Methane and Nitrous Oxide
AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

Goals :

- **CH_4**
  - **sources and sinks**
  - **lifetime**
  - **human influence**
- **N_2O**
  - **sources and sinks**
  - **human influence**
- **Connection of CH_4 & N_2O 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

22 September 2020

Announcements: Outside of Class

1) Thurs, 24 Sept : AOSC Weekly Seminar (3:30 pm)

Professor Nicole Riemer, University of Illinois

Aerosol Mixing State: Synthesizing Measurements and Models

Atmospheric aerosols are complex mixtures of different chemical species, and individual particles exist in many different shapes and morphologies. These characteristics contribute to the aerosol mixing state, which continuously evolves in the atmosphere.

Atmospheric models have become sufficiently complex to incorporate aspects of aerosol mixing state in their predictions. Concurrently, sophisticated measurement techniques have been developed to probe various physicochemical properties of particles. However, there is no single instrument that can characterize all aspects of aerosol mixing state, and it has proven challenging to quantitatively compare measured mixing state attributes with mixing state predictions.

This talk will present a framework to synthesize a picture of the ambient aerosol from models and observations and identify current gaps in this endeavor. We will focus on suitable metrics to quantify mixing state, sampling strategies to determine these metrics that are accessible for both models and observations, and modeling strategies to scale up detailed modeling results on the particle scale to global predictions of mixing state.

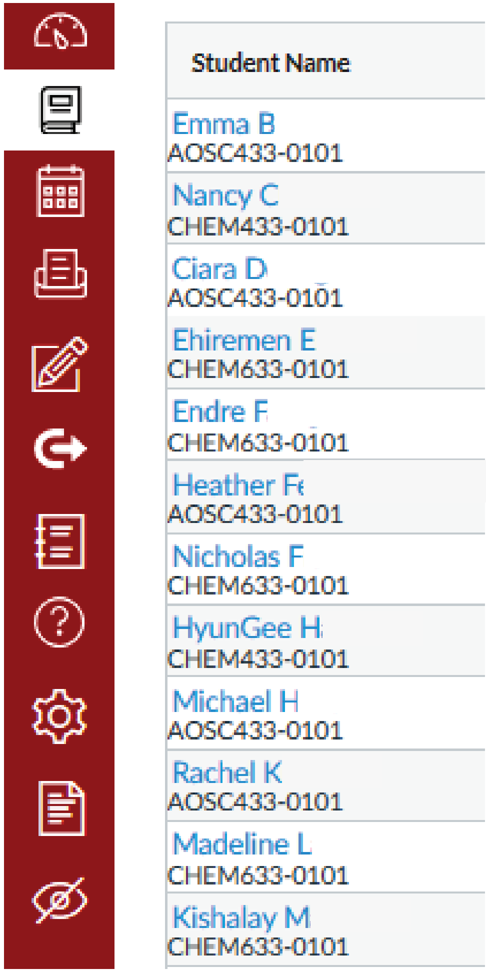
https://aosc.umd.edu/seminars/department-seminar

Email Joseph Knisely at jknisely@umd.edu for Zoom connection info

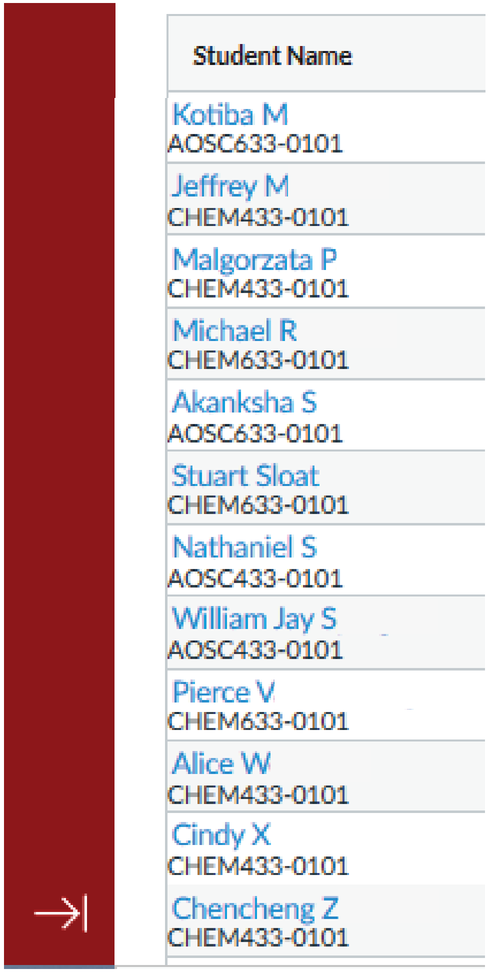
Announcements: Class

1) Starting on Thurs we will be using a password (distributed in announcement) to access class Zoom meetings

Roll call to state whether you know the password:



Student Name
Emma B AOSC433-0101
Nancy C CHEM433-0101
Ciara D AOSC433-0101
Ehiremen E CHEM633-0101
Endre F CHEM633-0101
Heather Fe AOSC433-0101
Nicholas F CHEM633-0101
HyunGee H CHEM433-0101
Michael H AOSC433-0101
Rachel K AOSC433-0101
Madeline L CHEM633-0101
Kishalay M CHEM633-0101



Student Name
Kotiba M AOSC633-0101
Jeffrey M CHEM433-0101
Malgorzata P CHEM433-0101
Michael R CHEM633-0101
Akanksha S AOSC633-0101
Stuart Sloat CHEM633-0101
Nathaniel S AOSC433-0101
William Jay S AOSC433-0101
Pierce V CHEM633-0101
Alice W CHEM433-0101
Cindy X CHEM433-0101
Chencheng Z CHEM433-0101

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 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.

CH_4 is the most reduced form of carbon

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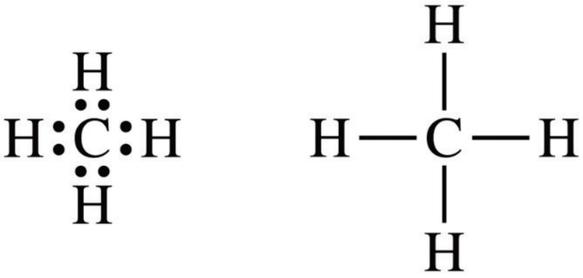

C in CH_4: has received an electron from each H atom.
All electrons are paired and hence this compound is relatively stable

CH_4 is the most reduced form of carbon

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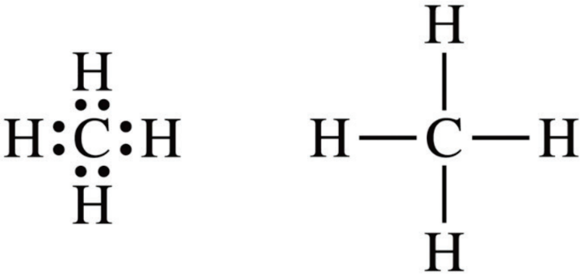
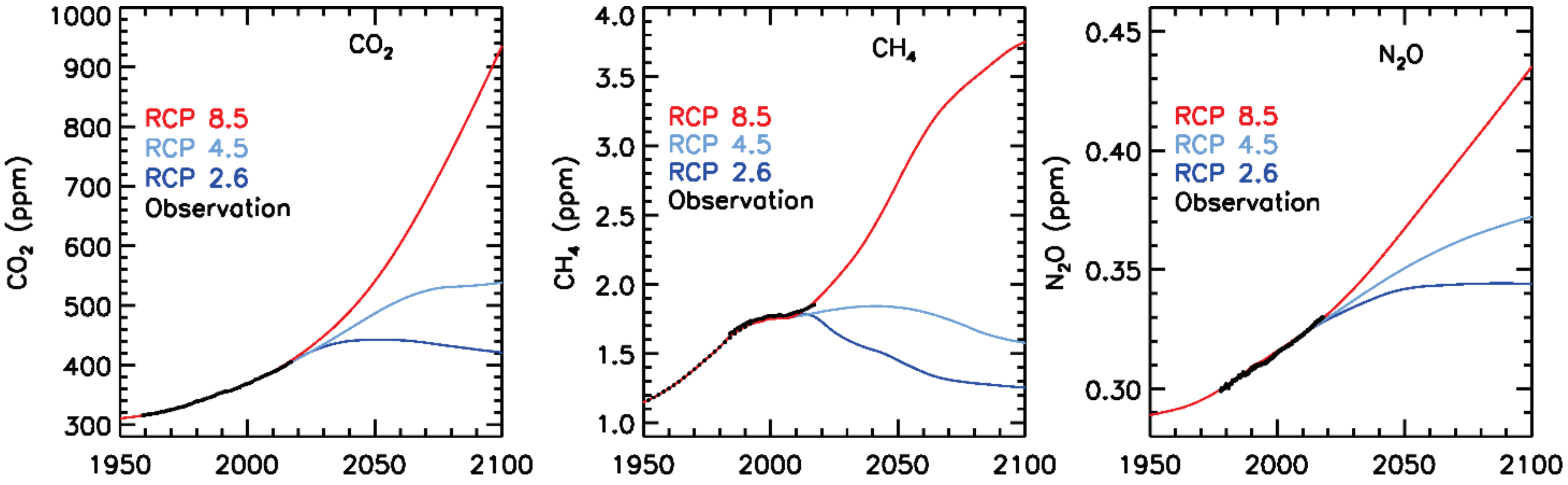


C in CH_4: has received an electron from each H atom.
All electrons are paired and hence this compound
is relatively stable: **until encountering OH : $H + OH \rightarrow H_2O$**

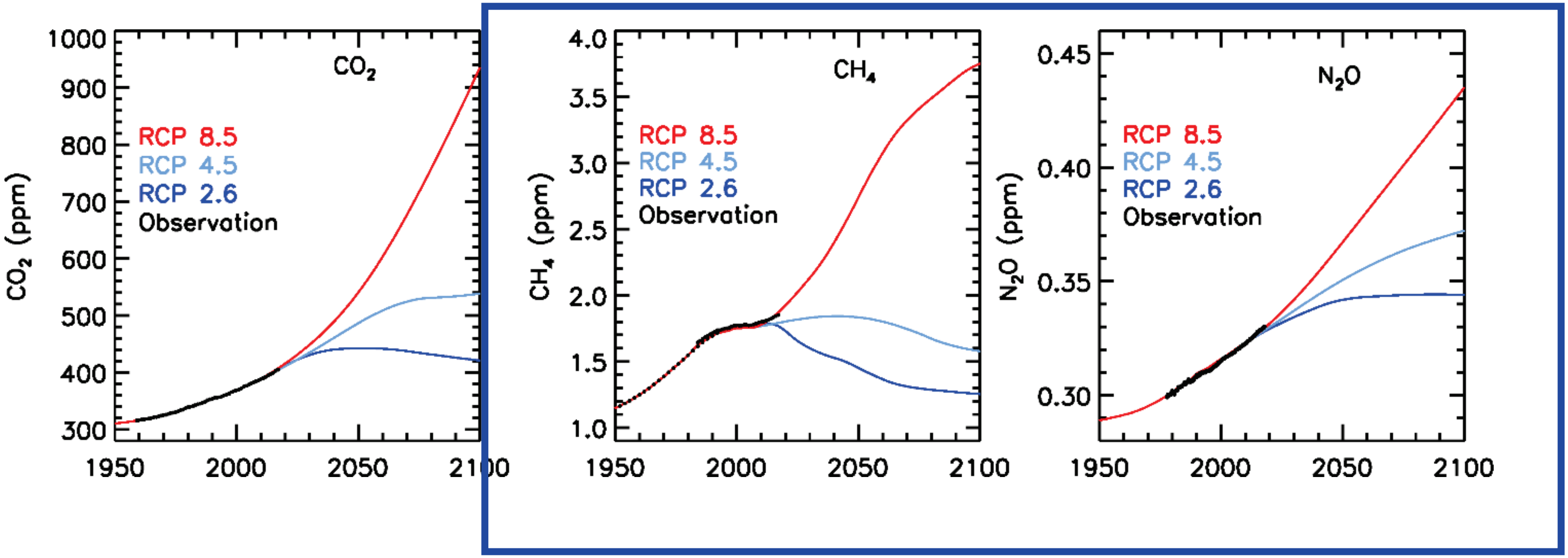
RCP Scenarios Forecast Wide Range of Possible Futures



- 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

Figure from Hope et al., 2020: https://www.essoar.org/pdfjs/10.1002/essoar.10504179.1

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



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Atmospheric CH_4

AT6, Q1:
According to Table 3.2 of Chemistry in Context, what was pre-industrial atmospheric abundance of CH_4 ***and*** is this consistent with Figure 3.7 of the Houghton reading?

