Effects of Hydroxyl Radical Chemistry on Methane Emissions Estimates

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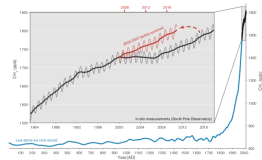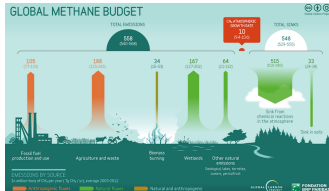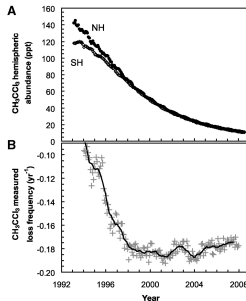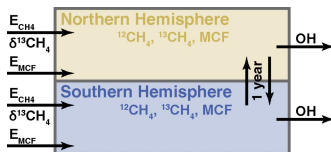- Second strongest anthropogenic greenhouse gas
- Precursor to tropospheric ozone

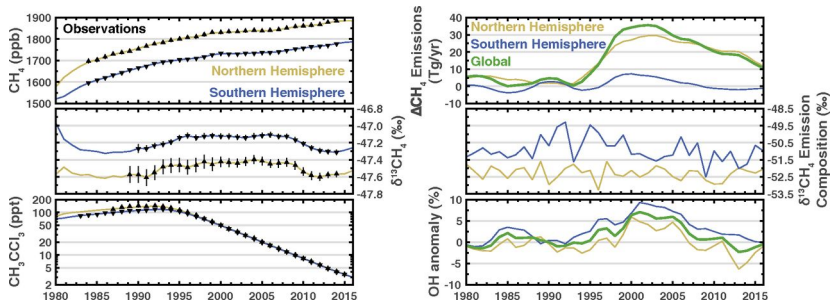- The Hydroxyl Radical (OH) is the main sink of methane in the troposphere
- OH is produced through photolysis
- MCF is used as a proxy for OH

The Box Model Approach

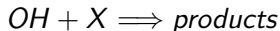## Most Likely Solution

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

- Inverted for S_{CH_4} based on observed $[CH_4]$ and infered values of [OH]
- Most likely solution is a 25 Tg/yr decrease in S_{CH_4} with a 7% decrease in [OH]

Chemical System

$$OH + CH_4 \implies (multiple\ steps) \implies CO + products$$
$$OH + CO \implies CO_2 + H$$
$$OH + X \implies products$$
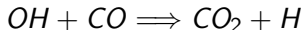
$$R_1 = k_1[OH][CH_4]$$
$$R_2 = k_2[OH][CO]$$
$$R_3 = k_3[OH][X]$$

- R_i is reaction rate (loss of reactants)
- K_i reaction rate constant (impirically obtained)
- x represents other sinks of OH

The System of Equations
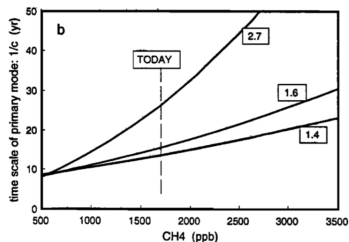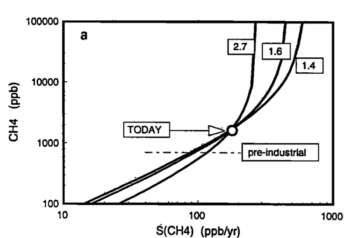
$$R_1 = k_1[OH][CH_4]$$
$$R_2 = k_2[OH][CO]$$
$$R_3 = k_3[OH][X]$$

$$\frac{d[CH_4]}{dt} = SCH_4 - R_1$$
$$\frac{d[CO]}{dt} = SCO + R_1 - R_2$$
$$\frac{d[OH]}{dt} = SOH - R_1 - R_2 - R_3$$

CH4 concentrations as a function of emission (left) and CH4 lifetime as a function of concentration. The system behaves nonlinearly at higher concentrations.
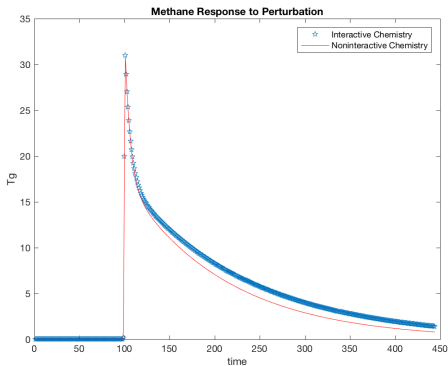
A test of our forward model by adding a large methane perturbation. The perturbation decays with a 13 year lifetime in the interactive chemistry case as compared to a 9 year lifetime in a noninteractive case.

- What is the effect of adding interactive chemistry (variable OH) on methane emissions estimates?
- What is the effect of adding CO+OH chemistry to our inversion?

