Sources of Atmospheric Methane

Global Anthropogenic CH₄ Budget by Source in 2000

Methane Sources

- Enteric Fermentation: 16%
- Coal & Oil Mining/Natural Gas: 19%
- Methane: 22%
- Termites: 4%
- CH₄ Hydrates and Ocean: 3%
- Animal Waste: 6%
- Landfills: 6%
- Biomass Burning: 4%
- Rice Cultivation: 12%
- Fuel Sat. & mobile: 10%
- Waste water: 13%
- Coal: 8%
- Oil: 1%
- Rice: 11%
- Manure: 4%
- Enteric fermentation: 28%
- Biomass burning: 6%
- Biofuel combustion: 4%
- Known: 96%
- Unidentified: 4%

Total CH₄ emissions in 2000 = 260 Tg CH₄

Atmospheric Chemistry Lecture 15
Methane is produced by anaerobic decomposition of organic matter

Floated Rice Paddy

Methane oxidation:
\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

Methanogenesis:
- Hydrogenotrophic:  \[ \text{CO}_2 + 4 \text{H}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CH}_4 \]
- Acetotrophic:  \[ \text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4 \]
Sources of Methane: Natural Gas Deposits
Sources of Methane: Clathrates or Natural Gas Hydrates
Atmospheric Methane History

- Graph showing the increase in methane parts per billion (ppb) from 1978 to 2010.
- Data points indicating a steady increase with some fluctuations.

Atmospheric Chemistry Lecture 15
CO₂ and CH₄ exhibit similar behavior over ice-age time scales.
Global Distribution of Atmospheric Methane
NOAA ESRL GMD Carbon Cycle

Three dimensional representation of the latitudinal distribution of atmospheric methane in the marine boundary layer. Data from the GMD cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Ed Dlugokencky, NOAA ESRL GMD Carbon Cycle, Boulder, Colorado, (303) 497-6228 (ed.dlugokencky@noaa.gov, http://www.cmdl.noaa.gov/ccgg).
Basic Oxidation of Methane

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

But, CH\(_4\) in a container with O\(_2\) will not burn unless ignited

What starts the “burning” in the free atmosphere?

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]

Hydrogen abstraction by the free radical OH
Methane Oxidation (continued)

Methyl radical adds an $O_2$ to make methyl peroxy

\[ CH_3 + O_2 + M \rightarrow CH_3O_2 + M \]

Two things can happen to methyl peroxy

\[ CH_3O_2 + NO \rightarrow CH_3O + NO_2 \]

or

\[ CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \]
Methane Oxidation (continued)

Ignore second channel to CH₃OOH for the time being:
CH₃O reacts rapidly with O₂ to lose another hydrogen atom

CH₃O + O₂ → CH₂O + HO₂

CH₂O is a relatively stable molecule, formaldehyde
Summarizing thus far

\[
\begin{align*}
  &\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
  &\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \\
  &\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
  &\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \\
\end{align*}
\]

\[
\begin{align*}
  \text{CH}_4 + \text{OH} + 2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2 + \text{H}_2\text{O}
\end{align*}
\]
What happens to formaldehyde?

Several pathways

Photolysis

\[ \text{CH}_2\text{O} + \text{hv} \rightarrow \text{CHO} + \text{H} \]
\[ \text{CH}_2\text{O} + \text{hv} \rightarrow \text{CO} + \text{H}_2 \]

or reaction with OH

\[ \text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O} \]

CHO reacts with \( \text{O}_2 \) to form CO

\[ \text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \]
Carbon monoxide, CO is a product of the oxidation of methane

All channels led to the formation of CO: depending on pathway, either H\textsubscript{2} was formed or 2 HO\textsubscript{2}