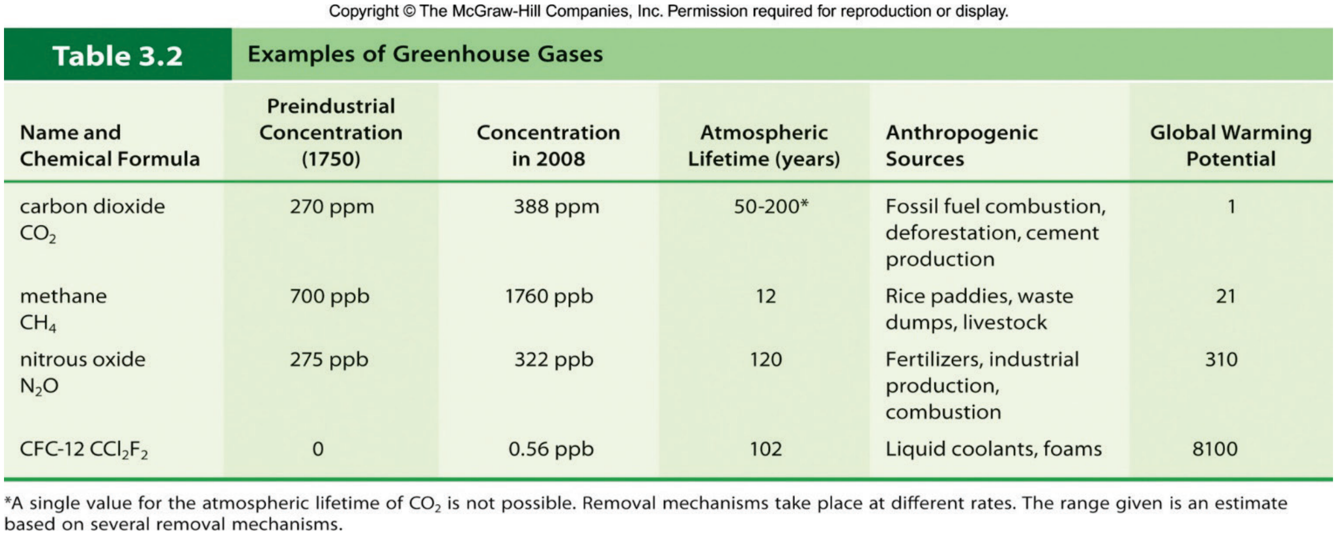

Table 3.2 Examples of Greenhouse Gases

Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
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methane CH_4	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
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CFC-12 CCl_2F_2	0	0.56 ppb	102	Liquid coolants, foams	8100

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Chapter 3, *Chemistry in Context*

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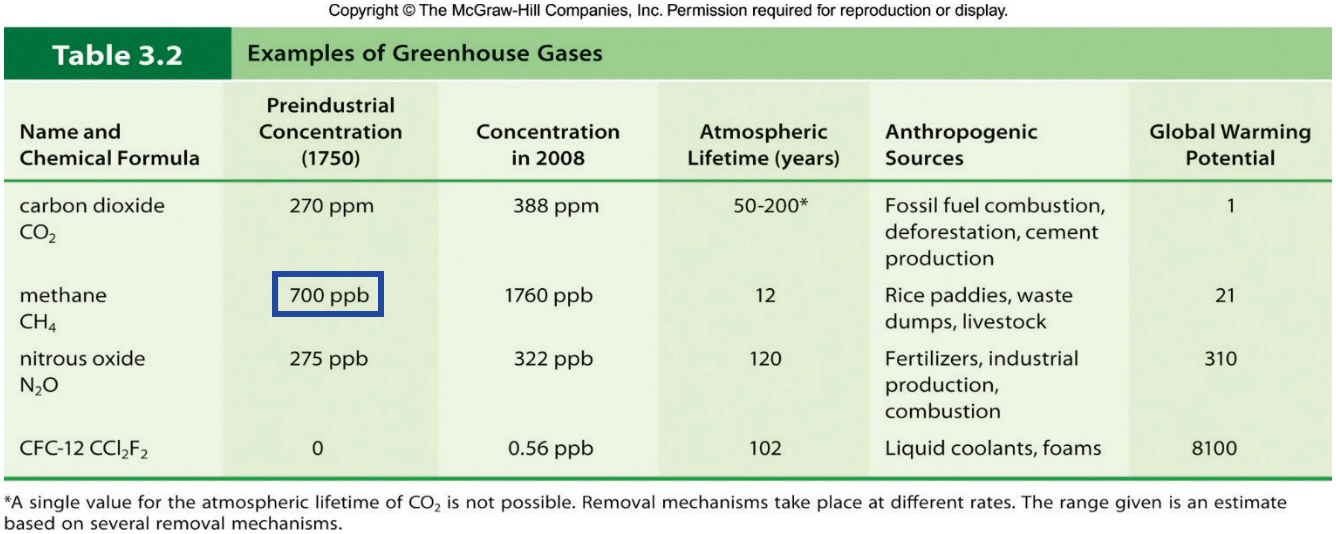

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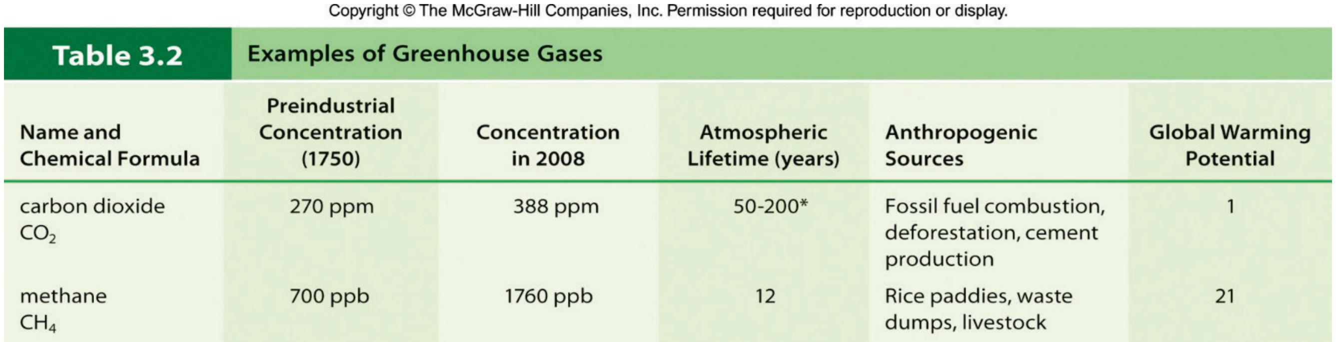
700 ppb

Broadly



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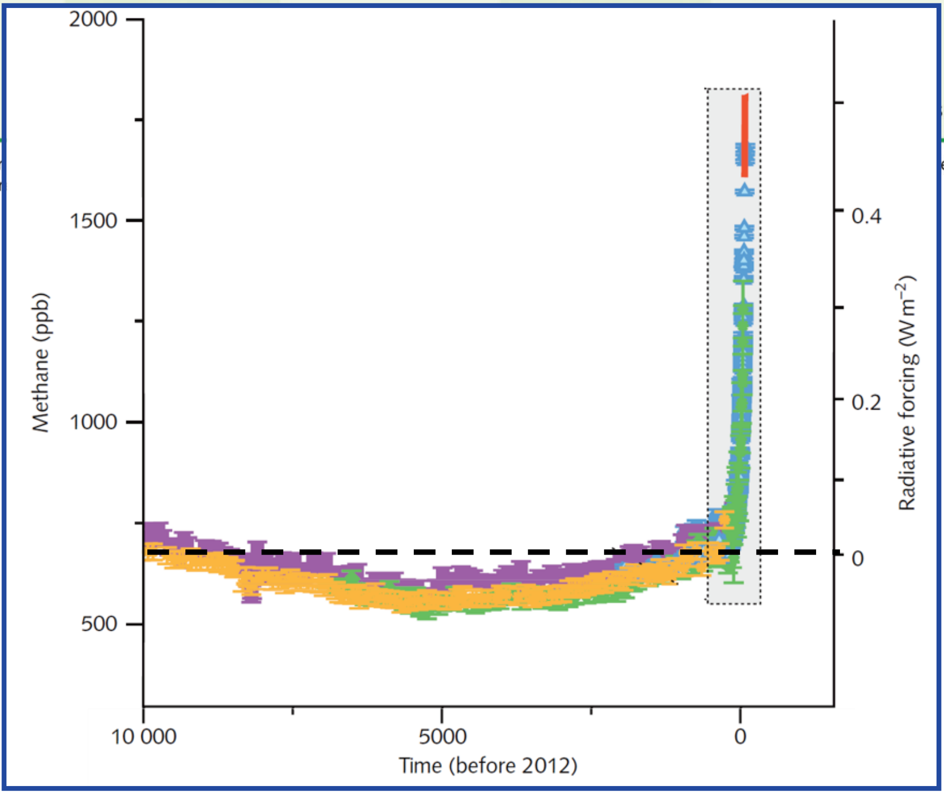
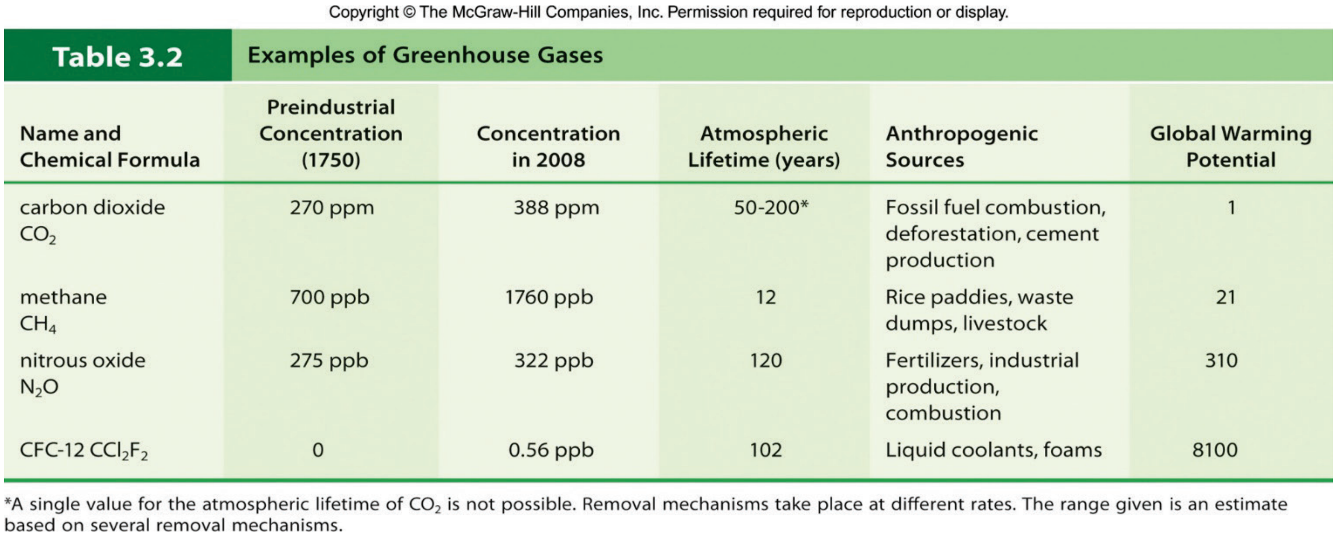


Figure 3.7, *Houghton*

Atmospheric CH_4

AT6, Q2:

What is the approximate current atmospheric abundance of CH_4?



