methane (NOAA), carbon monoxide (NOAA), and Methyl chloroform (NOAA, GAGE/AGAGE) concentrations.

Concentration measurements began in 1983 and continue into the present day. For our inversions, we take hemispheric averages by bootstrapping the deseasonalized data. These observations are combined by block averaging in 1 yr windows to form a timeseries. This process is repeated 50 times so that the mean and variance of these timeseries can be calculated. The data are then inputted into our inversion and emissions are derived by minimizing the cost function with our box model as the forward model.

3.2. Simulations

We first perform an idealized inversion test by globally prescribing fixed emissions until an arbitrary year and pre-



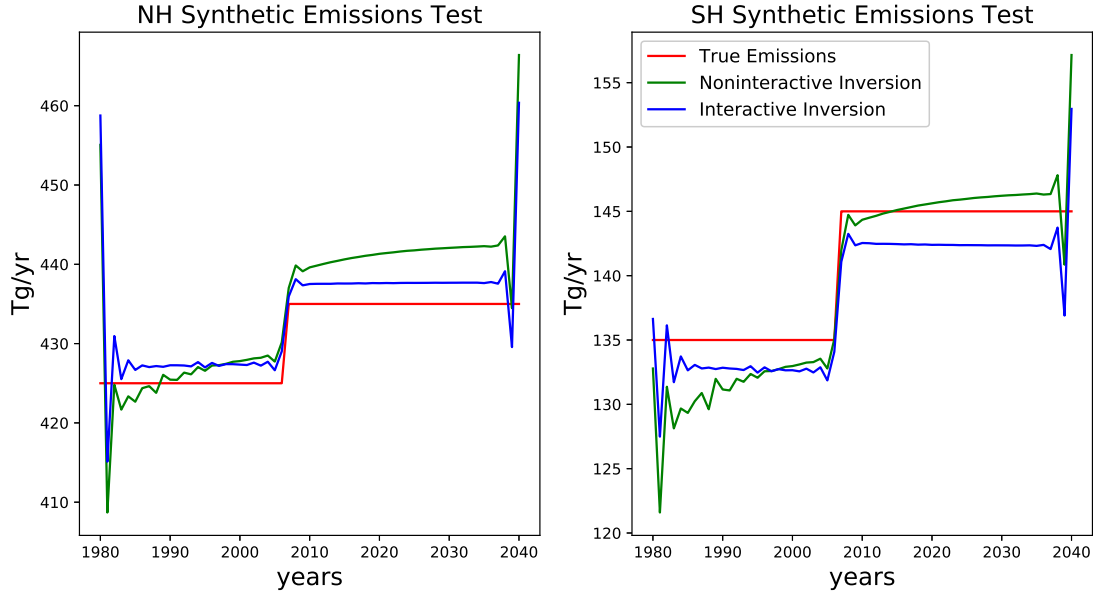


Figure 2. A test of our inversion. We prescribe emissions and increase it by 20 Tg/yr to test our inversion. We then run our inversion with interactive OH chemistry and non interactive OH chemistry

scribe an increase emissions by 20 Tg/yr in our forward model with interactive OH chemistry. The resulting concentrations are inverted for emissions in two different runs where we A), assume non interactive OH chemistry and B), assume interactive OH chemistry. This test serves two purposes: 1), We can test the performance of our inversion and 2), we can calculate the error when concentrations, calculated with interactive OH chemistry, are inverted for emissions while neglecting interactive OH chemistry. This is equivalent to computing the forward model error of using a simple fixed OH concentration in atmospheric methane inversions, which is common practice.

From the results of our Synthetic Emissions Test, Fig. 2, we find that the forward model error when not accounting for interactive OH chemistry is in close agreement with the prescribed emissions. This implies our inversion is accurately solving for emissions despite the added complexity to the forward model. However, the inversion without interactive OH chemistry begins changing sign when the prescribed emissions spike begins Fig. 2. This is due to the fact that increased Methane emissions decrease Hydroxyl concentrations. The noninteractive OH inversion does not account for this OH concentration response and results in an underestimation in an atmosphere with higher OH concentrations and an overestimation in an atmosphere with lower OH concentrations. This is discussed further in Section 4.

In addition, we run our inversions with increasing levels of complexity in order to obtain the biases associated with including (excluding) interactive OH chemistry and carbon

monoxide in emissions estimates. 1 shows the model runs. In our experiments, Case 1, our simplest run, assumes fixed OH concentrations (non interactive chemistry). Case 2 assumes fixed CO and OH sources with interactive chemistry while Case 3 accounts for the temporal variability of CO sources. Case 4 incorporates the variability of OH sources without variable CO sources while Case 5 accounts for the temporal variability of CO sources with variable OH sources. The results of these runs are plotted in Fig. 3.