- A test of the inversion with and without interactive OH chemistry
- Test

Adding Interactive OH
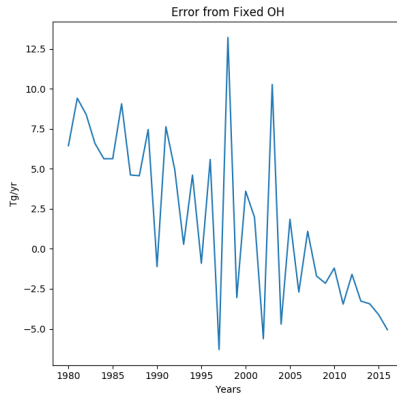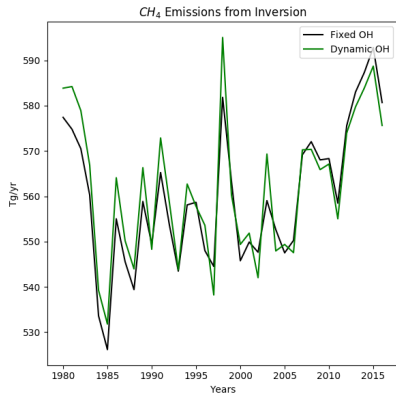
Results from inversion for both interactive and noninteractive OH chemistry. The trend is due to OH decreasing into the the 21st century.

Effects of Including CO
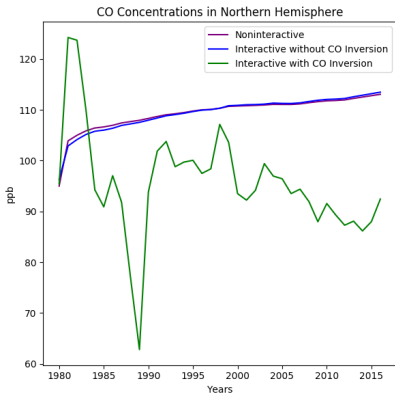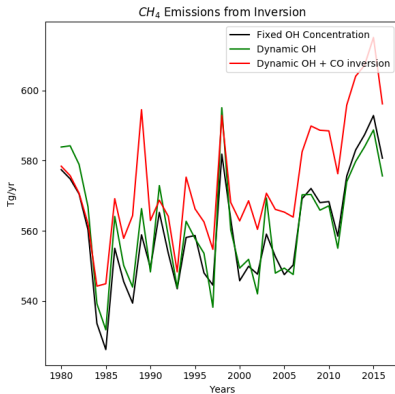
Methane emissions estimates with the inclusion of CO (left) and CO concentrations for each run in the northern hemisphere (right).

Key Conclusions

- Methane emissions estimates are biased to higher values when not accounting for interactive OH chemistry
- Methane emissions estimates are highly sensitive to CO concentrations

Mathematical formulation

$$\frac{d[CH_4]}{dt} = SCH_4 - R_1$$

$$\frac{d[CO]}{dt} = SCO + R_1 - R_2$$

$$\frac{d[OH]}{dt} = SOH - R_1 - R_2 - R_3$$

- Let $\mathbf{A}(V)$ be the matrix that represents the differential equation above
- Let V be the vector of concentrations of species and δV be a purturbation

$$[CH_4] \qquad [CO] \qquad [OH]$$

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$$[CH_4] \qquad [CO] \qquad [OH]$$

$$\frac{dV}{dt} = \mathbf{A}(V)$$

Remember Objective: Understand methane nonlinear variability

Hartmann-Brodman Theorem

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Hartmann-Grodman Theorem

A dynamical system near it's equalibrium point can be accurately represented by a linear Taylor Expansion in the neighborhood of its equalibrium. Additionally, from the expansion, Eigenvalues of the Jacobian correspond to the stability of the system and the Eigenvectors correspond to the modes of the system.
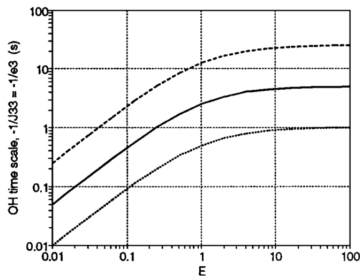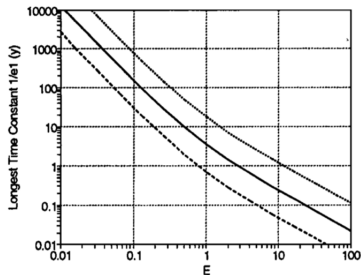
Derivation

$$\frac{dV}{dt} = \mathbf{A}(V)$$

$$\frac{d(V + \delta V)}{dt} = \frac{dV}{dt} + \frac{d\delta V}{dt} = \mathbf{A}(V + \delta V) = \mathbf{A}(V) + J\delta V$$

- $\mathbf{J}$ is the Jacobian Matrix
- Eigenvalues of $\mathbf{J}$ correspond to inverse of species lifetimes
- Eigenvectors correspond to modes

$$\mathbf{J} = \begin{matrix} \frac{\partial(d[CH_4]/dt)}{\partial[CH_4]} & \frac{\partial(d[CH_4]/dt)}{\partial[CO]} & \frac{\partial(d[CH_4]/dt)}{\partial[OH]} \\ \frac{\partial(d[CO]/dt)}{\partial[CH_4]} & \frac{\partial(d[CO]/dt)}{\partial[CO]} & \frac{\partial(d[CO]/dt)}{\partial[OH]} \\ \frac{\partial(d[OH]/dt)}{\partial d[CH_4]} & \frac{\partial(d[OH]/dt)}{\partial[CO]} & \frac{\partial(d[OH]/dt)}{\partial[OH]} \end{matrix}$$

Methane Lifetime

- Left: Methane lifetime $1/e_1$ as a function of E, excess OH.
- Right: OH lifetime as a function of reaction rate