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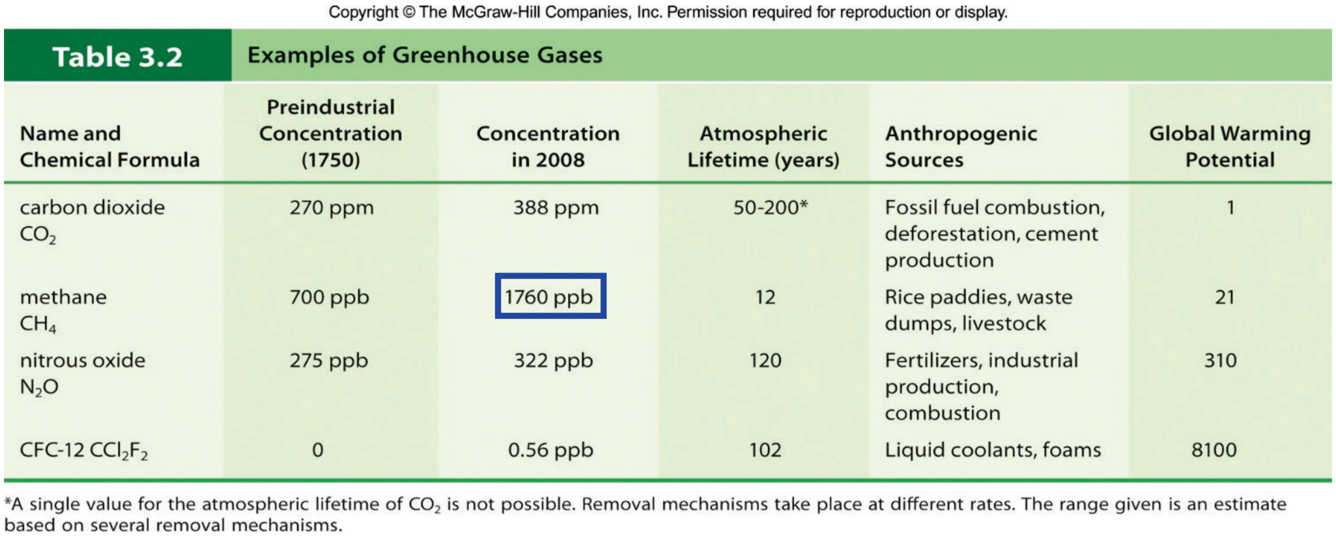

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Chapter 3, *Chemistry in Context*

***Chemistry in Context* gives 1760 ppb for year 2008**

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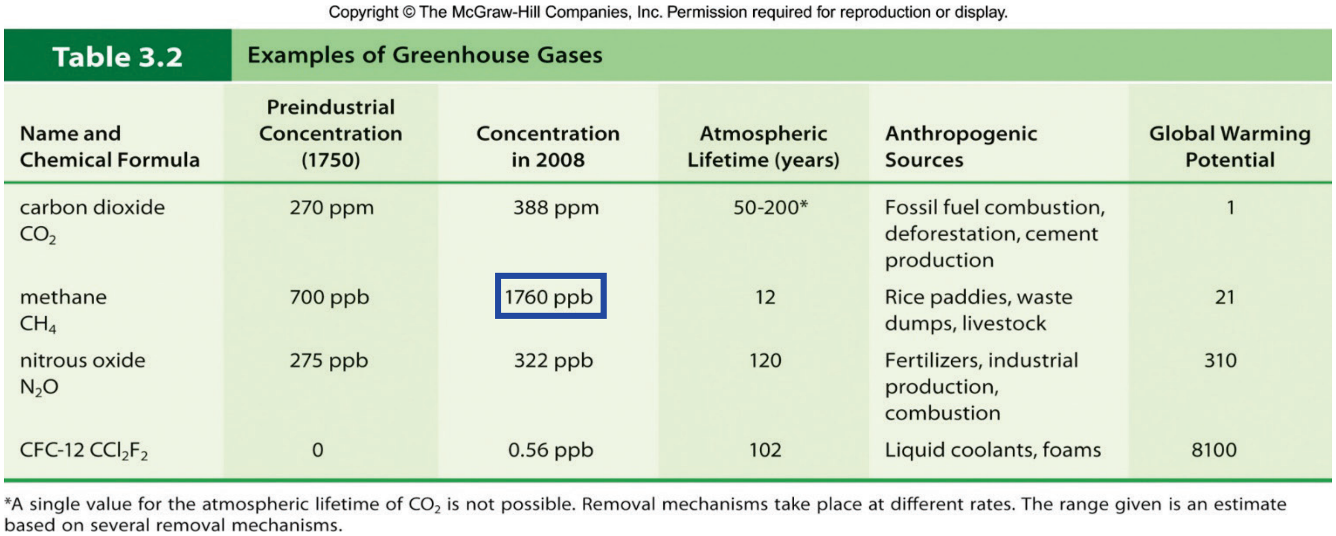

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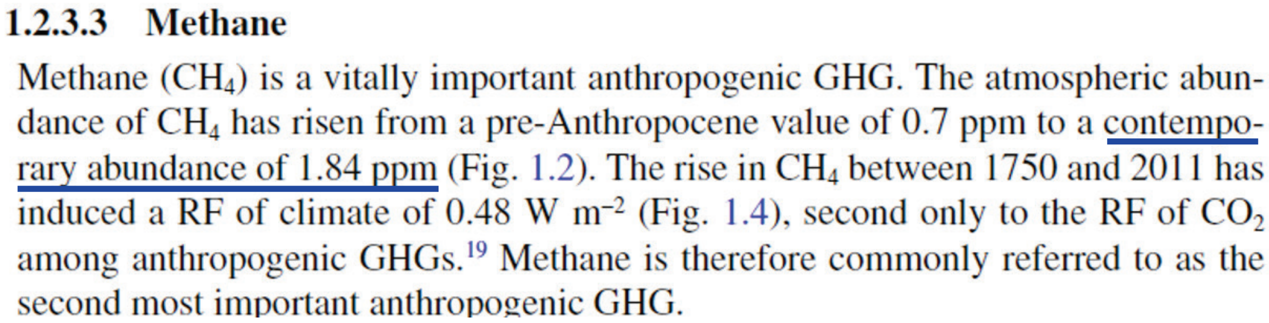
Chapter 3, *Chemistry in Context*

Chemistry in Context **gives 1760 ppb for year 2008**

Paris Climate Agreement: Beacon of Hope **gives 1.84 ppm for contemporary abundance of CH_4**



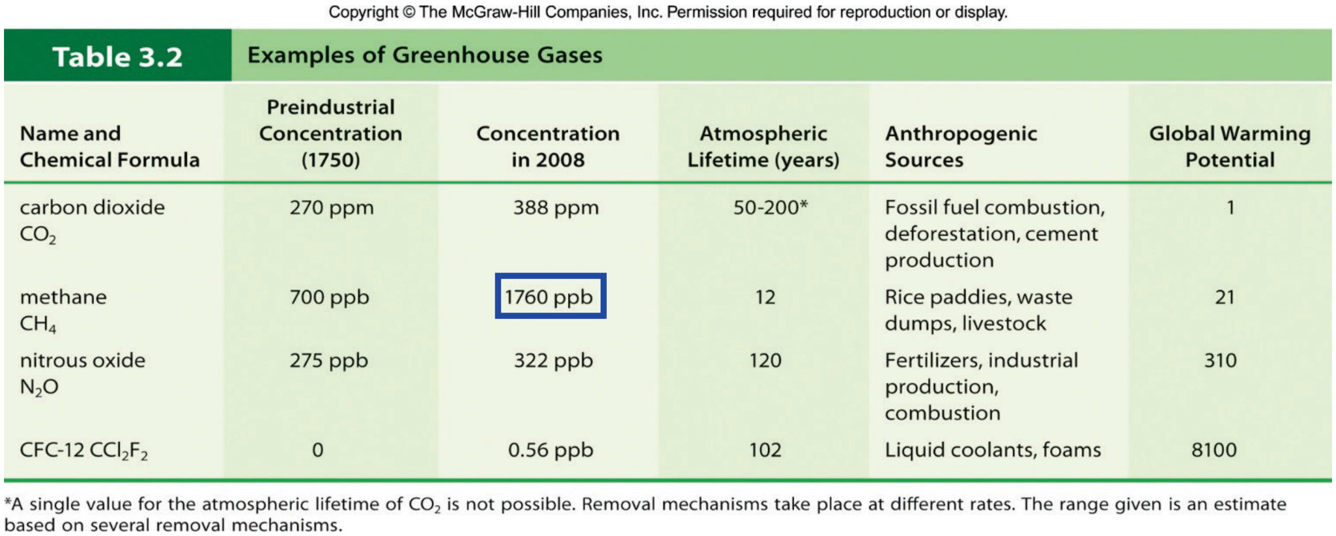
1.2.3.3 Methane

Methane (CH_4) is a vitally important anthropogenic GHG. The atmospheric abundance of CH_4 has risen from a pre-Anthropocene value of 0.7 ppm to a contemporary abundance of 1.84 ppm (Fig. 1.2). The rise in CH_4 between 1750 and 2011 has induced a RF of climate of 0.48 W m^{-2} (Fig. 1.4), second only to the RF of CO_2 among anthropogenic GHGs.[19] Methane is therefore commonly referred to as the second most important anthropogenic GHG.

Atmospheric CH_4

AT6, Q2:

What is the approximate current atmospheric abundance of CH_4?



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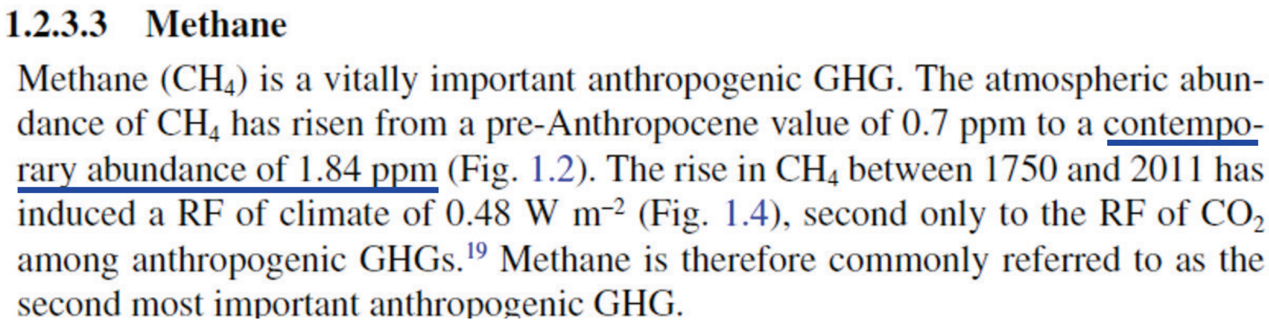
Chapter 3, *Chemistry in Context*

Chemistry in Context **gives 1760 ppb for year 2008**

Paris Climate Agreement: Beacon of Hope **gives 1.84 ppm for contemporary abundance of CH_4**

1760 ppb × (1 ppm / 1000 ppb) = 1.76 ppm

These values are similar (they differ by about 4.4%) and the difference does indeed reflect the recent growth in atmospheric CH_4.



