Biogeochemical Cycles of Methane and Nitrous Oxide

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

Goals :
- **CH_4**
  - **− sources and sinks**
  - **− lifetime**
  - **− human influence**
- **N_2O**
  - **− sources and sinks**
  - **− human influence**
  - **− connection to stratospheric O_3**

Note:
1 Gt (gigaton) = 10^9 tons, which also equals 10^{15} grams
1 Mt (megaton) = 10^6 tons, which also equals 10^{12} grams , or 1 Tg (Terra gram)

Lecture 6

19 February 2019

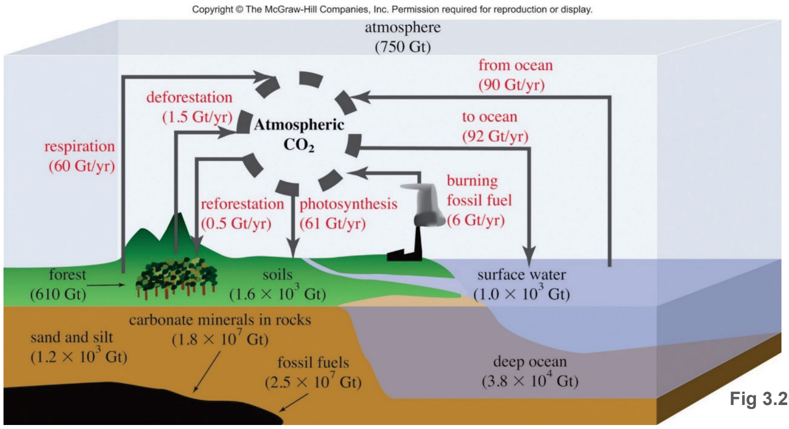


Fig 3.20, Chemistry in Context

Text from Houghton:

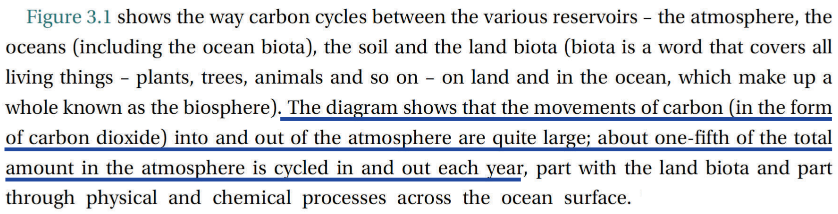


Figure 3.1 shows the way carbon cycles between the various reservoirs – the atmosphere, the oceans (including the ocean biota), the soil and the land biota (biota is a word that covers all living things – plants, trees, animals and so on – on land and in the ocean, which make up a whole known as the biosphere). The diagram shows that the movements of carbon (in the form of carbon dioxide) into and out of the atmosphere are quite large; about one-fifth of the total amount in the atmosphere is cycled in and out each year, part with the land biota and part through physical and chemical processes across the ocean surface.

Atmospheric Abundance: 750 Gt C

Gross Flux Out of the Atmosphere: 92 + 61 + 0.5 Gt C / yr = 153.3 Gt C / yr

Lifetime with respect to Gross Flux = (750 Gt C) / 153.3 Gt C / yr = 4.9 yr

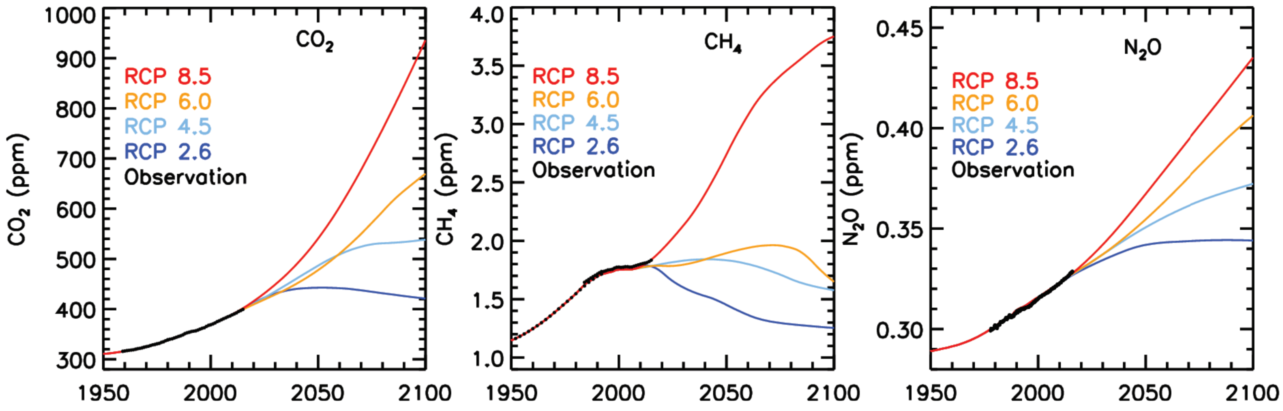
Net Flux Out of the Atmosphere = (92 – 90) + (61 – 60) + 0.5 Gt C / yr = 3.5 Gt C / yr

Lifetime with respect to Net Flux = (750 Gt C) / 3.5 Gt C / yr = 214 yr

Announcements

- Problem Set #1 due today
- Will hold problem set reviews during various evenings
  - Would like to hold review of Problem Set #1 Monday, 25 Feb, at 6 pm
  - How many interested in attending?
  - We will hand out solutions at the review … hence no credit for P Set #1 if we do not have by start of this review
- Problem Set #2 due Thurs, 28 Feb; will be posted this Thursday
- First exam is Tues, 5 Mar, in class:
  - Closed book, no calculator or e-device
  - Will focus on concepts rather than calculations
  - New exams every year; we will review prior exam in class on Thurs, 28 Feb to help you prepare

RCP Scenarios Forecast Wide Range of Possible Futures, Particularly for CH_4



- RCP: Representative Concentration Pathway
  Number represents ΔRF of climate (W m^{-2}) at the end of this century
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups

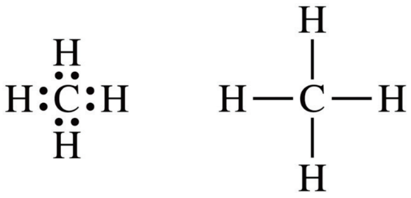
CH_4 is the most reduced form of carbon

Decreasing oxidation number (reduction reactions)

-4	0	+2	+4
CH_4 Methane	CH_2O Formaldehyde	CO Carbon Monoxide	CO_2 Carbon dioxide

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:
added to an element (negative #) or removed from an element (positive #)



C in CH_4: has received an electron from each H atom. All electrons are paired and hence this compound is relatively stable

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Decreasing oxidation number (reduction reactions)

-4	0	+2	+4
CH_4 Methane	CH_2O Formaldehyde	CO Carbon Monoxide	CO_2 Carbon dioxide

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:
added to an element (negative #) or removed from an element (positive #)

C in CO_2: has donated two electrons to each oxygen atom, completing the L shell of electrons & resulting in an electron configuration analogous to helium. This molecule is extremely stable.

Atmospheric CH_4

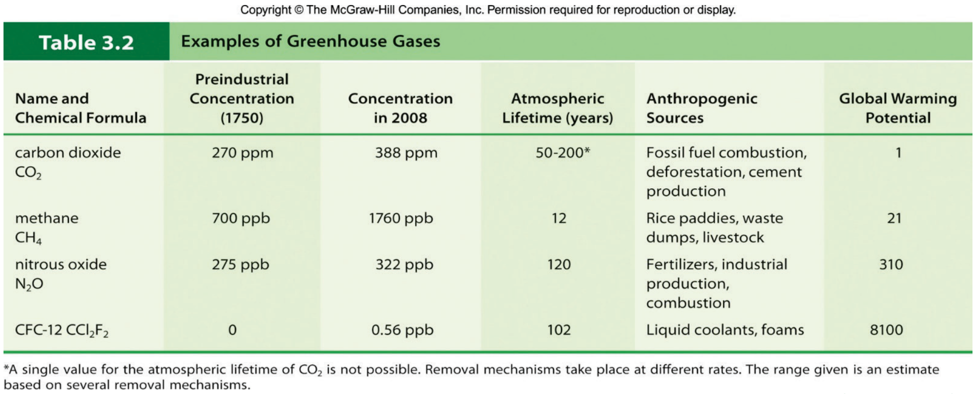


Table 3.2 Examples of Greenhouse Gases

Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
carbon dioxide CO_2	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH_4	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N_2O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl_2F_2	0	0.56 ppb	102	Liquid coolants, foams	8100

*A single value for the atmospheric lifetime of CO_2 is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.