4. Discussion

In this study, we estimated global methane emissions in a 2 hemispheres box model and quantify the biases associated with critical assumptions in decadal methane emissions estimates between the years 1980 to 2016 (Table 1). When excluding interactive OH chemistry, (fig. xx), our results indicate a bias that depends on the availability of OH radicals in the atmosphere.. When not accounting for interactive OH chemistry, higher OH concentrations result in a negative bias and low OH concentrations result in a positive bias. This can be seen in Fig xx where increased methane emissions at the turn of the century decrease the amount of OH radicals and an overestimation of emissions (Fig. 4). In case 1, with fixed OH concentrations, methane emissions increase by 6.6% between 1996 and 2016. In case 2, methane emissions increase by 6.9% while global mean OH concentrations decrease by 0.95%.

when CO emissions are increasing before the 1990s, increased emissions caused a decrease in OH concentration and a reduced estimation of methane emissions. However, with the decrease in CO emissions beginning in the 1990s, we see an increased availability of OH radicals to oxidize Methane, and hence, decreasing Methane lifetime results in increasing Methane emissions to match observations (Fig. 5-3. In case 3, global methane emissions increase by 7.4% with a decrease in OH concentrations by 0.5% between 1996 and 2016. This indicates that the reduction in CO more than compensates for the increased methane emissions in OH loss.

Table 1. Our simulations vary in complexity. Below are the assumptions in each model run.

Case	Interactive OH	Inverting with CO	Inverting for OH Source
1	no	no	no
2	yes	no	no
3	yes	yes	no
4	yes	no	yes
5	yes	yes	yes

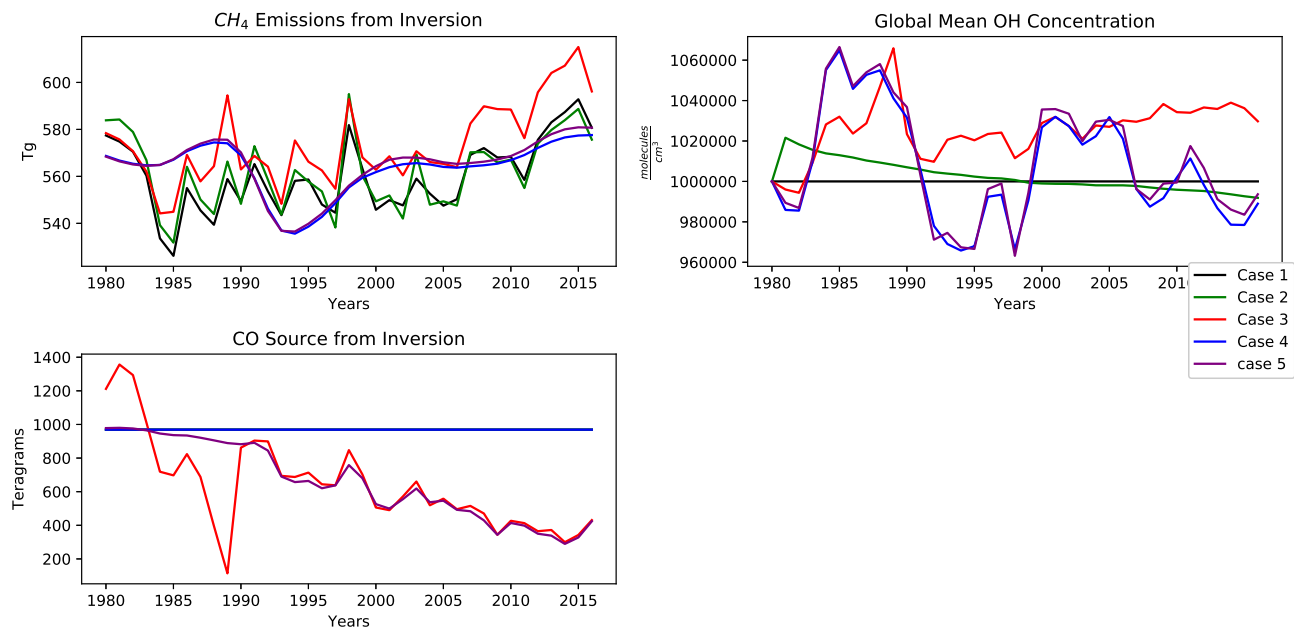


Figure 3. Plotted are the results from our inversion for all five cases in Table 1. Calculated methane emissions are on the top left panel, CO emissions are on the top right panel, and OH concentrations are on the bottom left panel.