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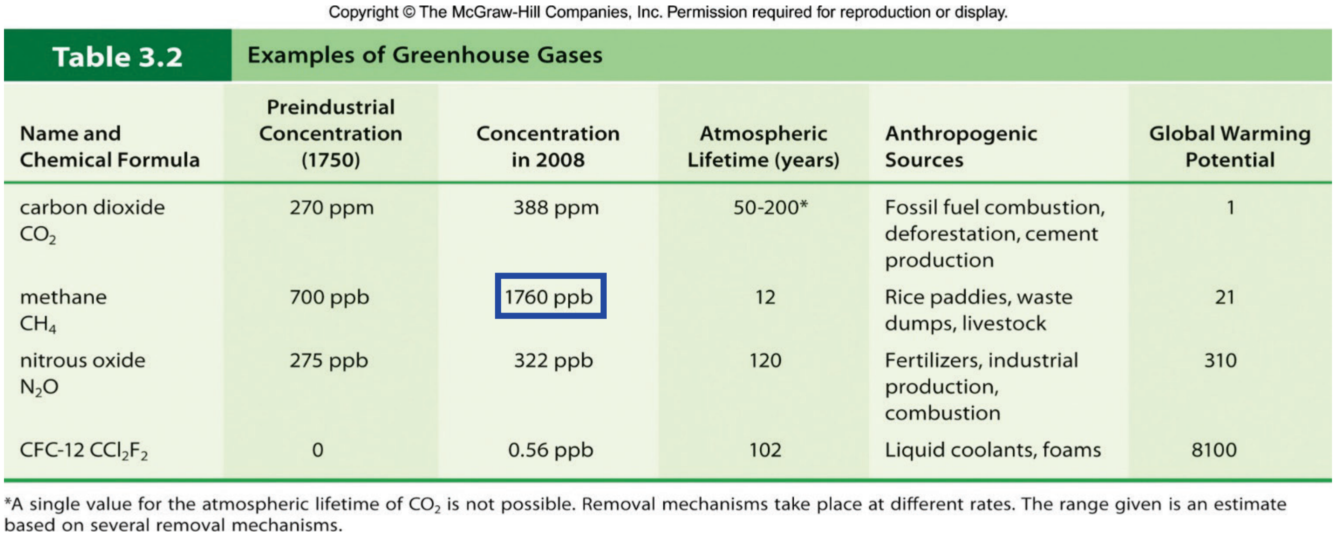

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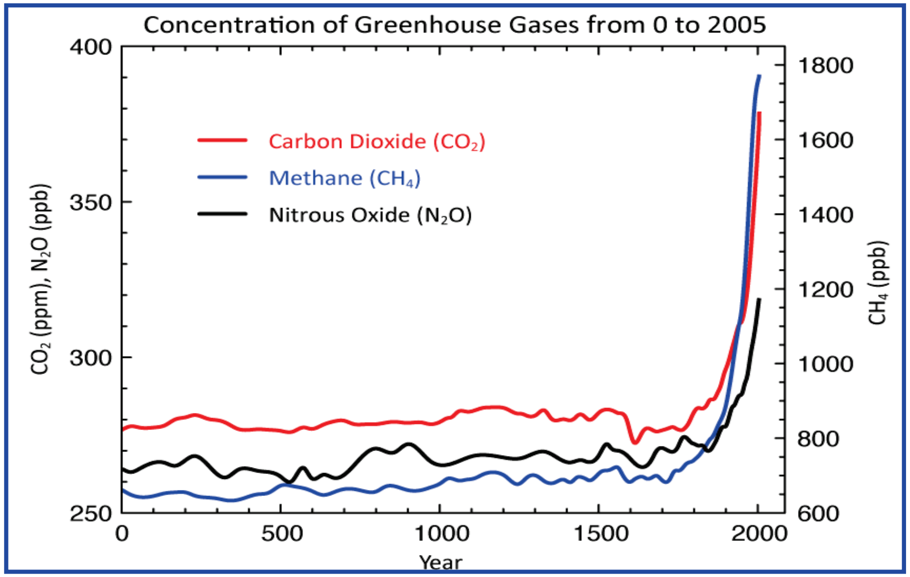
***Chemistry in Context* gives 1760 ppb for year 2008**

***Paris Climate Agreement: Beacon of Hope* gives 1.84 ppm for contemporary abundance of CH_4**

1760 ppb is consistent also with IPCC 2007 figure shown in Lecture 2



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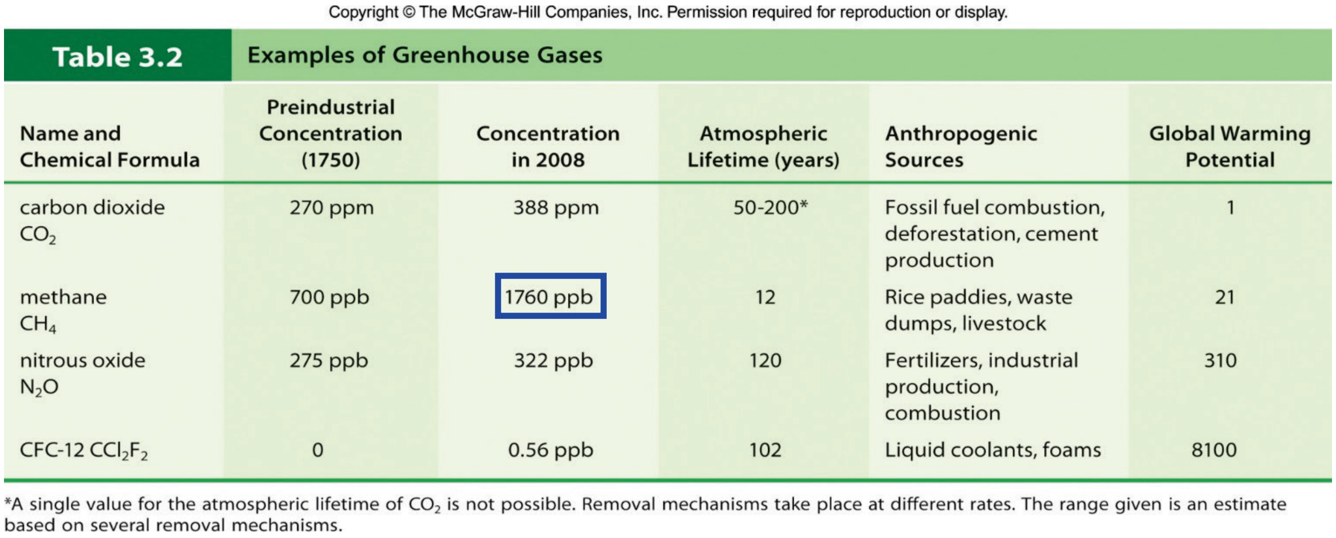

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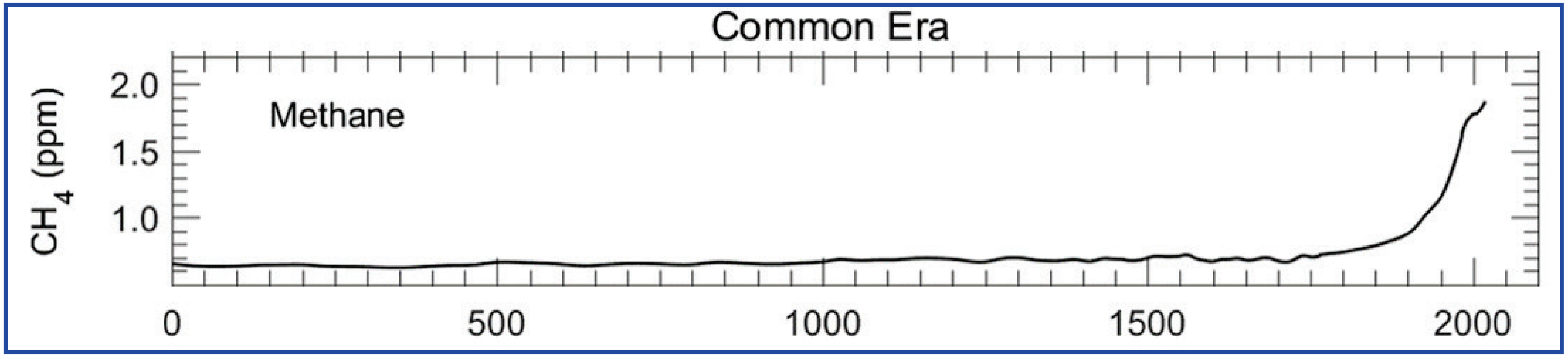
as well as Fig 1.2 from
Paris Climate Agreement: Beacon of Hope also shown in Lecture 2



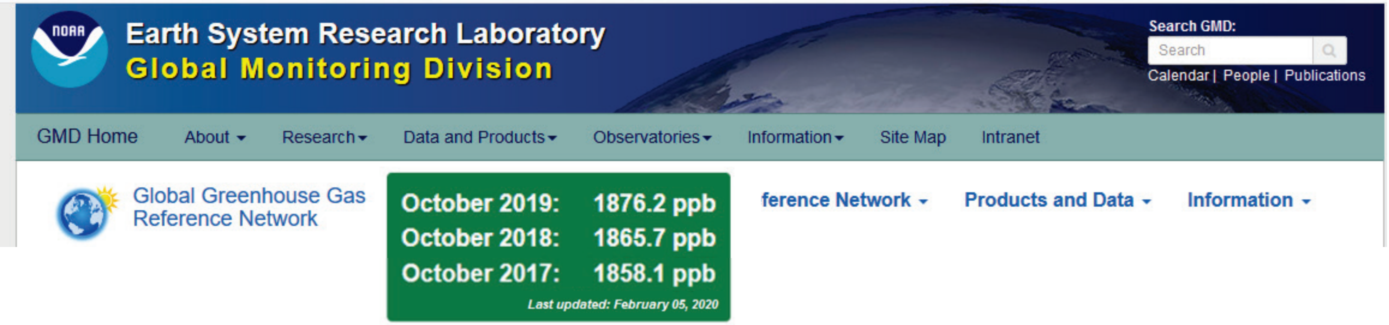
Atmospheric CH_4

AT6, Q2:

What is the approximate current atmospheric abundance of CH_4?

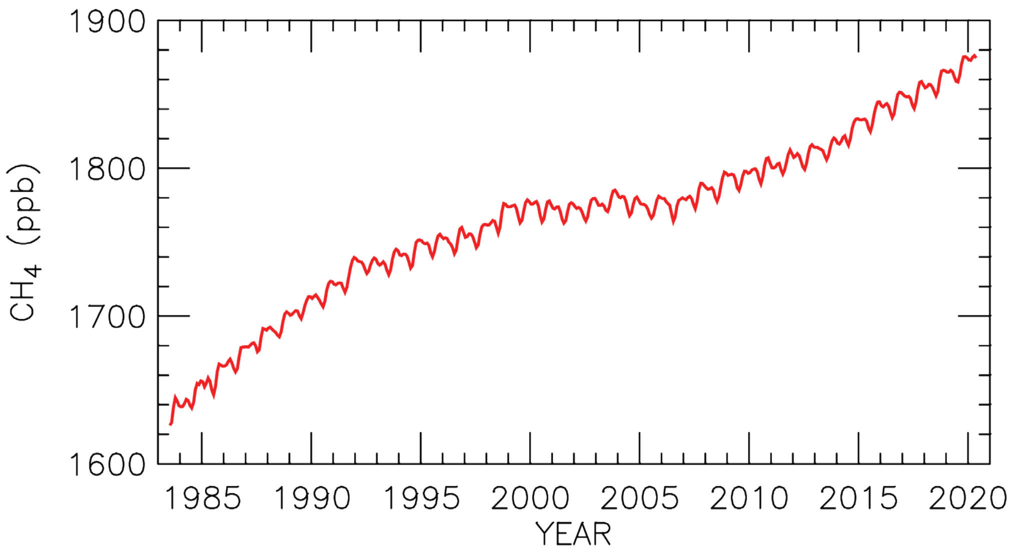
NOAA Earth System Research Laboratory (Boulder, Co) is “go to” place for information regarding GHGs

Latest data indicate CH_4 is at 1876.2 ppb and rising, and also that CH_4 exceeded 1760 ppb in late-1990s and exceeded 1.84 ppm in mid-2017.