Chapter 3, *Chemistry in Context*

Table 1.1 *Paris, Beacon of Hope*

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
100 Year Time Horizon				
CH_4	21	23	25	28, 34*
N_2O	310	296	298	265, 298*
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

Footnote 8, *Paris, Beacon of Hope*:

> Some textbooks and reports provide GWP values on a per molecule basis, rather than a per mass basis. A molecule of CO_2 with atomic mass of 44 weighs 2.75 times a molecule of CH_4 (atomic mass of 16). Using the IPCC (2013) value for the GWP of CH4 on a 100 year time horizon, without consideration of carbon cycle feedback, scientists would state CH_4 is 28 times more potent than CO_2 on a per mass basis and, at the same time, is 10.2 (28 ÷ 2.75) times more potent than CO_2 on a per molecule basis.

Atmospheric CH_4

AT6, Q4:
Page 47 of Houghton reads:

> That is because the enhanced greenhouse effect caused by a molecule of methane is about **eight** times that of a molecule of carbon dioxide.

Fill in the blank ***and*** then explain why the three values for the GWP of CH_4 given in Q3 above differ so much from the numerical value provided in the Houghton reading.

Endnote 9, Houghton:

> The ratio of the enhanced greenhouse effect of a molecule of methane compared to a molecule of carbon dioxide is known as its global warming potential (GWP) … **The figure of about 8 given here for the GWP of methane is for a time horizon of 100 years.** *The GWP is also often expressed as the ratio of the effect for unit mass of each gas in which case the GWP for methane (whose molecular mass is 0.36 of that of carbon dioxide) **becomes about 23 for the 100-year time horizon**.* **About 75% of the contribution of methane to the greenhouse effect is because of its direct effect on the outgoing thermal radiation**. **The other 25% arises because of its influence on the overall chemistry of the atmosphere. Increased methane eventually results in small increases in water vapour in the upper atmosphere, in tropospheric ozone and in carbon dioxide, all of which in turn add to the greenhouse effect.** For more information see IPCC WGI 2013, Chapter 8, p. 700.

Atmospheric CH_4

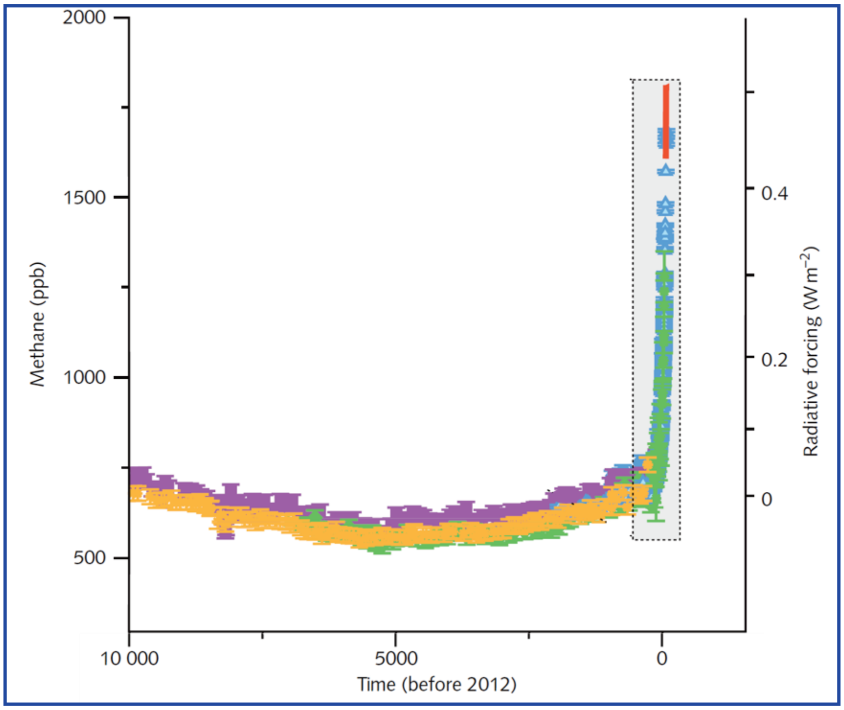


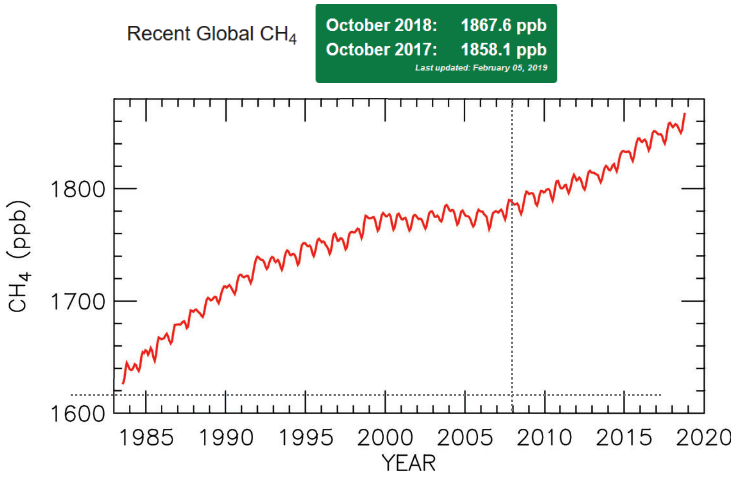
Figure 3.7, *Houghton*

Atmospheric CH_4

AT6, Q2:
What is the approximate current atmospheric abundance of CH_4 ***and*** what is the ratio of the current atmospheric CH_4 divided by the pre-industrial abundance?

NOAA Earth System Research Laboratory (Boulder, Co) is "go to" place for information regarding GHGs

Latest, greatest data indicate CH_4 is at 1876.6 ppb and rising, and also that CH_4 exceeded 1760 ppb in 2008



Recent Global CH_4

October 2018:	**1867.6 ppb**
October 2017:	**1858.1 ppb**

Last updated: February 05, 2019

https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4

Atmospheric CH_4

AT6, Q2:

What is the approximate current atmospheric abundance of CH_4 ***and*** what is the ratio of the current atmospheric CH_4 divided by the pre-industrial abundance?

The ratio of $CH_4^{\text{Preindustrial}}$ / CH_4^{Present} = (700 ppb) / (1760 ppb) = 0.4

CH_4 Sources:
Human: 335 Tg yr^{-1}
Natural: 218 Tg yr^{-1}
Total: 553 Tg yr^{-1}

Human ≈ 60% of total

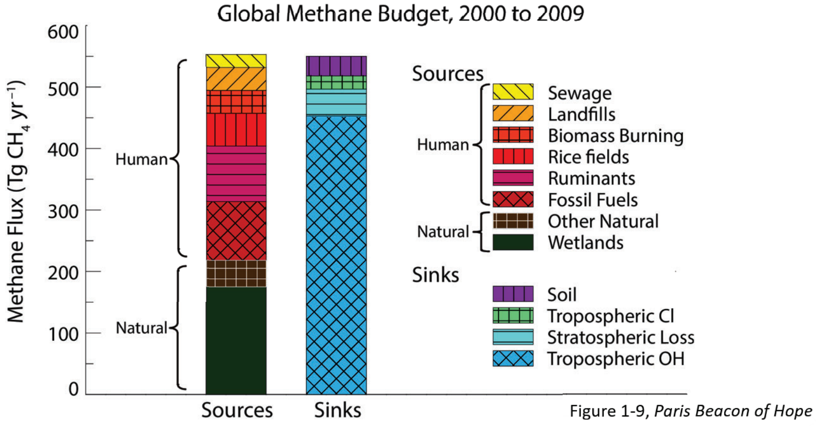


Figure 1-9, *Paris Beacon of Hope*

If:

Production of CH_4 = Loss of CH_4 *and* if the loss involves a chemical reaction of CH_4 with a Gas, then

Production of CH_4 = k [CH_4] [Gas], where k is the rate of a chemical reaction and [ ] denotes abundance

Assuming k and [Gas] are constant over time, we can write:

$\text{Production}^{\text{Preindustrial}}$= k $[CH_4]^{\text{Preindustrial}}$ [Gas] & $\text{Production}^{\text{Total}}$= k $[CH_4]^{\text{Present}}$ [Gas]

which can be re-arranged to yield:

k [Gas] = $\text{Production}^{\text{Preindustrial}}$ / $[CH_4]^{\text{Preindustrial}}$ & k [Gas] = $\text{Production}^{\text{Total}}$ / $[CH_4]^{\text{Present}}$

Atmospheric CH_4

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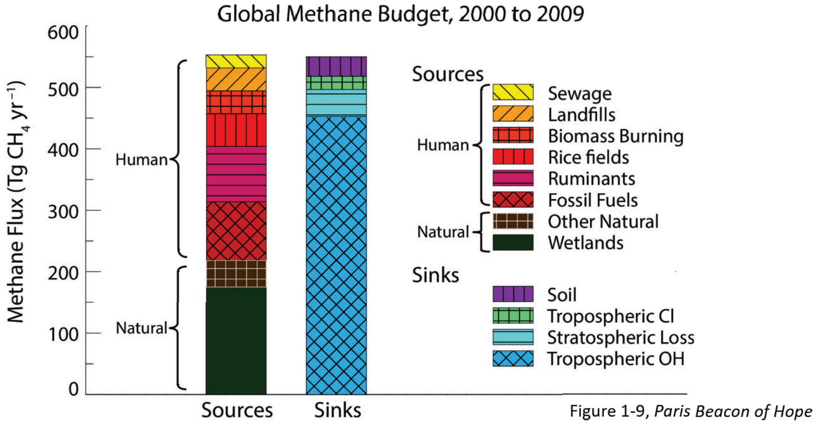