CO the reacts with OH to form CO\textsubscript{2}

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}
\]

and we have completely oxidized the carbon atom
Summarizing the second part of the oxidation (from formaldehyde)

\[
\begin{align*}
\text{CH}_2\text{O} + \text{hv} & \rightarrow \text{CHO} + \text{H} \\
\text{CHO} + \text{O}_2 & \rightarrow \text{CO} + \text{HO}_2 \\
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \\
2\text{x: H + O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{CH}_2\text{O} + 3\text{O}_2 + \text{OH} & \rightarrow \text{CO}_2 + 3\text{HO}_2 \\
\text{CH}_2\text{O} + \text{hv} & \rightarrow \text{CO} + \text{H}_2 \\
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{CH}_2\text{O} + 2\text{O}_2 + 2\text{OH} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{HO}_2 \\
\text{The net HO}_x \text{ formed will eventually combine via } \text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]
What have we done?

\[ \text{CH}_4 + \text{OH} + 2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2 + \text{H}_2\text{O} \]

\[ \text{CH}_2\text{O} + 2\text{O}_2 + 2\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{HO}_2 \]

\[ \text{CH}_4 + 4\text{O}_2 + 3\text{OH} + \text{NO} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 3\text{HO}_2 + \text{NO}_2 \]

Oxidized methane to \( \text{CO}_2 \) and \( 2\text{H}_2\text{O} \) plus used an extra 2 oxygen molecules to convert OH to \( \text{HO}_2 \) and NO to \( \text{NO}_2 \). Note that \( \text{NO}_2 \) photolyses easily to NO + O and the O atom forms ozone.
What have we done?

\[ \text{CH}_4 + \text{OH} + 2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2 + \text{H}_2\text{O} \]

\[ \text{CH}_2\text{O} + \text{O}_2 + \text{OH} \rightarrow \text{CO}_2 + 3\text{HO}_2 \]

\[ \text{CH}_4 + 4\text{O}_2 + 2\text{OH} + \text{NO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 4\text{HO}_2 + \text{NO}_2 \]

Oxidized \( \text{CH}_4 \) to \( \text{CO}_2 \) and one \( \text{H}_2\text{O} \). Have created 2 \( \text{HO}_x \) that will eventually recombine to form the second \( \text{H}_2\text{O} \). The \( \text{NO}_2 \) will photolyze to form \( \text{O} \) atoms and then ozone.
What have we done?

\[
\begin{align*}
\text{CH}_4 + \text{OH} + 2\text{O}_2 + \text{NO} & \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2 + \text{H}_2\text{O} \\
\text{CH}_2\text{O} + \text{O}_2 + \text{OH} & \rightarrow \text{CO}_2 + \text{HO}_2 + \text{H}_2
\end{align*}
\]

\[\text{CH}_4 + 3\text{O}_2 + 2\text{OH} + \text{NO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2 + 2\text{HO}_2 + \text{NO}_2\]

Oxidized CH₄ to CO₂ and one H₂O plus one H₂. Have converted 2OH to 2HO₂. The NO₂ will photolyze to form O atoms and then ozone.
What about the other channel for CH$_3$O$_2$ reaction?

CH$_3$O$_2$ + HO$_2$ $\rightarrow$ CH$_3$OOH + O$_2$

This can be followed by

CH$_3$OOH + hv $\rightarrow$ CH$_3$O + OH

which takes us back to the original chain reforming the O$_2$ that was used and converting HO$_2$ to OH, or it can be followed by

CH$_3$OOH + OH $\rightarrow$ CH$_3$O$_2$ + HO$_2$

This second channel forms a catalytic cycle that converts HO$_x$ back to H$_2$O
What about the other channel for CH$_3$O$_2$ reaction?

\[
\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \\
\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}
\]

\[
\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

This HO$_x$ destruction can counteract the HO$_x$ production in one of the above steps. The net effect depends on the ratio of the reaction rate of CH$_3$O$_2$ with NO to that with HO$_2$ and depends on the ratio of photolysis rate of CH$_3$OOH to the reaction rate with OH.
Summarizing Methane Oxidation

- Produces $CO_2 + 2H_2O$ with a minor channel that produces $H_2$ instead of the second $H_2O$

- Produces formaldehyde, $CH_2O$ and carbon monoxide, $CO$ as part of the degradation chain

- Can oxidize NO to $NO_2$ leading to $O$ atom production and hence ozone production

- Can produce $HO_x$ radicals or destroy them depending on conditions