Global Methane Cycle
Outline

- History and properties of Methane.
- Sources of methane.
- Methane sequestration and utilization.
- Oxidation pathway of Methane.
- Historical and potential future climate change ability.
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### Radiative Forcing Components

<table>
<thead>
<tr>
<th>RF Terms</th>
<th>RF values (W m⁻²)</th>
<th>Spatial scale</th>
<th>LOSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-lived greenhouse gases</td>
<td>1.66 [1.49 to 1.83]</td>
<td>Global</td>
<td>High</td>
</tr>
<tr>
<td>Stratospheric water vapour from CH₄</td>
<td>0.48 [0.43 to 0.53]</td>
<td>Global</td>
<td>High</td>
</tr>
<tr>
<td>Surface albedo</td>
<td>0.16 [0.14 to 0.18]</td>
<td>Continental</td>
<td>Med</td>
</tr>
<tr>
<td>Land use</td>
<td>0.34 [0.31 to 0.37]</td>
<td>Continental</td>
<td>Med</td>
</tr>
<tr>
<td>Ozone</td>
<td>-0.05 [-0.15 to 0.05]</td>
<td>Continental</td>
<td>Med</td>
</tr>
<tr>
<td>Stratospheric</td>
<td>0.35 [0.25 to 0.65]</td>
<td>Continental</td>
<td>Med</td>
</tr>
<tr>
<td>Tropospheric</td>
<td>0.07 [0.02 to 0.12]</td>
<td>Global</td>
<td>Low</td>
</tr>
<tr>
<td>Black carbon on snow</td>
<td>-0.2 [-0.4 to 0.0]</td>
<td>Local</td>
<td>Med</td>
</tr>
<tr>
<td>Direct effect</td>
<td>0.1 [0.0 to 0.2]</td>
<td>Local</td>
<td>Low</td>
</tr>
<tr>
<td>Total Aerosol</td>
<td>-0.5 [-0.9 to -0.1]</td>
<td>Continental</td>
<td>Med</td>
</tr>
<tr>
<td>Cloud albedo effect</td>
<td>-0.7 [-1.8 to -0.3]</td>
<td>Continental</td>
<td>Low</td>
</tr>
<tr>
<td>Linear contrails</td>
<td>0.01 [0.003 to 0.03]</td>
<td>Continental</td>
<td>Low</td>
</tr>
<tr>
<td>Solar irradiance</td>
<td>0.12 [0.06 to 0.30]</td>
<td>Global</td>
<td>Low</td>
</tr>
<tr>
<td>Total net anthropogenic</td>
<td>1.6 [0.6 to 2.4]</td>
<td>Global</td>
<td>High</td>
</tr>
</tbody>
</table>

**Radiative Forcing (W m⁻²)**

-2  -1  0  1  2
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- History and properties of Methane.
- Sources of methane.
- Methane sequestration and utilization.
- Oxidation of Methane in the atmosphere.
- Historical and potential future climate change ability.
Over the past two decades, CH4 growth rates in the atmosphere have generally decreased.

Currently, atmospheric concentration of methane is 1774 ppb
• Unprecedented in last 650 kyr, avg (320 – 790 ppb)
Methane: A more Potent Gas
over Shorter Periods—Rate of emission!

The GWP depends on the following factors:
• the absorption of infrared radiation by a given species
• the spectral location of its absorbing wavelengths
• the atmospheric lifetime of the species

\[ \text{GWP} = \frac{\int_0^T I_{\text{gas}} M_{\text{gas}} \, dt}{\int_0^T I_{\text{CO}_2} M_{\text{CO}_2} \, dt} \]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Lifetime (years)</th>
<th>GWP for time horizon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 years</td>
</tr>
<tr>
<td>CO₂</td>
<td>~100</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>12</td>
<td>63</td>
</tr>
</tbody>
</table>

Methane 23 times “hotter” than CO₂ (100 yr time period)
Methane 63 times “hotter” than CO₂ (20 yr time period)

The decrease in GWP associated with longer times is due to the fact that the methane is degraded to water and CO₂ by chemical reactions in the atmosphere.

IPCC 2007
CH$_4$ is much more dilute than CO$_2$ in the atmosphere—therefore it’s absorption band is much less saturated.

• More potent RF gas, molecule per molecule.

• Only competition CH$_4$ has for radiation absorption is N$_2$O and H$_2$O.

What happens when NOx emissions are low?

What happens when they are high?

CO$_2$ = 6,103 Tg / Yr emitted.
CH$_4$ = 597 Tg / Yr emitted.
Methanogenesis and Enteric Fermentation contribute to 30% of total sources, while Partial combustion, Mining/processing/transport emissions contribute to 70%.
Imbalance of Sources vs. Sinks

$\text{CO}_2 = 6,103 \text{ Tg / Yr emitted.}$
$\text{CH}_4 = 597 \text{ Tg / Yr emitted.}$

- Sources total $\quad 597 \text{ Tg/yr}$
- Sinks total $\quad 560 \text{ Tg/yr}$
- Imbalance $\quad +37 \text{ Tg/yr}$
Natural Sources of Methane
Anaerobic Methane Production

- Microbial degradation of cellulose, proteins, lipids in oxygen suppressed environments form CH\(_4\) and CO\(_2\) as a terminating product—terminus of the anaerobic food chain.
- Terminus of anaerobic food chain.