Figure 1-9, *Paris Beacon of Hope*

If:

k [Gas] = $\text{Production}^{\text{Preindustrial}}$ / $[CH_4]^{\text{Preindustrial}}$ & k [Gas] = $\text{Production}^{\text{Total}}$ / $[CH_4]^{\text{Present}}$

Then:

$\text{Production}^{\text{Preindustrial}}$ / $[CH_4]^{\text{Preindustrial}}$ = $\text{Production}^{\text{Total}}$ / $[CH_4]^{\text{Present}}$

Or:

$[CH_4]^{\text{Preindustrial}}$ / $[CH_4]^{\text{Present}}$ = $\text{Production}^{\text{Preindustrial}}$ / $\text{Production}^{\text{Total}}$

Or:

$[CH_4]^{\text{Preindustrial}}$ / $[CH_4]^{\text{Present}}$ = $\text{Source}^{\text{Preindustrial}}$ / $\text{Source}^{\text{Total}}$

Atmospheric CH_4

AT6, Q2:
What is the approximate current atmospheric abundance of CH_4 ***and*** what is the ratio of the current atmospheric CH_4 divided by the pre-industrial abundance?

The ratio of $CH_4^{\text{Preindustrial}}$ / CH_4^{Present} = (700 ppb) / (1760 ppb) = 0.4

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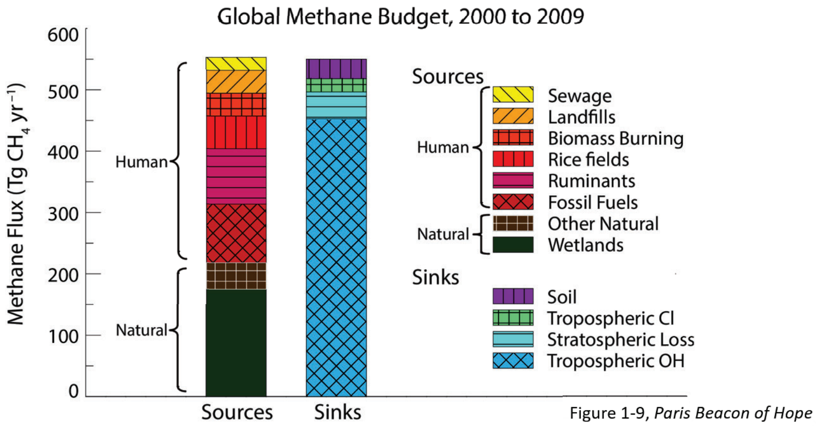

Global Methane Budget, 2000 to 2009

Figure 1-9, *Paris Beacon of Hope*

From prior slide:

$$[CH_4]^{\text{Preindustrial}} / [CH_4]^{\text{Present}} = \text{Source}^{\text{Preindustrial}} / \text{Source}^{\text{Total}}$$

Presumably:

$$\text{Source}^{\text{Preindustrial}} = \text{Source}^{\text{Total}} - \text{Source}^{\text{Human}}$$ **(i.e., presumably "nature" has not changed)**

If so, then top equation can be written as:

$$[CH_4]^{\text{Preindustrial}} / [CH_4]^{\text{Present}} = (\text{Source}^{\text{Total}} - \text{Source}^{\text{Human}}) / \text{Source}^{\text{Total}}$$
$$= 1 - \text{Source}^{\text{Human}} / \text{Source}^{\text{Total}} = 1 - (335\ \text{Tg yr}^{-1}) / (553\ \text{Tg yr}^{-1})$$
$$= 1 - 0.6 = 0.4$$

CH_4 is in fact lost by reaction with OH, the hydroxyl radical

$$CH_4 + OH \rightarrow H_2O + CH_3$$

$$\frac{d\text{CH}_4}{dt} = \text{Production} - \text{Loss} = \text{Production} - k\,[\text{OH}][\text{CH}_4]$$

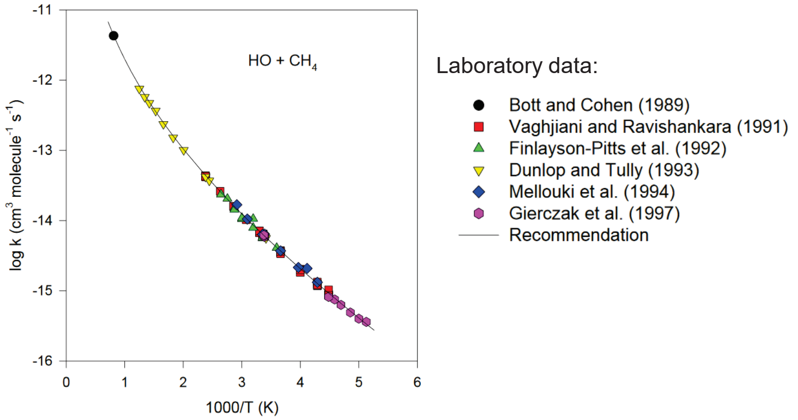
Rates constant represents the speed at which OH reacts with CH_4:

Arrhenius:

$$k^{\text{NASA}} = 2.45\times10^{-12} \times e^{-1775/T}\ \text{cm}^3\ \text{sec}^{-1}$$
$$k^{\text{IUPAC}} = 1.85\times10^{-12} \times e^{-1690/T}\ \text{cm}^3\ \text{sec}^{-1}$$

Non-Arrhenius

$$k^{\text{NASA}} = 2.80\times10^{-14} \times \text{T}^{0.667} e^{-1575/T}\ \text{cm}^3\ \text{sec}^{-1}$$
$$k^{\text{IUPAC}} = 1.85\times10^{-20} \times \text{T}^{2.82} e^{-987/T}\ \text{cm}^3\ \text{sec}^{-1}$$



http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf

CH_4 is in fact lost by reaction with OH, the hydroxyl radical

$CH_4 + OH \rightarrow H_2O + CH_3$

$$\frac{d\mathrm{CH_4}}{dt} = \mathrm{Production} - \mathrm{Loss} = \mathrm{Production} - k\,[\mathrm{OH}][\mathrm{CH_4}]$$

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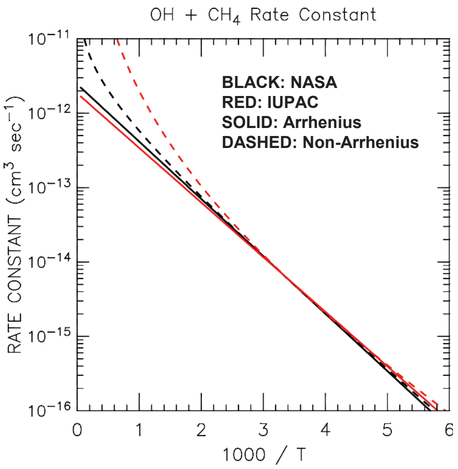

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$$\frac{d\mathrm{CH_4}}{dt} = \mathrm{Production} - \mathrm{Loss} = \mathrm{Production} - k\,[\mathrm{OH}][\mathrm{CH_4}]$$

Arrhenius Expressions for rate constant: i.e., speed at which OH reacts with CH_4:

$$k^{\mathrm{NASA}} = 2.45\times10^{-12}\times e^{-1775/T}\ \mathrm{cm^3\ sec^{-1}}$$

$$k^{\mathrm{IUPAC}} = 1.85\times10^{-12}\times e^{-1690/T}\ \mathrm{cm^3\ sec^{-1}}$$

$$\mathrm{Lifetime\ of\ CH_4} = \frac{\mathrm{Abundance}}{\mathrm{Loss}} = \frac{[\mathrm{CH_4}]}{k[\mathrm{OH}][\mathrm{CH_4}]} = \frac{1}{k\,[\mathrm{OH}]}$$

Commonly T = 272 K and **$[OH] = 1 \times 10^6$ molec cm^{-3}** are used yielding:

$$\mathrm{Lifetime\ of\ CH_4} = \frac{1}{k\,[\mathrm{OH}]} = \frac{1}{3.59\times10^{-15}\ \mathrm{cm^3\ sec^{-1}}\ \times\ 1\times10^{6}\ \mathrm{molec\ cm^{-3}}}$$