October 2019:	1876.2 ppb
October 2018:	1865.7 ppb
October 2017:	1858.1 ppb

Last updated: February 05, 2020



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

Atmospheric CH_4

AT6, Q3:

What are the values given for:

a) enhanced greenhouse effect caused by a molecule of CH_4 relative to that of a molecule of CO_2 given on pg 47 of Houghton

b) the GWP for CH_4 given in Table 3.2 of *Chemistry in Context*

c) the GWP for CH_4 over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

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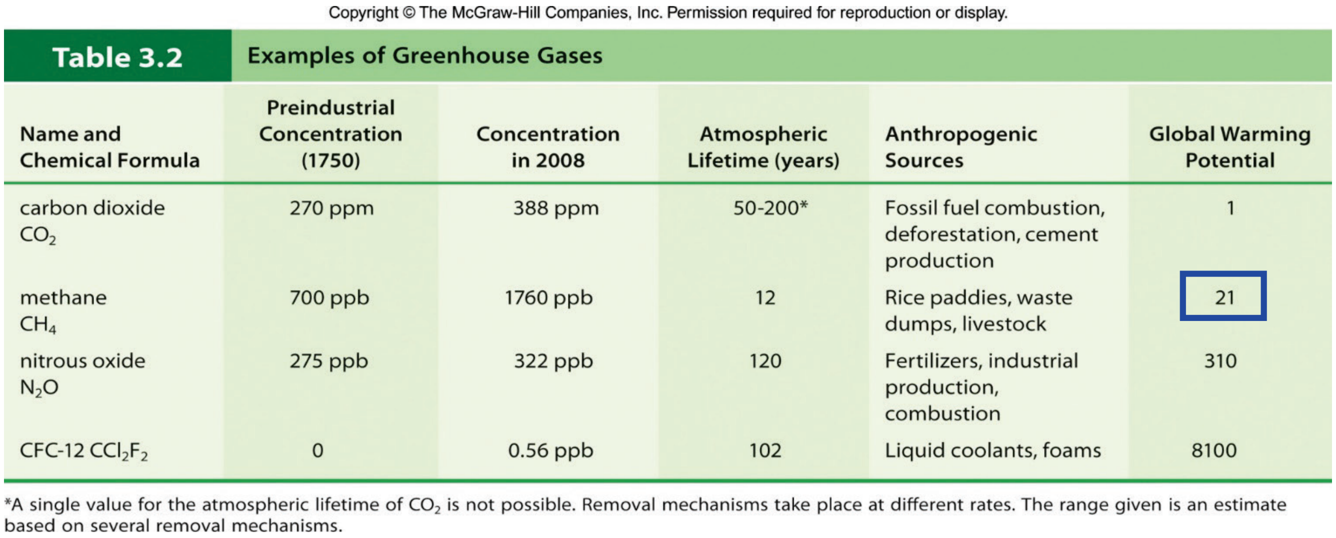

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Chapter 3, *Chemistry in Context*

Atmospheric CH_4

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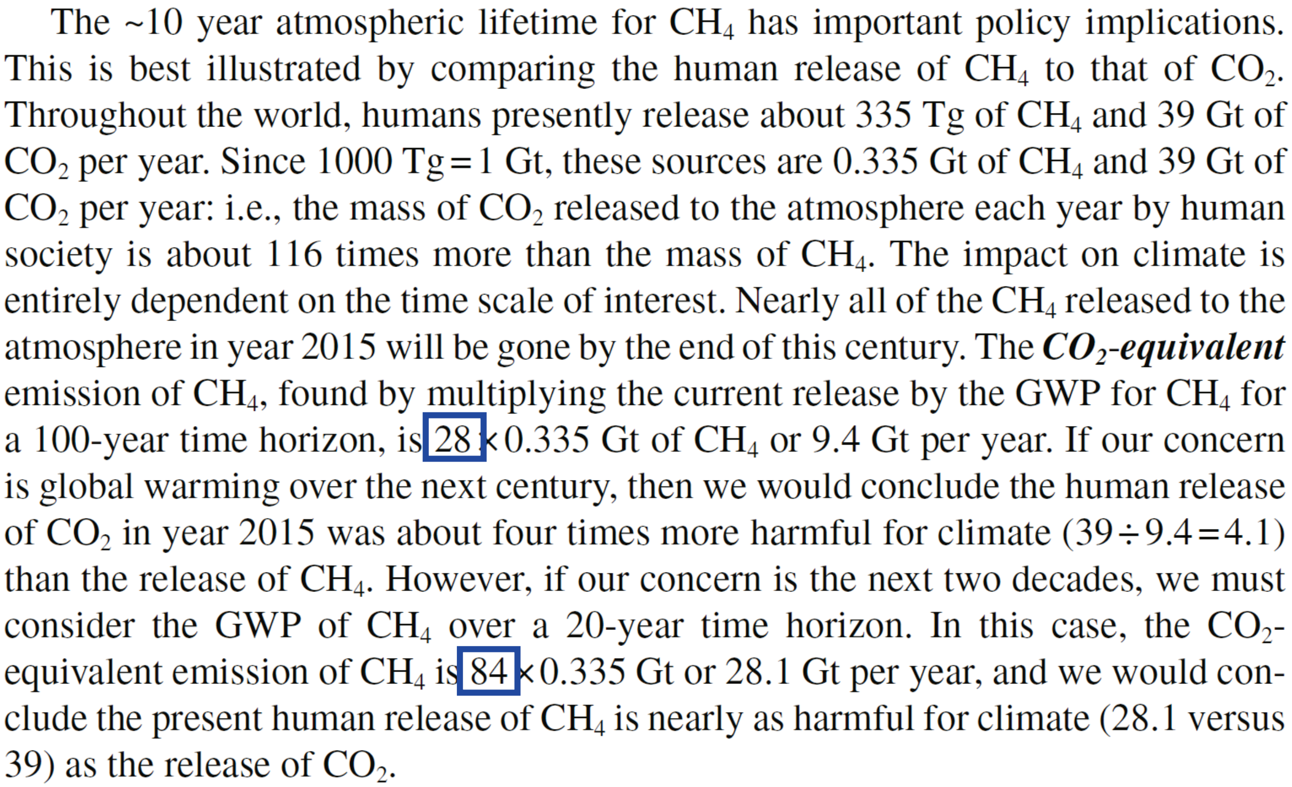

The ~10 year atmospheric lifetime for CH_4 has important policy implications. This is best illustrated by comparing the human release of CH_4 to that of CO_2. Throughout the world, humans presently release about 335 Tg of CH_4 and 39 Gt of CO_2 per year. Since 1000 Tg = 1 Gt, these sources are 0.335 Gt of CH_4 and 39 Gt of CO_2 per year: i.e., the mass of CO_2 released to the atmosphere each year by human society is about 116 times more than the mass of CH_4. The impact on climate is entirely dependent on the time scale of interest. Nearly all of the CH_4 released to the atmosphere in year 2015 will be gone by the end of this century. The ***CO_2-equivalent*** emission of CH_4, found by multiplying the current release by the GWP for CH_4 for a 100-year time horizon, is 28 × 0.335 Gt of CH_4 or 9.4 Gt per year. If our concern is global warming over the next century, then we would conclude the human release of CO_2 in year 2015 was about four times more harmful for climate (39 ÷ 9.4 = 4.1) than the release of CH_4. However, if our concern is the next two decades, we must consider the GWP of CH_4 over a 20-year time horizon. In this case, the CO_2-equivalent emission of CH_4 is 84 × 0.335 Gt or 28.1 Gt per year, and we would conclude the present human release of CH_4 is nearly as harmful for climate (28.1 versus 39) as the release of CO_2.

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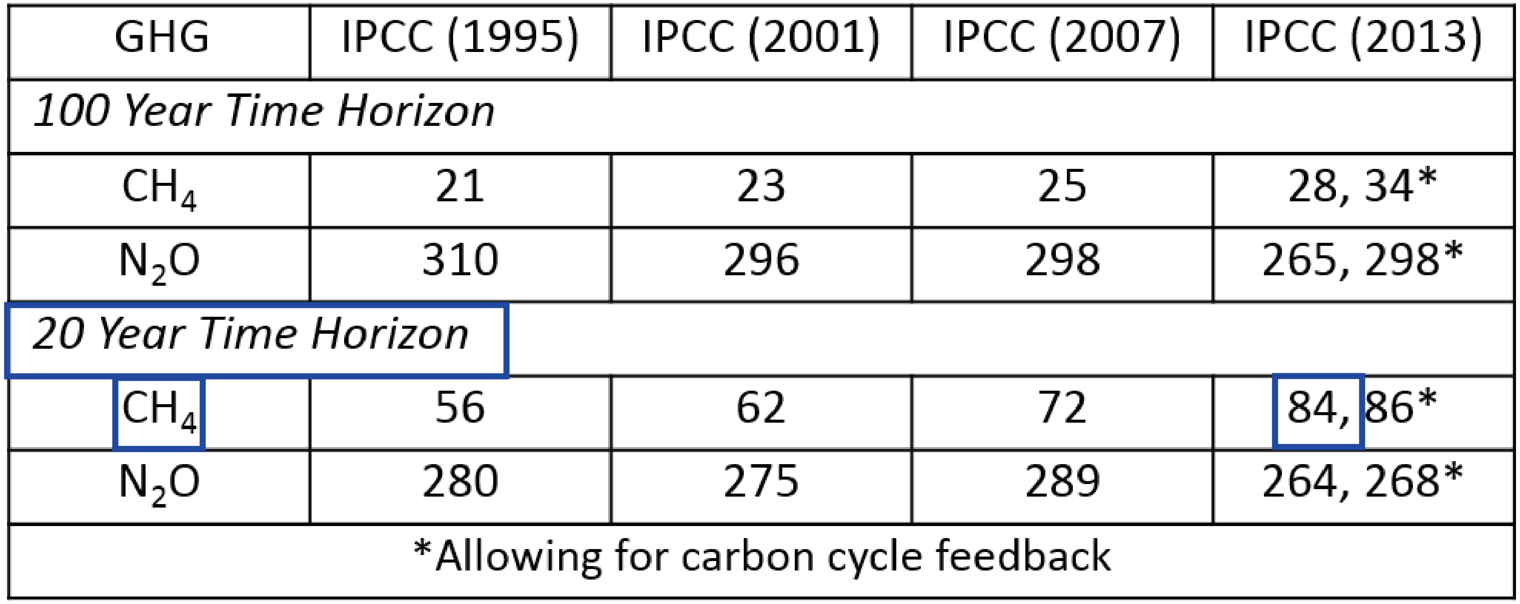
c) the GWP for CH_4 over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

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				

Atmospheric CH_4

AT6, Q3:

What are the values given for:

- a) enhanced greenhouse effect caused by a molecule of CH_4 relative to that of a molecule of CO_2 given on pg 47 of Houghton
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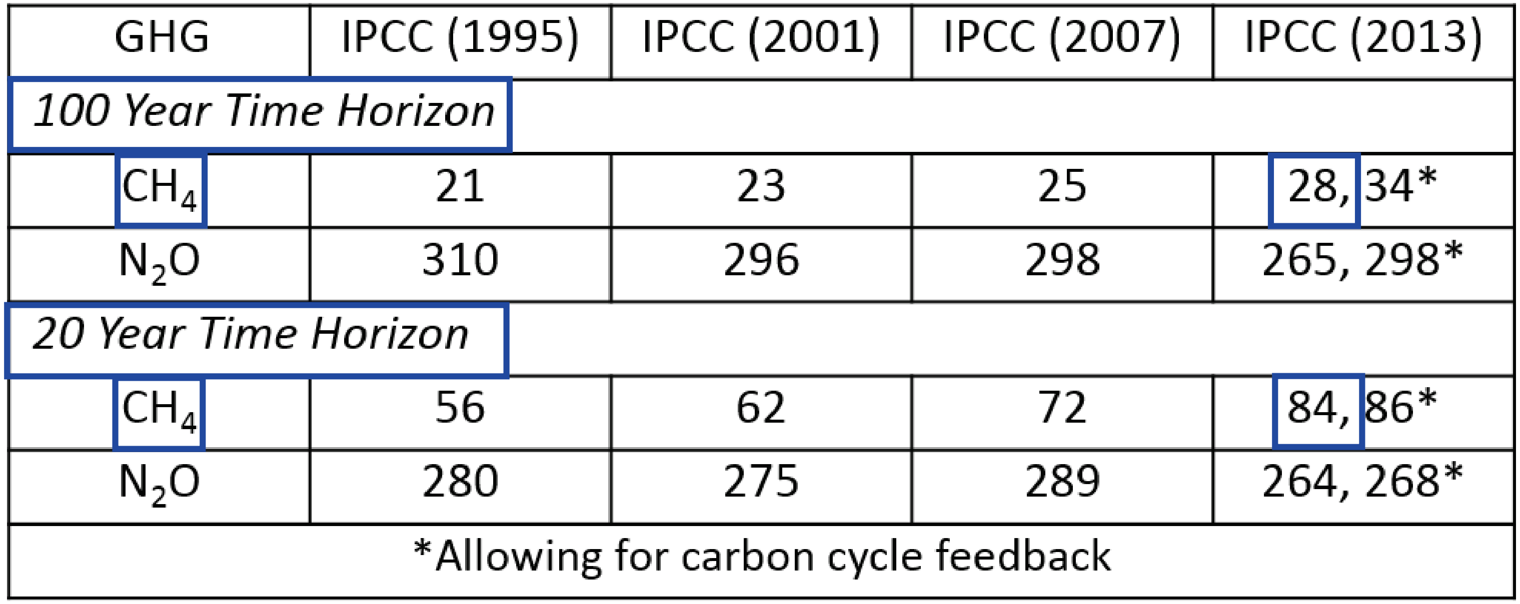

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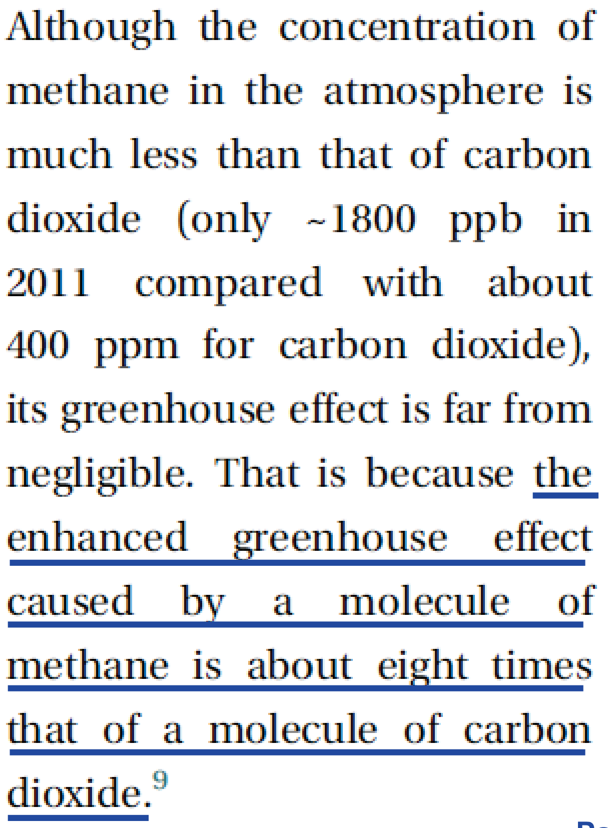

Although the concentration of methane in the atmosphere is much less than that of carbon dioxide (only ~1800 ppb in 2011 compared with about 400 ppm for carbon dioxide), its greenhouse effect is far from negligible. That is because the enhanced greenhouse effect caused by a molecule of methane is about eight times that of a molecule of carbon dioxide.[9]

Page 47, Houghton

Atmospheric CH_4

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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.

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Dang, Houghton is still using 23 !

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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 CH_4 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

Scientific utility of quantifying the human and natural sources of CH_4

CH_4 Sources:

Human: 335 Tg yr^{-1}

Natural: 218 Tg yr^{-1}

Total: 553 Tg yr^{-1}

Human ≈ 60% of total

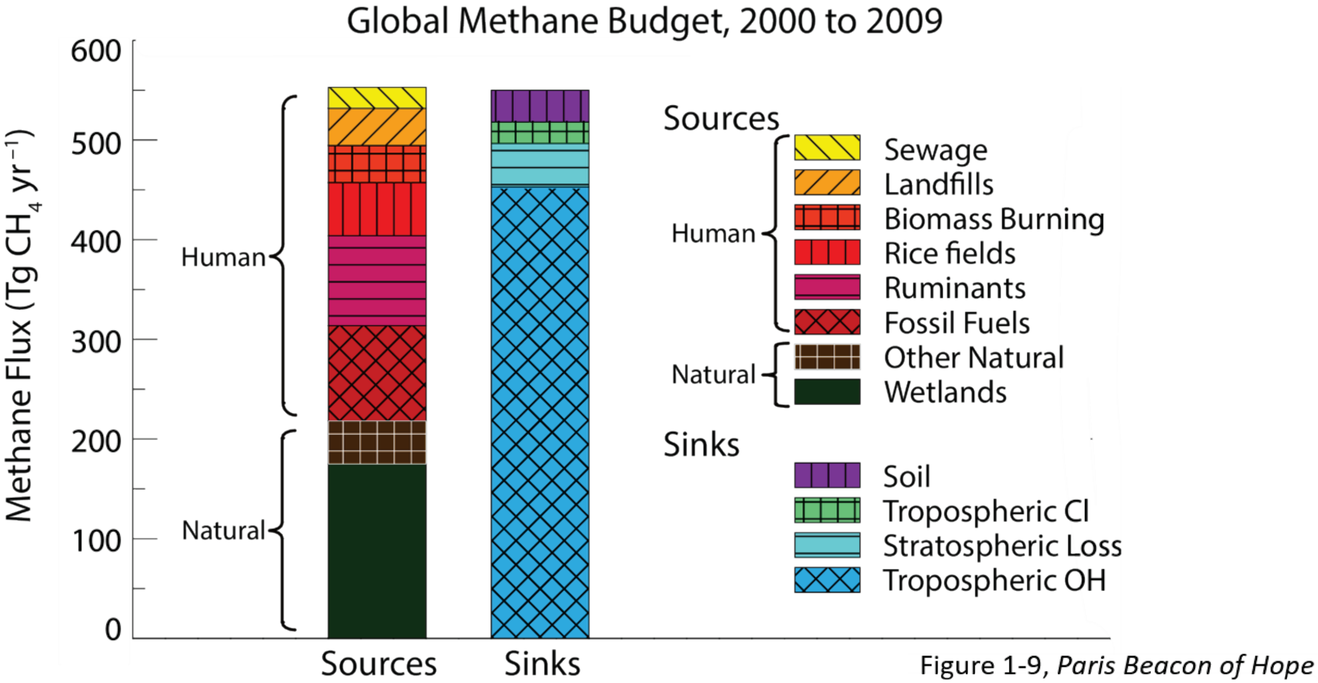

Figure 1-9, *Paris Beacon of Hope*

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

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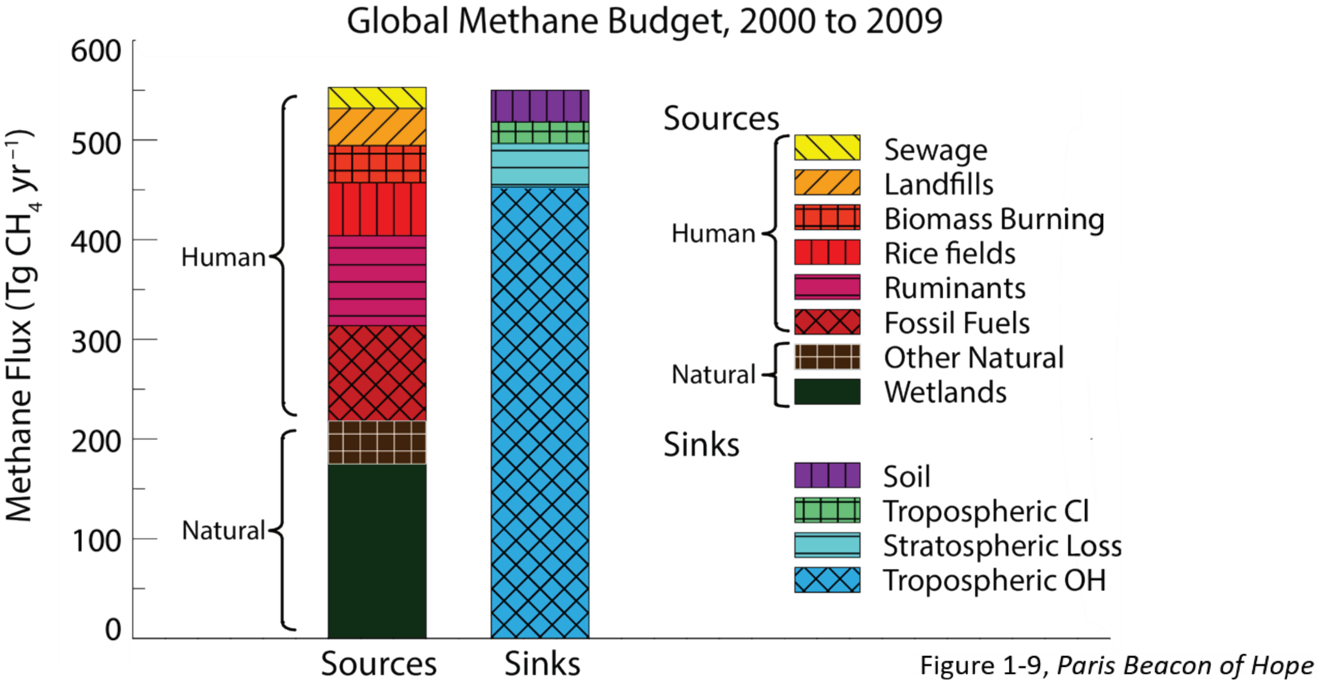

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Assuming k and [Gas] are constant over time, we can write:

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

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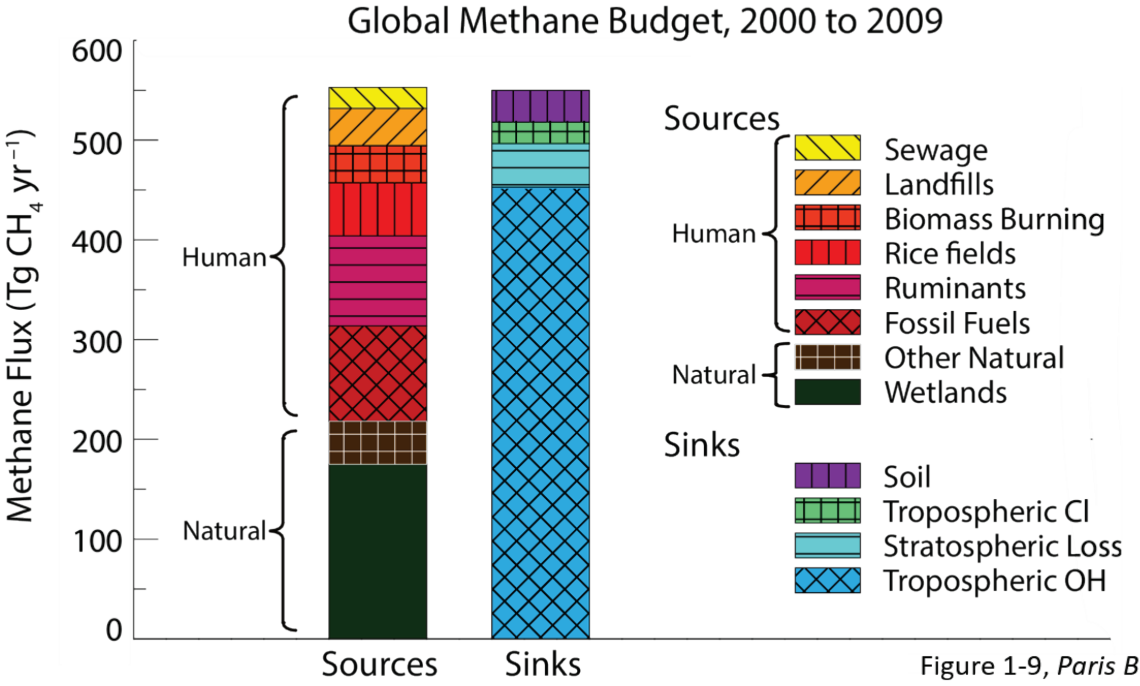