1. In oxygen deprived environments, methanogens ferment plant material (glucose) to acetate, CO\(_2\), H\(_2\), and H+.

\[
\text{Glucose} + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COO}^- + 2\text{H}^+ + 2\text{CO}_2, + 4\text{H}_2 \quad \Delta G^0 = -215.7 \text{ kJ mol}^{-1}
\]

2. These products are then converted to carbon dioxide and methane.

\[
\begin{align*}
\text{CH}_3\text{COO}^- + \text{H}^+ & \rightarrow \text{CO}_2 + \text{CH}_4, \quad \Delta G^0' = -36 \text{ kJ mol}^{-1} \\
4\text{H}_2 + \text{CO}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \quad \Delta G^0 = -131 \text{ kJ mol}^{-1} \\
\text{CH}_3\text{COO}^- + 9\text{H}^+ & \rightarrow 2\text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G^0 = -144.5 \text{ kJ mol}^{-1}
\end{align*}
\]

Wetlands produce 225 Tg (CH\(_4\)) / year
Ruminants produce 115 Tg (CH\(_4\)) / year

*IPCC Third Assessment Report 2003*
Anthropogenic Sources of Methane
Methane emissions declined steadily from 1990 to 2001, as emissions from coal mining and landfills fell.


http://www.eia.doe.gov/oiaf/1605/ggrpt/methane.html#total
Being a gas at STP, Methane is difficult to contain and transport as natural gas.

27% Ventilation of methane pockets from drilling and extraction methods in the oil, and coal sectors. Abandoned Mines.

24% Compression of gas leaks.

37% Pipe leaks, container leaks, underground storage seepage.

24% Consumer neglect, leaks.
Opportunities to reduce methane emissions and make a profit

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

- Combustion of methane is not green overall.

- Comparatively, natural gas burns cleaner than oil or coal—emitting virtually no air pollutants like sulfur oxides, nitrogen oxides, or partially combusted materials.
Coalbed Methane Outreach Program

• Primarily from ventilation of mine shafts, an estimated 40 – 50 Tg / Yr. of Methane are thought to be released from coalbed mining.

• With the help of the EPA and their Coalbed Methane Outreach Program (CMOP), methane extraction from coalbed mining is now viewed as an economically viable source.

• Reduced Coalbed methane emissions by 16% (216 million metric tons of CO$_2$ equivalent).

http://www.epa.gov/cmop

• This and landfill capture programs are two of the components attributed towards the recent atmospheric steady state of methane.
Principle of Ventilation Air Methane (VAM) Operation

- Electric heating element brings the temperature to 1000 °C (1832 °F) at startup.
- Process fan forces the air into the plenum and through the bed.
- Methane is Oxidized (800-900 °C).
- Thermal energy released by oxidation is recovered by the bed medium—heating the water input.
- Air flow is reversed, and the heat recovered in the first cycle heats the incoming ventilation air.
Biogas Recovery Systems

- EPA heads the Landfill Methane Outreach Program (LMOP).
- Partnership program which promotes the use of landfill gas as a renewable, green energy system.
- Methane emissions (60 – 70 %) occur whenever animal waste is managed in anaerobic conditions.
- Gas can be used to run engines, boilers, irrigation pumps, or be flared to minimize odor.
- NO decreases as NO₂ increases
- NO₂ photolyzes (<420nm) as sun comes out

- RH (CH4) seems to be a major player in all of this too!
High NOx, no CH₄

\[ \text{NO}_2 + h\nu (<420\text{nm}) (+\text{O}_2) \rightarrow \text{NO} + \text{O}_3 \quad J_1 \]
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad K_1 \]

- Ignoring other reactions, during daylight this forms a fast cycle in steady-state
  \[ \frac{d[\text{NO}_2]}{dt} = \text{Prod} - \text{Loss} = 0 \]
  \[ K_1[\text{NO}][\text{O}_3] = J_1[\text{NO}_2] \]
  \[ \frac{[\text{NO}]}{[\text{NO}_2]} = \frac{J_1}{K_1[\text{O}_3]} \]

- Partitioning of NOₓ between NO and NO₂ has important implications for removal of O₃ from the atmosphere
High NOx, High CH₄

- Methane is oxidized first to a methyl radical via OH condensation rxn.
- It is further oxidized by oxygen to produce a peroxy radical.
- These radicals have a high rate of NO → NO₂ production—thereby significantly increasing the overall rate of NO₂ production.