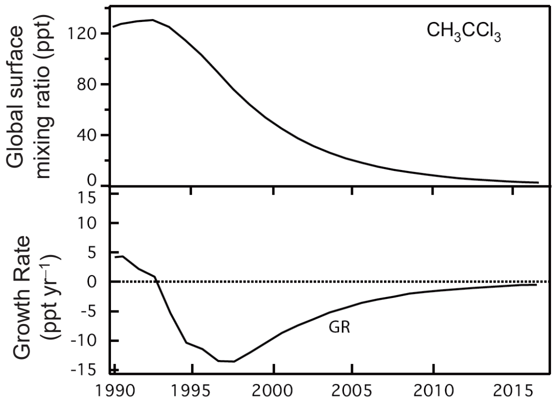
$$= 2.79\times10^{8}\ \mathrm{sec} = 8.8\ \mathrm{yr}\ \ \mathrm{using}\ k^{\mathrm{NASA}}$$

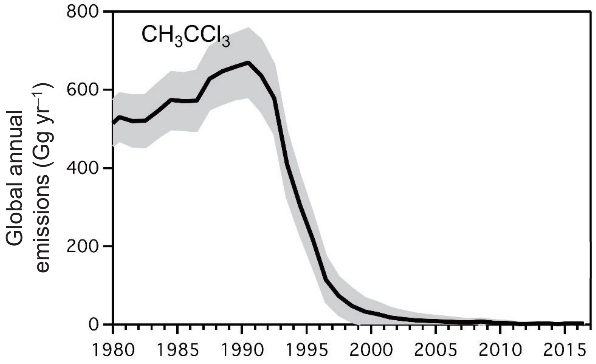
lifetime of 8.6 yr found using k^{IUPAC}

CH_3CCl_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

CH_3CCl_3 + OH → CH_2CCl_3+H_2O

$$\frac{d\mathrm{CH_3CCl_3}}{dt} = \text{Production} - \text{Loss} = \text{Production} - k\,[\mathrm{OH}][\mathrm{CH_3CCl_3}]$$





https://www.esrl.noaa.gov/csd/assessments/ozone/2018/report/Chapter1_2018OzoneAssessment.pdf

Methyl chloroform (1,1,1-trichloroethane) is an excellent solvent and one of the least toxic of the chlorinated hydrocarbons. Prior to the Montreal Protocol, it was widely used for cleaning metal parts and circuit boards, as an aerosol propellant, and as a solvent for inks, paints, and adhesives. It was also the standard cleaner for photographic film (movie/slide/negatives, etc.). Methyl chloroform was also used as a thinner in correction fluid products such as Liquid Paper.

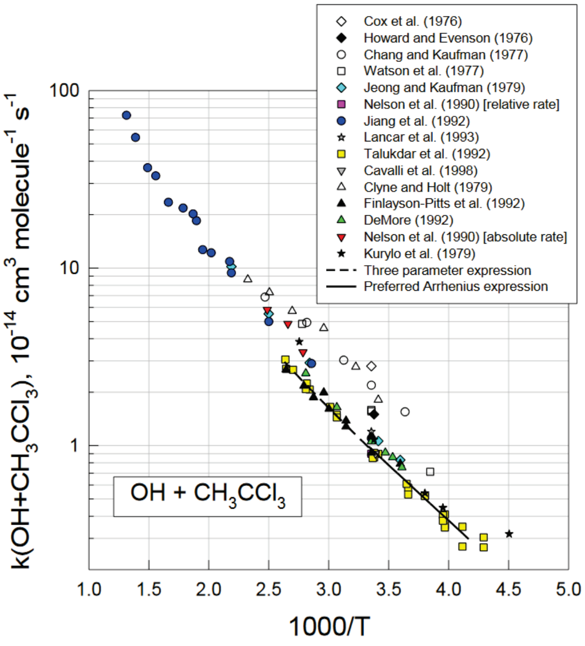
Montreal Protocol banned the use of methyl chloroform and it was **rapidly phased out, throughout the world**.

See http://en.wikipedia.org/wiki/1,1,1-Trichloroethane

CH_3CCl_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

CH_3CCl_3 + OH → CH_2CCl_3+H_2O

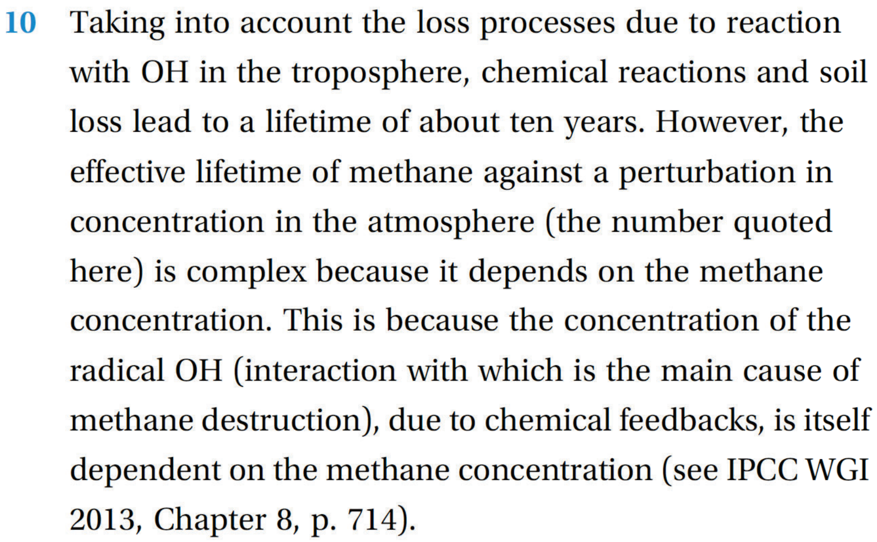
$$\frac{d\mathrm{CH_3CCl_3}}{dt} = \text{Production} - \text{Loss} = \text{Production} - k\,[\mathrm{OH}][\mathrm{CH_3CCl_3}]$$



$$k^{\mathrm{NASA}} = 1.64\times10^{-12}\times e^{-1520/T}\ \ \mathrm{cm^3\ \ sec^{-1}}$$

$$k^{\mathrm{IUPAC}} = 1.2\times10^{-12}\times e^{-1440\ /T}\ \ \mathrm{cm^3\ \ sec^{-1}}$$

Houghton & CC give a Lifetime for CH_4 of 12 Years
What's up with that?



10 Taking into account the loss processes due to reaction with OH in the troposphere, chemical reactions and soil loss lead to a lifetime of about ten years. However, the effective lifetime of methane against a perturbation in concentration in the atmosphere (the number quoted here) is complex because it depends on the methane concentration. This is because the concentration of the radical OH (interaction with which is the main cause of methane destruction), due to chemical feedbacks, is itself dependent on the methane concentration (see IPCC WGI 2013, Chapter 8, p. 714).

Endnote #10, Chapter 3, Houghton

Lots of interesting photochemistry takes place in the tropics

https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/2018JD028388
https://www.nasa.gov/feature/goddard/2018/greenhouse-gas-detergent-recycles-itself-in-atmosphere-nasa-study

Journal of Geophysical Research: Atmospheres

Changes in Global Tropospheric OH Expected as a Result of Climate Change Over the Last Several Decades

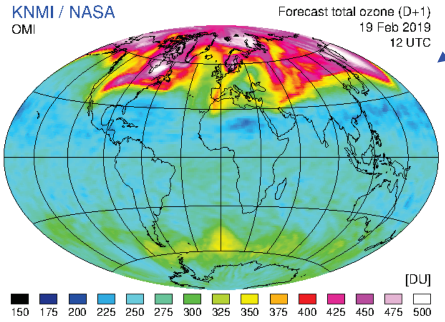
Julie M. Nicely[1,2,3], Timothy P. Canty[4], Michael Manyin[2,5], Luke D. Oman[2], Ross J. Salawitch[1,4,6], Stephen D. Steenrod[2,3], Susan E. Strahan[2,3], and Sarah A. Strode[2,3]

Primary production of OH occurs via O_3 photolysis to excited state $O(^1D)$ followed by reaction with water vapor:

$$O_3 + h\nu\ (\lambda \le 336\ \text{km}) \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow 2\ OH$$

See https://three.jsc.nasa.gov/articles/RadChemO2Sidebar.pdf
for an explanation of $O(^1D)$

Because this formation pathway depends on the abundance of H_2O and the actinic flux at wavelengths ≤ 336 nm, the highest concentrations of OH are found in the tropical lower and middle troposphere. **Overhead column O_3 is low in the tropics**, allowing greater penetration of ultraviolet (UV) photons to the troposphere than in the extratropics. This, along with more H_2O due to higher temperatures, results in loss of methane being dominated by OH in the tropics (**Figure 1**).



http://www.temis.nl/protocols/o3field/data/omi/forecast/today_wd.gif

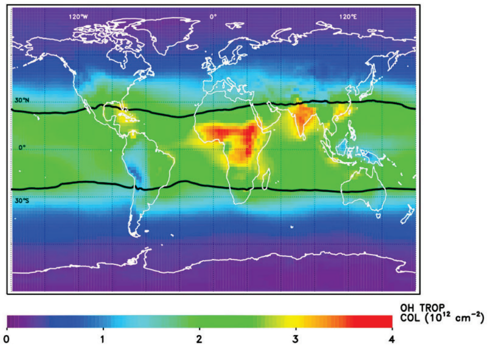


Figure 1. Annual average tropospheric OH columns are shown from the Global Modeling Initiative model for year 1980, used as a baseline in this analysis. Annual average tropical boundaries are indicated as black lines.