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which can be re-arranged to yield:

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

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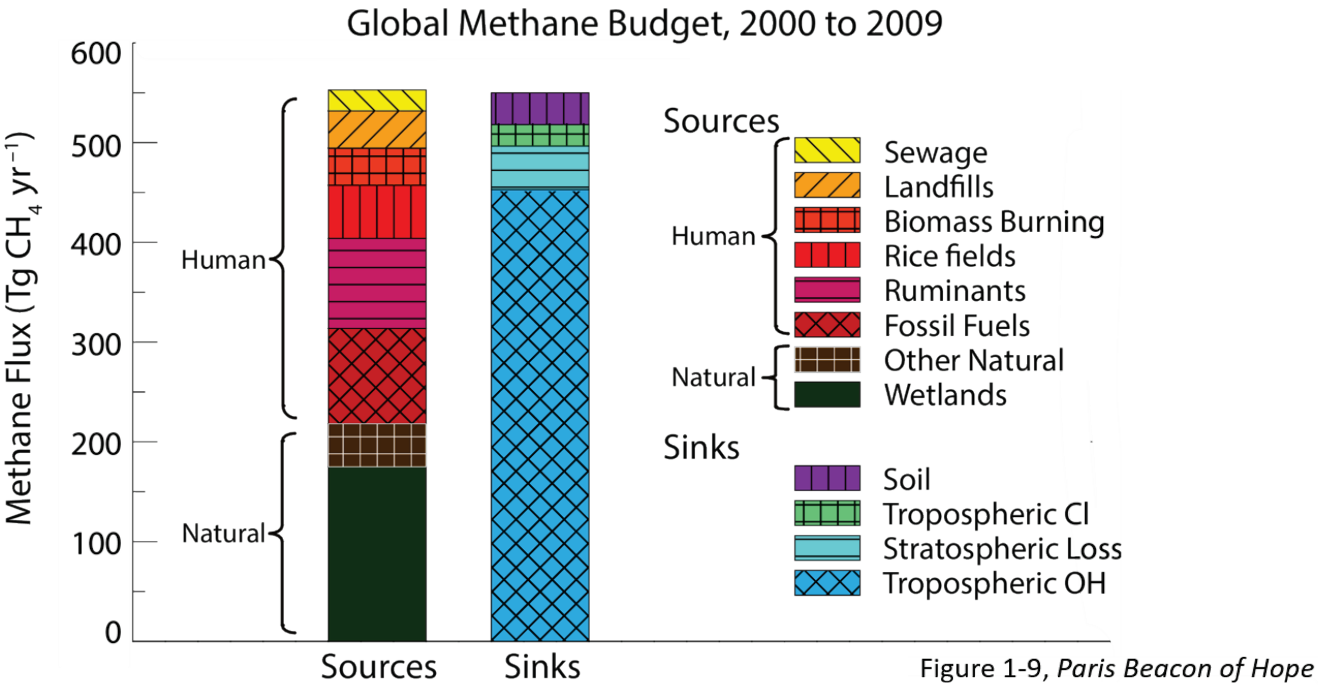

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If:

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

Then:

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

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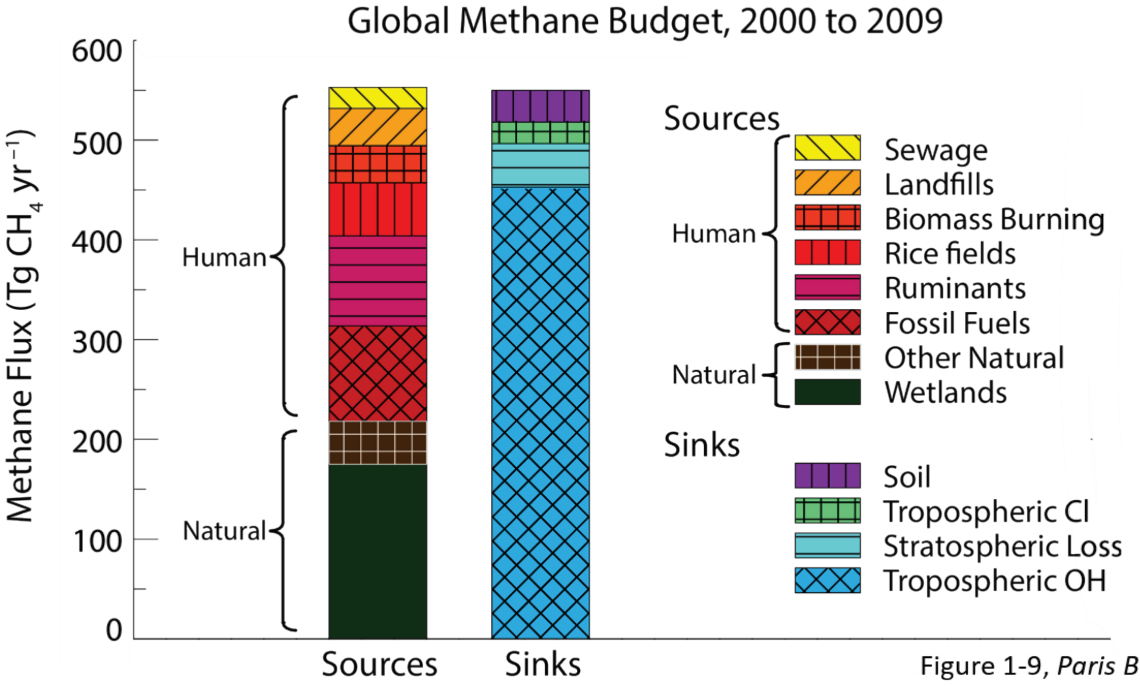

Figure 1-9, *Paris Beacon of Hope*

If:

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

Then:

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

Or:

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

Or:

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

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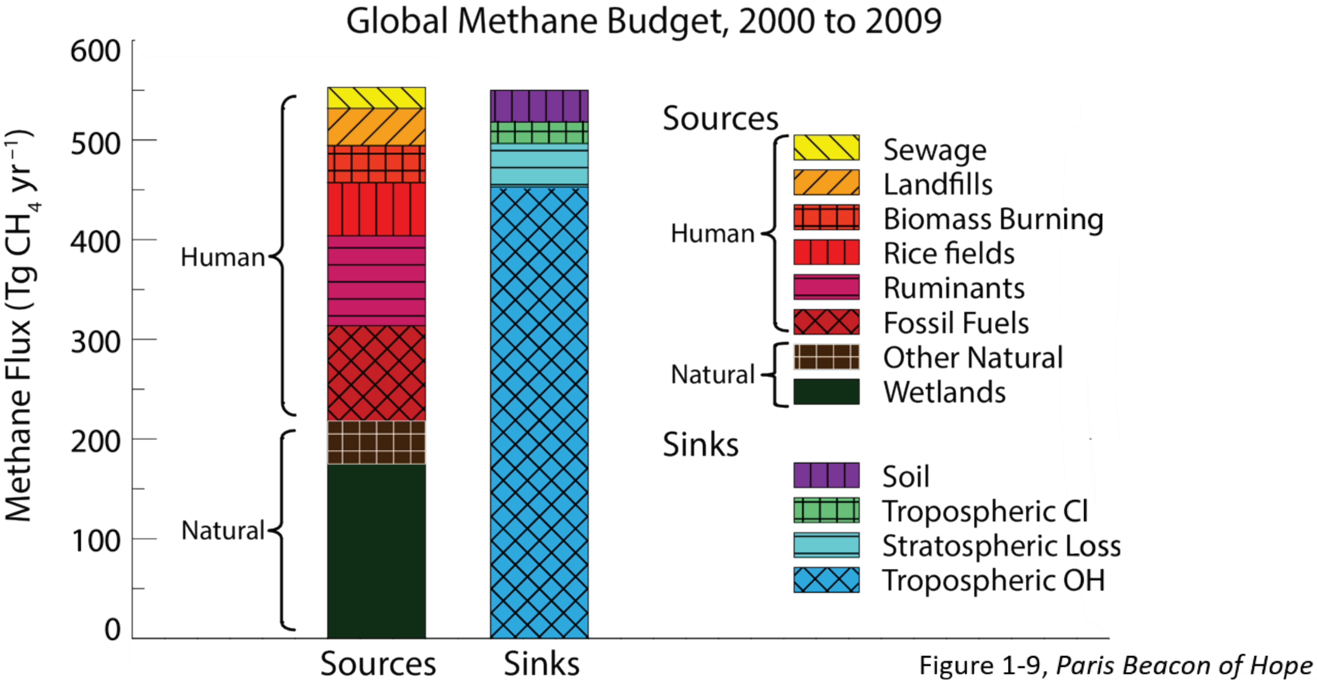

Figure 1-9, *Paris Beacon of Hope*

From prior slide:

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

Presumably:

$Source^{Preindustrial} = Source^{Present} – Source^{Human}$ (i.e., presumably "natural state" has not changed)

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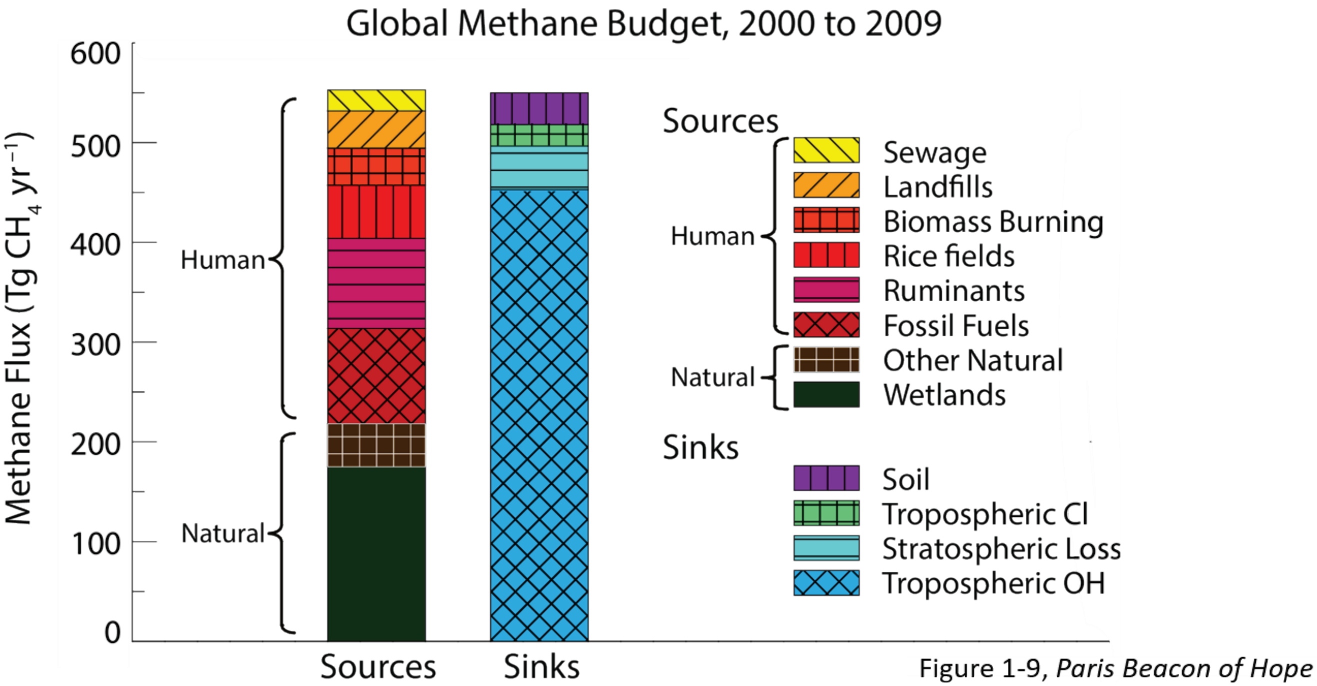

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Presumably:

$$Source^{Preindustrial} = Source^{Present} - Source^{Human}$$ **(i.e., presumably “natural state” has not changed)**

If so, then top equation can be written as:

$$[CH_4]^{Preindustrial} \, / \, [CH_4]^{Present} = (Source^{Present} - Source^{Human}) / Source^{Present}$$
$$= 1 - Source^{Human} / Source^{Present} = 1 - (335 \text{ Tg yr}^{-1}) / (553 \text{ Tg yr}^{-1})$$
$$= 1 - 0.61 = 0.39$$

Atmospheric CH_4

AT6, Q1:

According to Table 3.2 of Chemistry in Context what was pre-industrial atmospheric abundance of CH_4 ? ⇒ 700 ppb

AT6, Q2:

What is the approximate current atmospheric abundance of CH_4? ⇒ 1800 ppb

700 ppb / 1800 ppb = 0.39 !!!