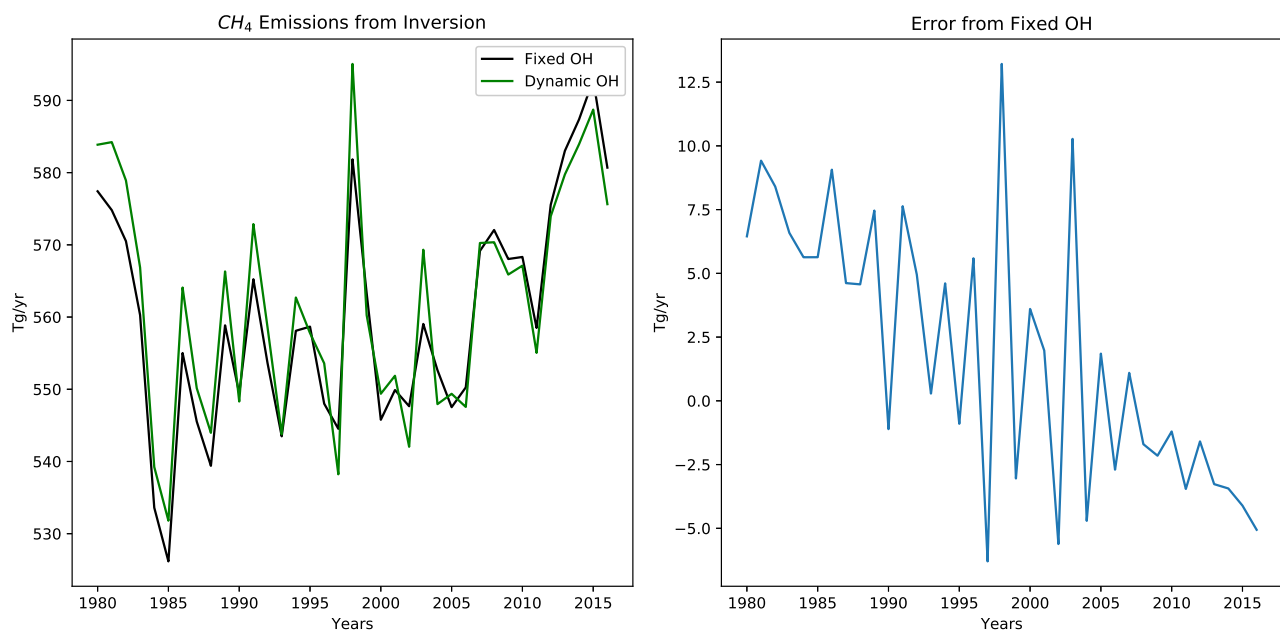
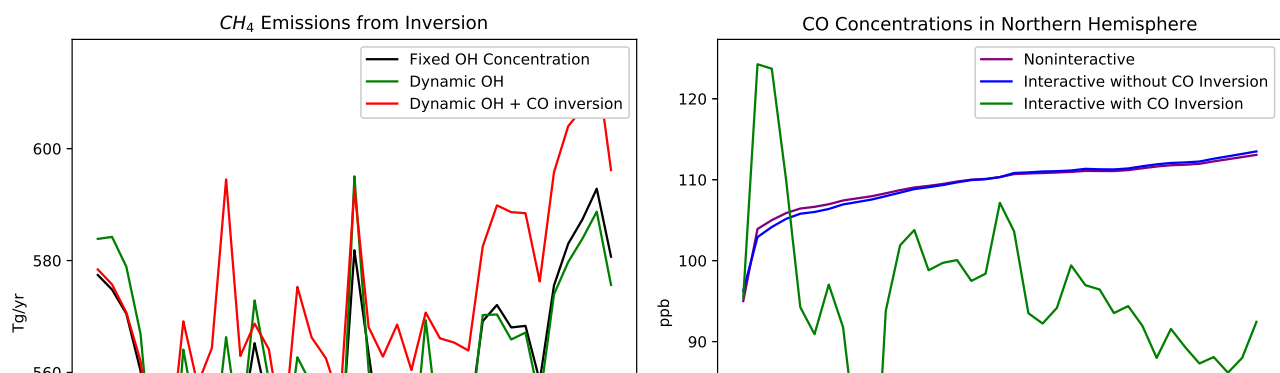


Figure 4. Above are inversion results from ignoring interactive OH chemistry (Case 1) and accounting for interactive OH chemistry with assuming a fixed CO emission (Case 2). The left panel shows calculated emissions from 1980 to 2016. The right panel shows the difference in CH_4 emissions with the assumptions outlined in Table 1.



in both cases is small. They also generally agree with the solution obtained by [Turner et al., 2017, @].

In summary, we find that not accounting for interactive OH chemistry and the variability of CO emissions biases the results of methane emissions estimates in opposing ways. Methane lifetime depends on the concentration of the Hydroxyl Radical which, in turn, depends on the concentration of CO and CH₄. In decadal Methane emissions estimates, we find a systematic negative bias in inversions that do not account for this chemical system. This is due to the decline of CO emissions starting in the 1990s overcompensating for the loss of OH due to CH₄. However, when allowing for a varying OH source term, our results match that of [Turner et al., 2017, @] because of compensating OH production accounting for variabilities in OH concentrations due to interactive chemistry.

We conclude that future work in estimating methane emissions in the decadal timescale should account for the interactive OH chemistry that takes place in the troposphere, and more work should be done to constrain trends in the concentration and production of Hydroxyl radicals due to its effect on the methane lifetime.

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