CH_4-induced change in [OH] is one of several “hot ticket items” in modern atmospheric chemistry

https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/2018JD028388
https://www.nasa.gov/feature/goddard/2018/greenhouse-gas-detergent-recycles-itself-in-atmosphere-nasa-study

Journal of Geophysical Research: Atmospheres

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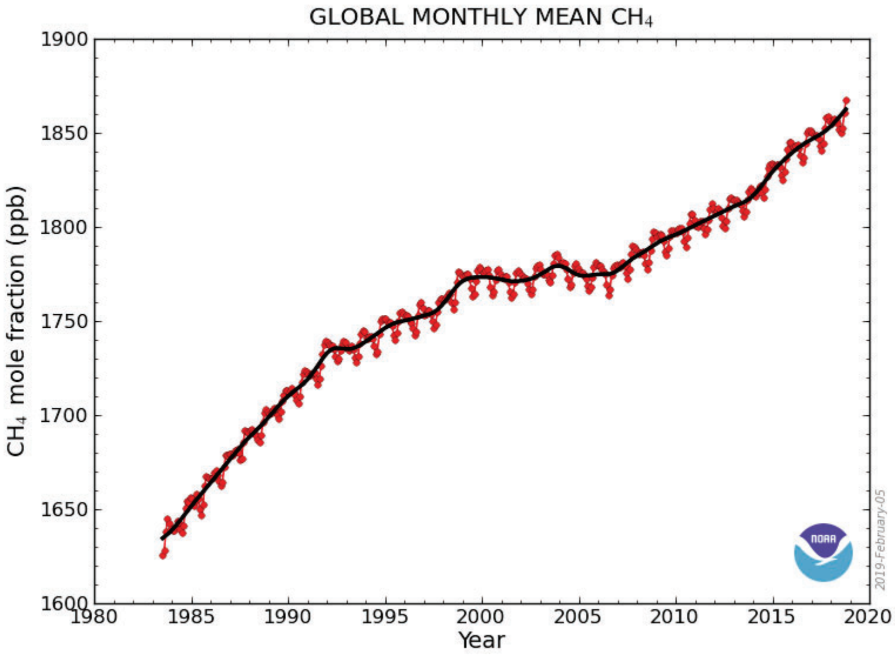
- **Trends in OH between 1980 and 2015 were modeled using observed total column ozone, H_2O, CH_4, model-simulated NO_x ($NO+NO_2$) and a widening of the Hadley cell**
- **Nearly all (i.e., 94%) of the expected CH_4-induced decline in tropospheric OH was offset by increases due to H_2O, NO_x, overhead O_3, and tropical widening**
- **Trends depend on time frame examined; NO_x and overhead O_3 drive most of OH increase between 1980 and 2005**
- **In this framework, the trends in NO_x are driven nearly entirely by human set fires**

Understanding the observed time series of CH_4 is another “hot ticket item” in modern atmospheric chemistry



https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4

See also https://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html

Recent trends in CH_4

These papers offer conflicting views on the cause of the recent rise in CH_4

- Kirschke *et al.*, *Nature Geoscience*, 2013:

:

Methane is an important greenhouse gas, responsible for about 20% of the warming induced by long-lived greenhouse gases since pre-industrial times. By reacting with hydroxyl radicals, methane reduces the oxidizing capacity of the atmosphere and generates ozone in the troposphere. Although most sources and sinks of methane have been identified, their relative contributions to atmospheric methane levels are highly uncertain. As such, the factors responsible for the observed stabilization of atmospheric methane levels in the early 2000s, and the renewed rise after 2006, remain unclear. Here, we construct decadal budgets for methane sources and sinks between 1980 and 2010, using a combination of atmospheric measurements and results from chemical transport models, ecosystem models, climate chemistry models and inventories of anthropogenic emissions. The resultant budgets suggest that data-driven approaches and ecosystem models overestimate total natural emissions. We build three contrasting emission scenarios — which differ in fossil fuel and microbial emissions — to explain the decadal variability in atmospheric methane levels detected, here and in previous studies, since 1985. Although uncertainties in emission trends do not allow definitive conclusions to be drawn, we show that the observed stabilization of methane levels between 1999 and 2006 can potentially be explained by decreasing-to-stable fossil fuel emissions, combined with stable-to-increasing microbial emissions. **We show that a rise in natural wetland emissions and fossil fuel emissions probably accounts for the renewed increase in global methane levels after 2006, although the relative contribution of these two sources remains uncertain.**

Recent trends in CH_4

These papers offer conflicting views on the cause of the recent rise in CH_4

- Wolf *et al.*, *Carbon Balance and Management,* 2017:

Livestock play an important role in carbon cycling through consumption of biomass and emissions of methane. Recent research suggests that existing bottom-up inventories of livestock methane emissions in the US, such as those made using 2006 IPCC Tier 1 livestock emissions factors, are too low. This may be due to outdated information used to develop these emissions factors. …

Using the new emissions factors, we estimate global livestock emissions of 119.1 ± 18.2 Tg methane in 2011; this quantity is 11% greater than that obtained using the IPCC 2006 emissions factors, encompassing an 8.4% increase in enteric fermentation methane, a 36.7% increase in manure management methane, and notable variability among regions and sources. …

Our results suggest that livestock methane emissions, while not the dominant overall source of global methane emissions, may be a major contributor to the observed annual emissions increases over the 2000s to 2010s. Differences at regional and local scales may help distinguish livestock methane emissions from those of other sectors in future top-down studies. The revised estimates allow improved reconciliation of top-down and bottom-up estimates of methane emissions, will facilitate the development and evaluation of Earth system models, and provide consistent regional and global Tier 1 estimates for environmental assessments.

Recent trends in CH_4

These papers offer conflicting views on the cause of the recent rise in CH_4

- Schaefer *et al.*, *Science*, 2016 :

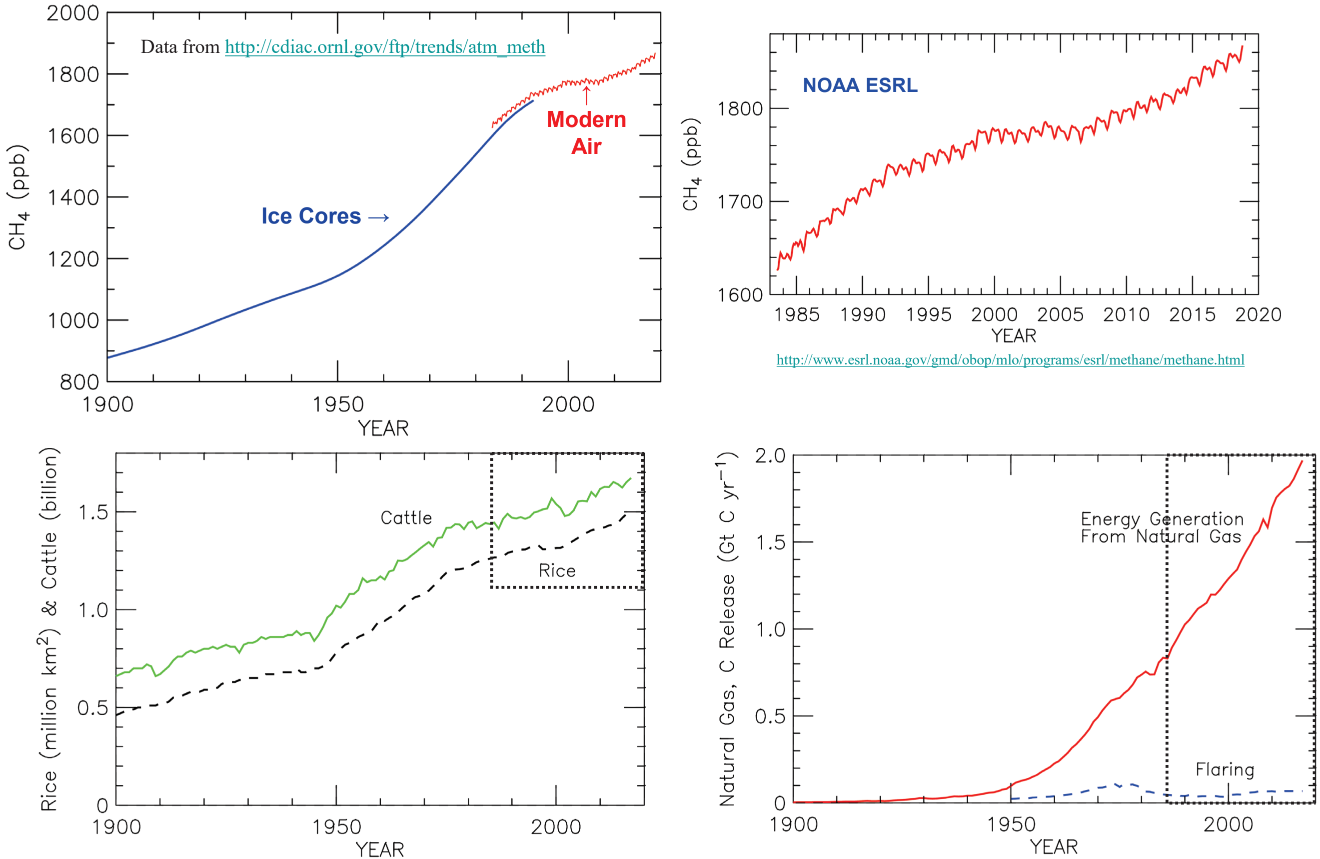
  Between 1999 and 2006, a plateau interrupted the otherwise continuous increase of atmospheric methane concentration [CH_4] since preindustrial times. Causes could be sink variability or a temporary reduction in industrial or climate-sensitive sources. We reconstructed the global history of [CH_4] and its stable carbon isotopes from ice cores, archived air, and a global network of monitoring stations. A box-model analysis suggests that diminishing thermogenic emissions, probably from the fossil-fuel industry, and/or variations in the hydroxyl CH_4 sink caused the [CH_4] plateau. Thermogenic emissions did not resume to cause the renewed [CH_4] rise after 2006, which contradicts emission inventories. **Post-2006 source increases are predominantly biogenic, outside the Arctic, and arguably more consistent with agriculture than wetlands.** If so, mitigating CH_4emissions must be balanced with the need for food production.