- The added NO₂ to the system results in a positive increase in tropospheric O₃.
PSC formation via Methane

- Water Vapor has an average lifetime of ~ 2 weeks in the troposphere before it condenses and precipitates.
- The oxidation of methane into various species can culminate in the release of water vapor near the tropopause. CH4 undergoes chemical destruction in the stratosphere, producing a small amount of water vapor.
- The RF from the increase in stratospheric water vapor due to oxidation of CH₄ is estimated to be +0.07 [± 0.05] W m⁻².

IPCC 2007
Isotopic Oxygen composition: $^{16}\text{O}$ (99.76%), $^{17}\text{O}$ (0.04%), and $^{18}\text{O}$ (0.2%).

As evaporation occurs, lighter molecules are preferentially evaporated.

This causes the vapor to be depleted in heavy molecules but enriched in lighter ones.

As the air mass cools and condensation occurs, the heavier molecules preferentially condense due to the same principle.

The condensation is then assumed to fall out of the cloud as precipitation.

Oxygen isotopic ratio of rain and snow $\rightarrow$ strongly related to condensation temperature.

Therefore, low temps $\rightarrow$ a depletion of $^{18}\text{O}$ relative to precipitation that condensed in a warmer environment.
Not only does methane affect climate through greenhouse effects, but it in turn can be affected by climate itself.

• “Clathrate gun hypothesis”:

  • Clathrate compounds store methane during cold periods.

  • Methane is released at a high rate—aggressively increasing the global climate temperature.

  • Not widely accepted.

  • Precise, relatively young ice core records show methane lagging behind drastic increasing in global temperature.
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- **Wetland / Permafrost explanation:**

  As climate warms from total RF factors → rate of water evaporation increases

  Increases rain in tropical wetland areas

  Induced anaerobic conditions from newly formed wetlands → increased methane emissions → global temperature
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- **Wetland / Permafrost explanation:**

  \[
  \text{Methanogenesis:} \quad \text{CO}_2 + 4\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4
  \]
  \[
  \text{CH_3COOH} \rightarrow \text{CO}_2 + \text{CH}_4
  \]
Not only does methane affect climate through greenhouse effects, but it in turn can be affected by climate itself.

- **Wetland / Permafrost explanation:**

Permafrost melts (northern hemisphere), increasing methane emissions drastically → wetland model is reinforced—inducing further global warming, and cycle repeats.
So Far…….

1. Methane has a high global warming potential with and a short lifetime.
   → Rate of methane emissions matter—more methane abundance = less oxidized methane, increased initial specie lifetime, and higher GWP.

2. Oxidative pathway contributes to many other forcing species in the atmosphere.

1. Historically, methane can be involved in a positive feedback loop triggered by initial stages of climate change.
   → Rate of methane emissions can be catalyzed to create abrupt glacial / interglacial changes in overall climate.
What is Permafrost?

- **Permafrost**: Bedrock, organic or earth material that has temperatures below 0 °C persisting over at least two consecutive years.
- Defined solely by temperature.
- **Yedoma**: Windblown organic carbon containing dust which was deposited during the last glacial ice age—covering 1 million km² over northern Siberia and Alaska and having an average depth of 25 m.

- Avg. carbon content of 2 – 5%.
- ~20 x the carbon content found in mineral, non-permafrost soil.
What is Permafrost?

- Permafrost underlies approximately 22.79 million square kilometers (about 24 percent of the exposed land surface) of the Northern Hemisphere.
- It occurs as far north 84° N in northernmost Greenland, and as far south as 26° N in the Himalayas.
- Frozen and anaerobic conditions merely suspend organic matter decomposition time.
“It’s coming out a lot and there’s a lot more to come out.”

–Katey Walter U. of Alaska-Fairbanks
When permafrost ice thaws, it forms thermokarst lakes. The yedoma carbon below the lakes produces methane under anaerobic conditions—eventually emitting into the atmosphere via ebullition. Decomposition happens rapidly—producing 40g of C / m$^3$ / day.

Near eroding lake shores, methane bubbling is so high that channels through the lake ice remain open all winter.

*NATURE, Vol 443, 7 September 2006*
Interestingly Enough.....

IPCC [2007]

El Nino  La Nina  No Longer in a methane steady state!
What I hope you have taken from this

- Methane is a very powerful GHG! One that indirectly contributes to many RF factors.
- The rate which methane is released is a primary factor in understanding its GW ability.
- Observing methane on a short timescale will display a more accurate GWP—one which climate history may show is involved in a quick paced positive feedback loop—and a top candidate for the source of abrupt climate change.
- Sequestration and combustion of anthropogenic induced methane decreases overall methane emissions, yet still releases CO$_2$ into the atmosphere.
- The climate trends we are currently observing with tropical storms, wetland creation, and an increased rate deviation from the recent methane steady state may be a preview of drastic CH$_4$ increases—yet it is too soon to tell.
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