- Worden *et al.*, *Nature Communications*, 2017:

  Several viable but conflicting explanations have been proposed to explain the recent ~8 ppb per year increase in atmospheric methane after 2006, equivalent to net emissions increase of ~25 Tg CH_4 per year. A concurrent increase in atmospheric ethane implicates a fossil source; a concurrent decrease in the heavy isotope content of methane points toward a biogenic source, while other studies propose a decrease in the chemical sink (OH). Here we show that biomass burning emissions of methane decreased by 3.7 (±1.4) Tg CH_4 per year from the 2001–2007 to the 2008–2014 time periods using satellite measurements of CO and CH_4, nearly twice the decrease expected from prior estimates. After updating both the total and isotopic budgets for atmospheric methane with these revised biomass burning emissions (and assuming no change to the chemical sink), **we find that fossil fuels contribute between 12–19 Tg CH_4 per year to the recent atmospheric methane increase, thus reconciling the isotopic- and ethane-based results**.

See also https://insideclimatenews.org/news/10032016/mysterious-global-methane-rise-asian-agriculture-or-us-fracking

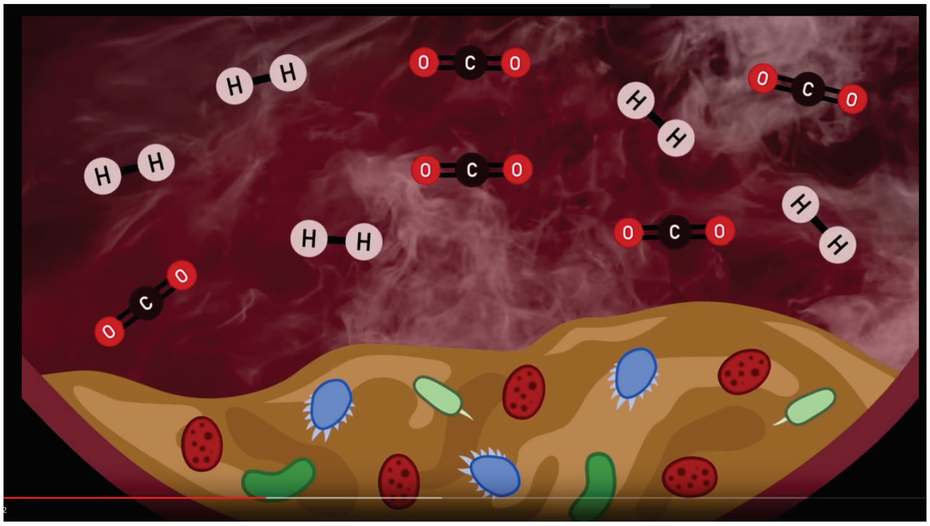
Atmospheric CH_4 and Energy from Gas, Rice, Cattle Trends



Data from http://faostat.fao.org

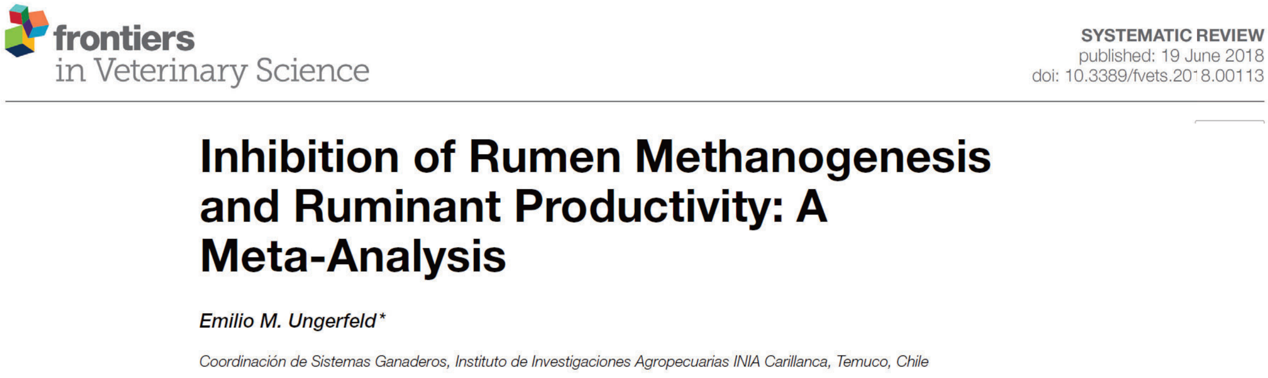
Data from http://cdiac.ornl.gov

Time for Another YouTube Video



https://www.youtube.com/watch?v=MnRFUSGz_ZM

Fascinating Paper For Those Who Are Interested



frontiers
in Veterinary Science

SYSTEMATIC REVIEW
published: 19 June 2018
doi: 10.3389/fvets.2018.00113

Inhibition of Rumen Methanogenesis and Ruminant Productivity: A Meta-Analysis

*Emilio M. Ungerfeld**

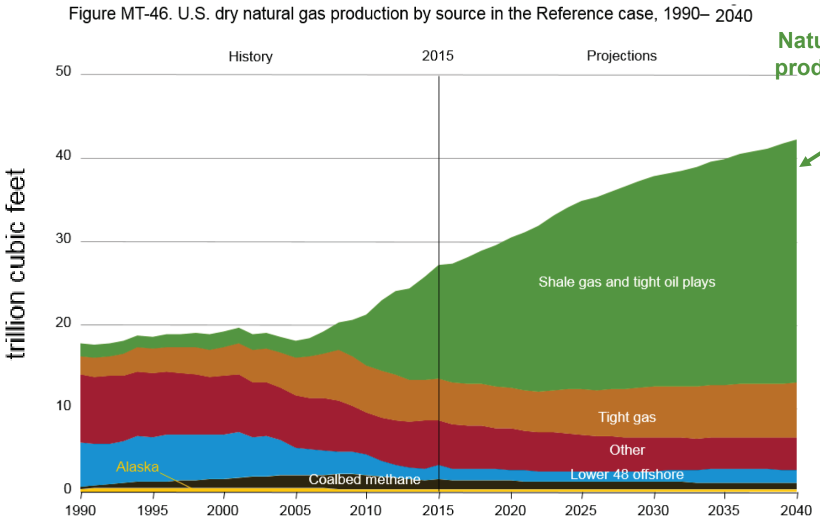
Coordinación de Sistemas Ganaderos, Instituto de Investigaciones Agropecuarias INIA Carillanca, Temuco, Chile

Methane (CH_4) formed in the rumen and released to the atmosphere constitutes an energy inefficiency to ruminant production. Redirecting energy in CH_4 to fermentation products with a nutritional value to the host animal could increase ruminant productivity and stimulate the adoption of CH_4-suppressing strategies. …

A more complete understanding of changes in the flows of nutrients caused by inhibiting rumen methanogenesis and their effect on intake also seems necessary to effectively re-channel energy gained from CH_4 suppression toward consistent gains in productivity.

https://www.frontiersin.org/articles/10.3389/fvets.2018.00113/full#h5

Fracking



Natural gas (mainly CH_4) production from fracking

https://www.eia.gov/outlooks/archive/aeo16/images/fig_mt-46.pn

Combustion of CH_4 yields ~70% more energy, per CO_2 released to the atmosphere, than combustion of coal

Break even point for "climate", natural gas versus coal, is leakage of:
2.3% of CH4 for GWP over a 20-yr time horizon
6.9% of CH4 for GWP over a 100-yr time horizon

Footnote #35, Chapter 4, *Paris Beacon of Hope*

Nitrous Oxide: N_2O

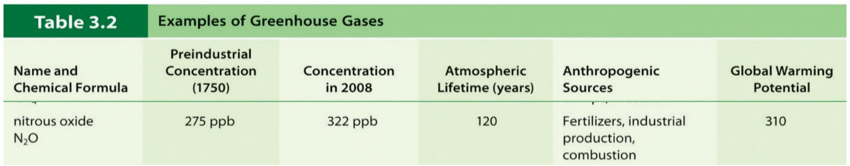


Table 3.2 Examples of Greenhouse Gases

Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
nitrous oxide N_2O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

Chapter 3, *Chemistry in Context*

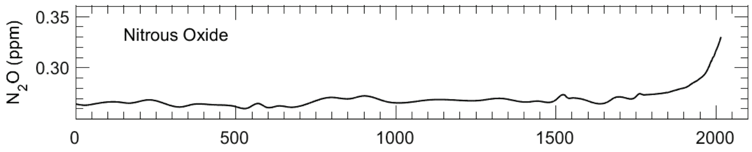


Figure 1.2, *Paris, Beacon of Hope*

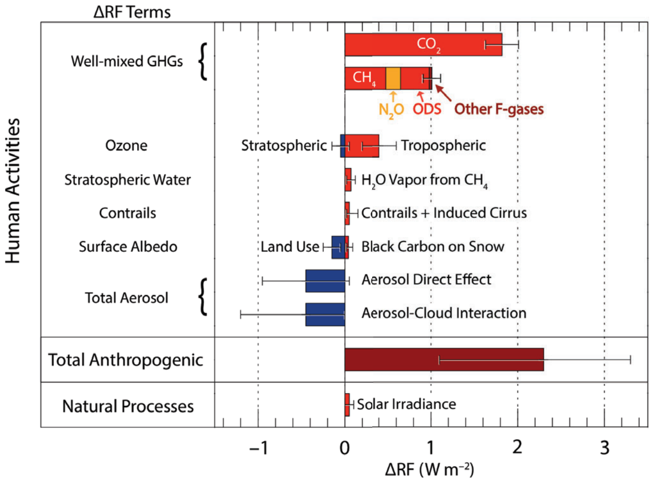


Figure 1.4, *Paris, Beacon of Hope*

Nitrous Oxide: N_2O

Table 3.2 Examples of Greenhouse Gases

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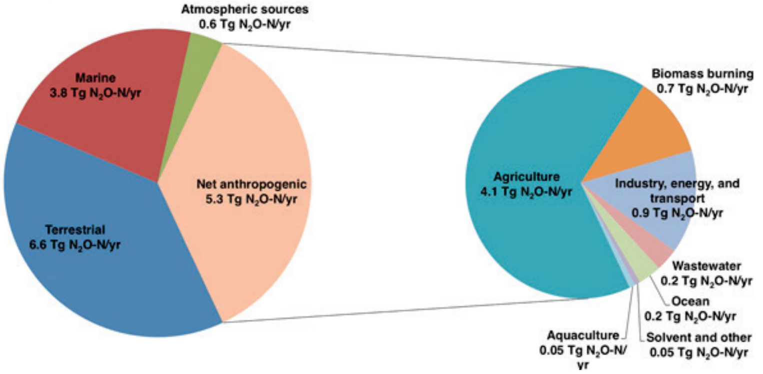
Chapter 3, *Chemistry in Context*

Davidson and Kanter, *ERL*, 2014:



https://iopscience.iop.org/article/10.1088/1748-9326/9/10/105012/meta

$[N_2O]^{Preindustrial}$ / $[N_2O]^{Present}$ = 1 – $Source^{Human}$ / $Source^{Total}$ = 1 – (5.3 Tg yr^{-1}) / (16.3 Tg yr^{-1})

= 1 – 0.32 = 0.67

From above, $[N_2O]^{Preindustrial}$ / $[N_2O]^{Present}$ = (275 ppb) / (322 ppb) = 0.85

Difference between these two values could reflect a short-coming in our understanding of the net anthropogenic source of N_2O, but more likely is due to the fact that with a 120 year lifetime, the fundamental assumption of Production = Loss is not true for N_2O

Sources and Sinks of N_2O

Table 6.9, IPCC 2013

SECTION 2 (N_2O)	All units for N_2O fluxes are in Tg N yr^{-1}
	AR5 (2006/2011)
Anthropogenic sources	
Fossil fuel combustion and industrial processes	0.7 (0.2–1.8)[a]
Agriculture	4.1 (1.7–4.8)[b]
Biomass and biofuel burning	0.7(0.2–1.0)[a]
Human excreta	0.2 (0.1–0.3)[a]
Rivers, estuaries, coastal zones	0.6 (0.1–2.9)[c]
Atmospheric deposition on land	0.4 (0.3–0.9)[d]
Atmospheric deposition on ocean	0.2 (0.1–0.4)[e]
Surface sink	–0.01 (0– -1)[f]
Total anthropogenic sources	**6.9 (2.7–11.1)**
Natural sources[a]	
Soils under natural vegetation	6.6 (3.3–9.0)
Oceans	3.8(1.8–9.4)
Lightning	—
Atmospheric chemistry	0.6 (0.3–1.2)
Total natural sources	**11.0 (5.4–19.6)**
Total natural + anthropogenic sources	**17.9 (8.1–30.7)**
Stratospheric sink	**14.3 (4.3–27.2)**[g]
Observed growth rate	**3.61 (3.5–3.8)**[h]
Global top-down (year 2011)[i]	
Burden (Tg N)	1553
Atmospheric Loss	11.9±0.9
Atmospheric Increase	4.0±0.5
Total Source	15.8±1.0
Natural Source	9.1±1.0
Anthropogenic Source	6.7±1.3

Prior slide:
16.3 (Total)
11.0 (Natural)
5.3 (Human)

Sources and Sinks of N_2O

Table 6.9 Notes:

a All units for N_2O fluxes are in TgN yr^{-1} as in AR4 (not based on 2006 IPCC Guidelines). Lower end of range in the natural ocean from Rhee et al. (2009); higher end of the range from Bianchi et al. (2012) and Olivier and Janssens-Maenhout (2012); natural soils in line with Stocker et al. (2013).

b Direct soil emissions and emissions from animal production; calculated following 2006 IPCC Guidelines (Syakila and Kroeze, 2011); range from AR4 (Olivier and Janssens-Maenhout, 2012).

c Following 2006 IPCC Guidelines (Kroeze et al., 2010; Syakila and Kroeze, 2011). Higher end of range from AR4; lower end of range from 1996 IPCC Guidelines (Mosier et al., 1998). Note that a recent study indicates that emissions from rivers may be underestimated in the IPCC assessments (Beaulieu et al., 2011).

d Following 2006 IPCC Guidelines (Syakila and Kroeze, 2011).

e Suntharalingam et al. (2012).

f Syakila et al. (2010).

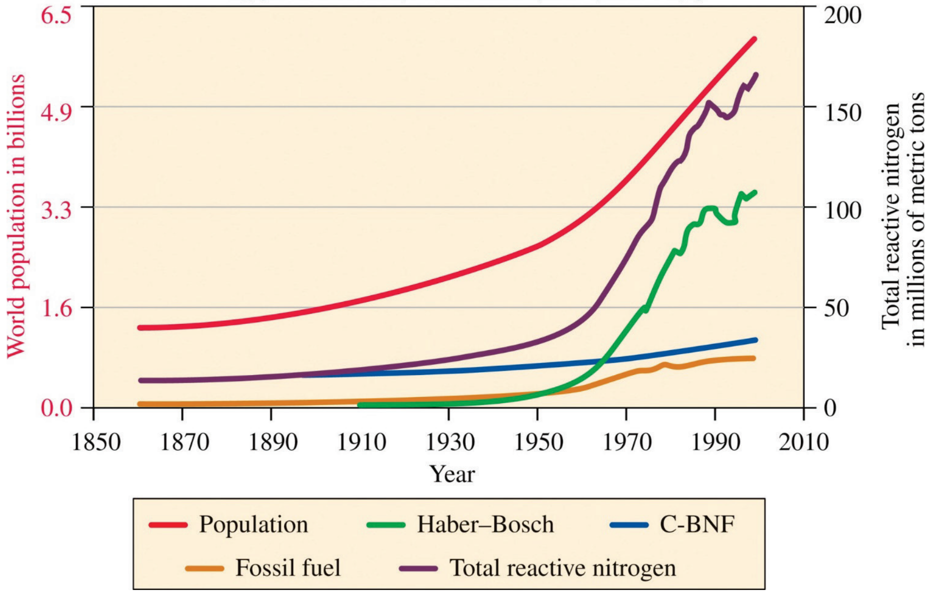
g *The stratospheric sink regroups losses via photolysis and reaction with O(^{1}D) that account for 90% and 10% of the sink, respectively (Minschwaner et al., 1993)*. The global magnitude of the stratospheric sink was adjusted in order to be equal to the difference between the total sources and the observed growth rate. This value falls within literature estimates (Volk et al., 1997).

h Data from Sections 6.1 and 6.3 (see Figure 6.4c). The range on the observed growth rate in this table is given by the 90% confidence interval of Figure 6.4c.

i Based on Prather et al. (2012), updated to 2011 (Table 2.1) and used in Chapter 11 projections; uncertainties evaluated as 68% confidence intervals, N_2O budget reduced based on recently published longer lifetimes of 131±10 yrs, see Annex II.2.3 and II.4.3.

The Nitrogen Cycle

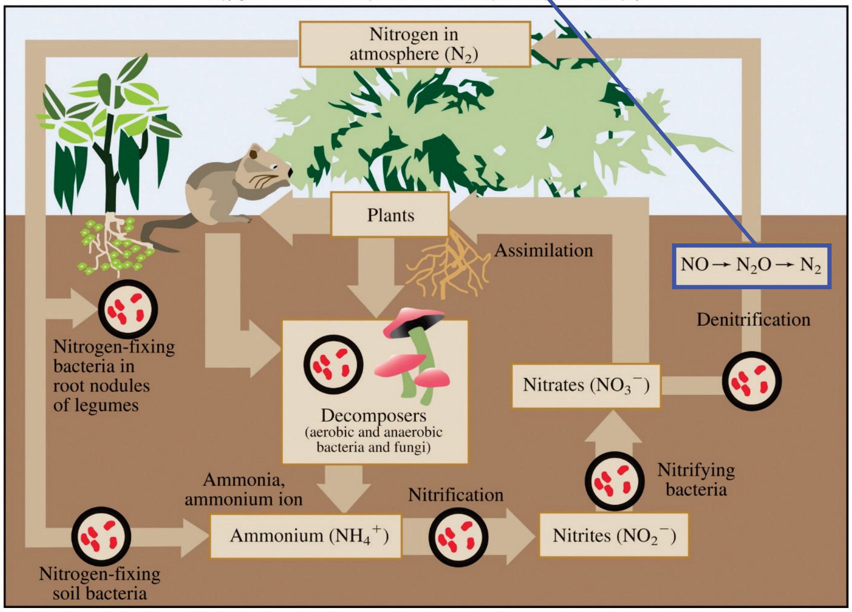
Haber-Bosch: N_2(gas) + 3 H_2 (gas) → 2 NH_3 (gas)
Led to large scale, economical production of ammonia based fertilizer



Chapter 6, *Chemistry in Context*

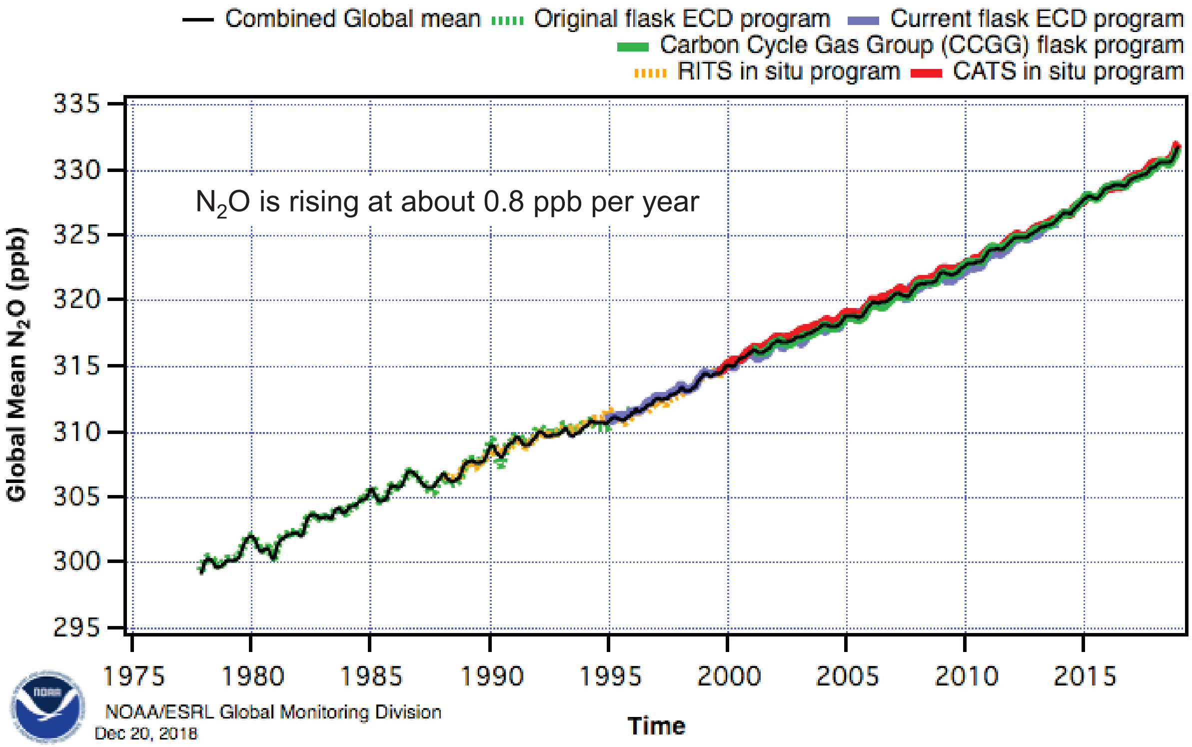
The Nitrogen Cycle

The reactive forms of nitrogen in this cycle continuously change chemical forms. Thus, the ammonia that starts out as fertilizer may end up as NO, in turn increasing the acidity of the atmosphere. Or the NO may end up as N_2O, a GHG that is currently rising.



Chapter 6, *Chemistry in Context*

N_2O Time Series



N_2O is rising at about 0.8 ppb per year

http://www.esrl.noaa.gov/gmd/hats/combined/N2O.html

N_2O and NO_y

Loss of N_2O occurs mainly in the stratosphere due to:
photolysis – main sink
reaction with electronically excited $O(^1D)$ – minor sink

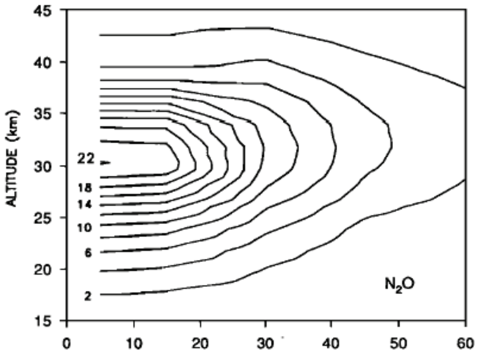


Fig. 11. Diurnally averaged loss rate for N_2O (10^2 molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N_2O by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

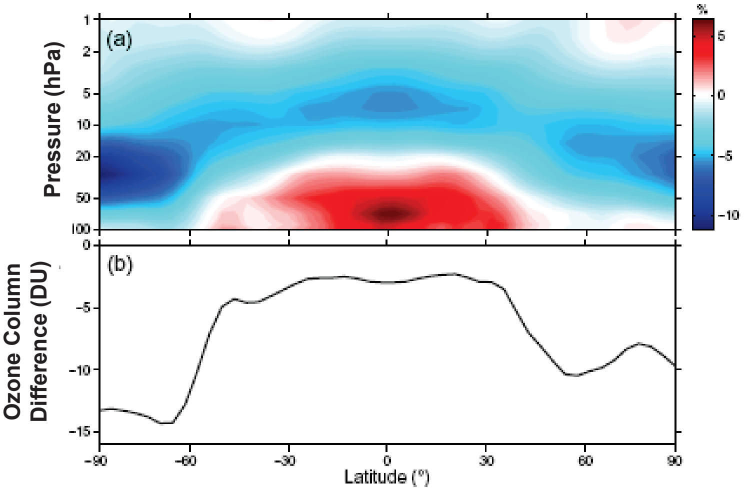
The minor sink for N_2O loss has a path that results in "fixed nitrogen":

$$N_2O + O(^1D) \rightarrow NO + NO$$

Fixed nitrogen (NO_y) is crucial to stratospheric chemistry

Oxides of nitrogen catalyze loss of stratospheric O_3 & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.

N_2O and Stratospheric Ozone



Revell *et al.*, *ACP*, 2012

Difference of stratospheric O_3 in the 2090s for a computer simulation run using N_2O from RCP 8.5 minus that of a simulation using N_2O from RCP 2.6

Rising N_2O leads to:
a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO_2 mediated loss cycles.

b) speeds up the rate of $OH+NO_2+M \rightarrow HNO_3$ & $ClO+NO_2+M \rightarrow ClNO_3+M$ in the lowermost stratosphere, leading to slower ozone loss by these cycles & less O_3 where these cycles dominate total loss of O_3

Computer models project stratospheric column O_3 will decline as N_2O rises