From prior slide:

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

Presumably:

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

If so, then top equation can be written as:

$$\begin{aligned}[CH_4]^{\mathrm{Preindustrial}} / [CH_4]^{\mathrm{Present}} &= (\mathrm{Source}^{\mathrm{Present}} - \mathrm{Source}^{\mathrm{Human}}) / \mathrm{Source}^{\mathrm{Present}} \\ &= 1 - \mathrm{Source}^{\mathrm{Human}} / \mathrm{Source}^{\mathrm{Present}} = 1 - (335\ \mathrm{Tg\ yr^{-1}}) / (553\ \mathrm{Tg\ yr^{-1}}) \\ &= 1 - 0.61 = 0.39\end{aligned}$$

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

$CH_4 + OH \rightarrow H_2O + CH_3$

$$\frac{d\mathrm{CH}_4}{dt} = \mathrm{Production} - \mathrm{Loss} = \mathrm{Production} - k^{\mathrm{CH4+OH}}\,[\mathrm{CH}_4]\,[\mathrm{OH}]$$

Rate constant (speed at which CH_4 reactions with OH):

$$k^{\mathrm{CH4+OH}} = 1.85\times10^{-20}\times \mathrm{T}^{2.82} e^{-987/T}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$$

which is obtained from analysis of laboratory measurements

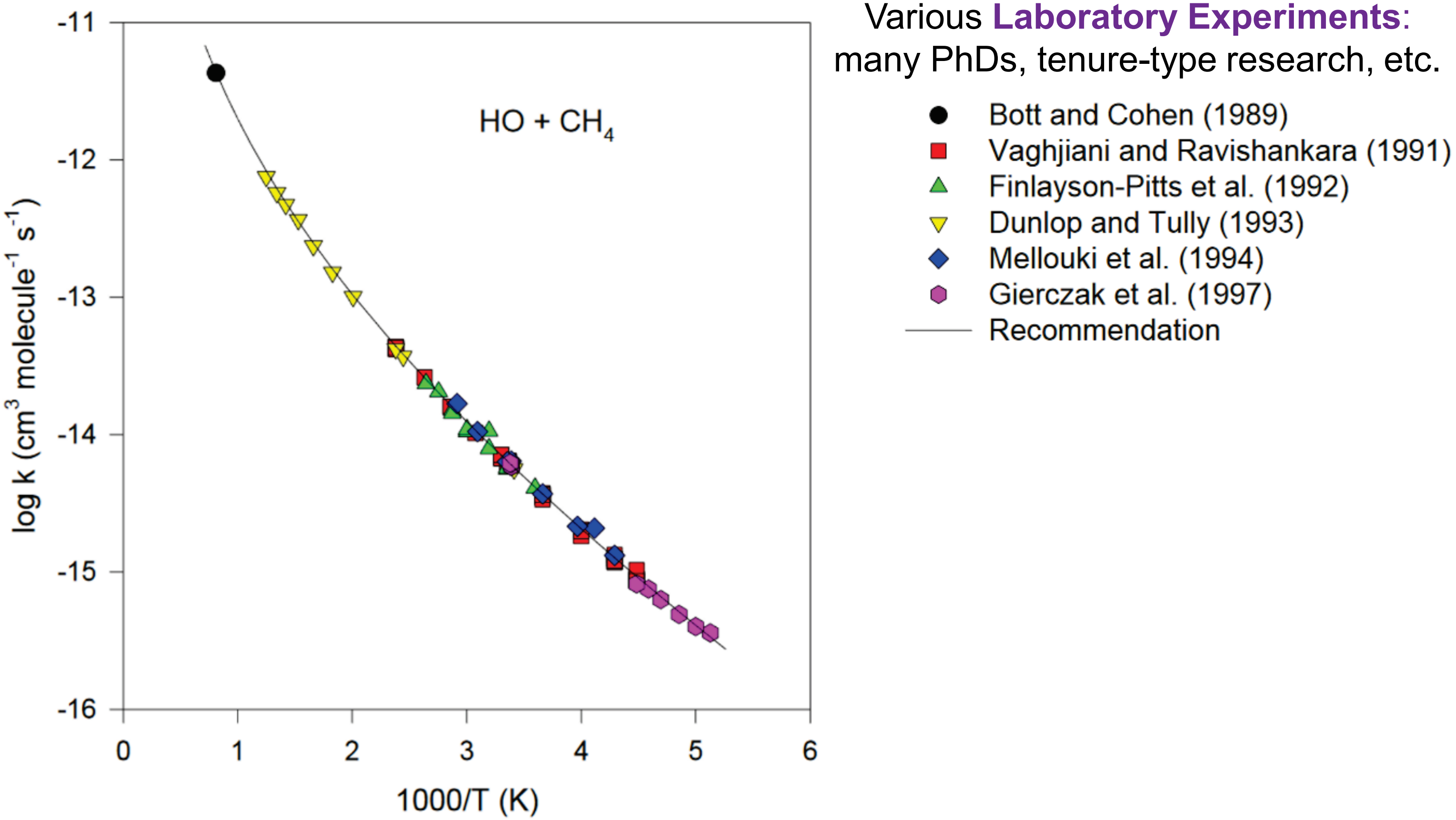
Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

Rate constant recommended by IUPAC

$$k^{\mathrm{OH+CH4}} = 1.85\times10^{-20} \times \mathrm{T}^{2.82} e^{-987/T} \ \mathrm{cm}^3 \ \mathrm{molecule}^{-1} \ \mathrm{sec}^{-1}$$

Various **Laboratory Experiments**:
many PhDs, tenure-type research, etc.



IUPAC: International Union of Pure and Applied Chemistry website
http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf

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$$\mathrm{Lifetime\ of\ CH}_4 = \frac{\mathrm{Abundance}}{\mathrm{Loss}} = \frac{[\mathrm{CH}_4]}{k^{\mathrm{CH4+OH}}[\mathrm{OH}][\mathrm{CH}_4]} = \frac{1}{k^{\mathrm{CH4+OH}}\,[\mathrm{OH}]}$$

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

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$$= 2.77\times10^8\ \mathrm{sec} = 8.80\ \mathrm{yr}$$

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

$CH_4 + OH \rightarrow H_2O + CH_3$

$$\frac{d\mathrm{CH_4}}{dt} = \text{Production} \; - \; \text{Loss} = \text{Production} \; - \; k^{\mathrm{CH4+OH}} \, [\mathrm{CH_4}] \, [\mathrm{OH}]$$

Rate constant (speed at which CH_4 reactions with OH):

$$k^{\mathrm{CH4+OH}} = 1.85\times10^{-20} \times \mathrm{T}^{2.82} e^{-987/T} \;\; \mathrm{cm^3} \;\; \mathrm{molecule^{-1}} \;\; \mathrm{sec^{-1}}$$

which is obtained from analysis of laboratory measurements

$$\text{Lifetime of } \mathrm{CH_4} = \frac{\text{Abundance}}{\text{Loss}} = \frac{[\mathrm{CH_4}]}{k^{\mathrm{CH4+OH}}[\mathrm{OH}][\mathrm{CH_4}]} = \frac{1}{k^{\mathrm{CH4+OH}}\,[\mathrm{OH}]}$$

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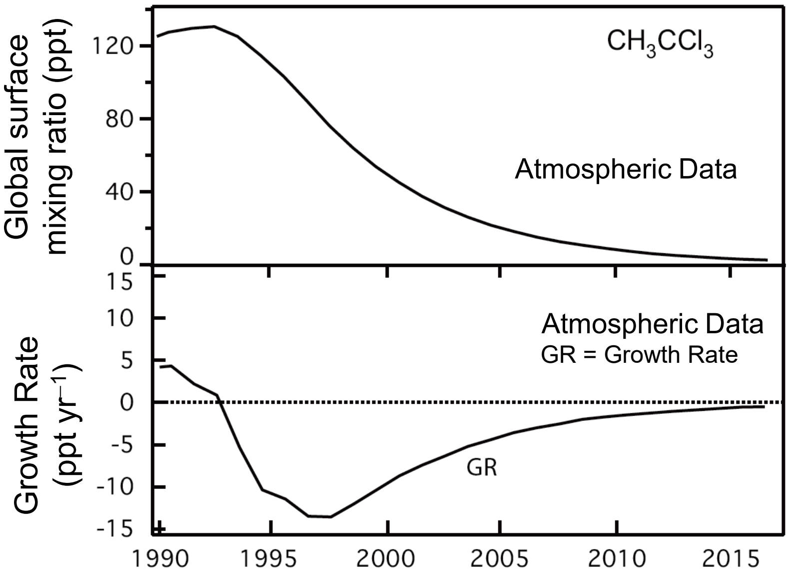
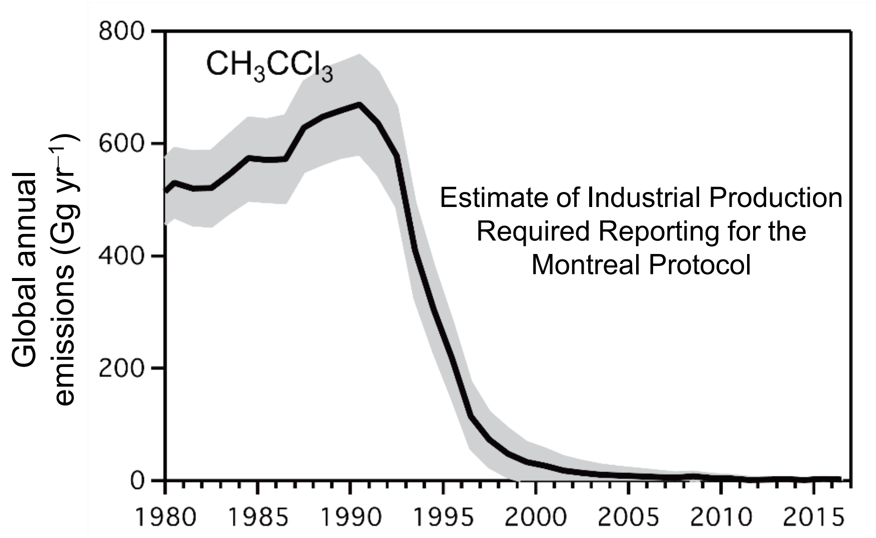
The determination of [OH] is a fascinating story!

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

$$\mathrm{CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O}$$

$$\frac{d\mathrm{CH_3CCl_3}}{dt} = \mathrm{Production} - \mathrm{Loss} = \mathrm{Production} - k^{\mathrm{CH3CCl3\,+\,OH}}\,[\mathrm{CH_3CCl_3}]\,[\mathrm{OH}]$$





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

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$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$

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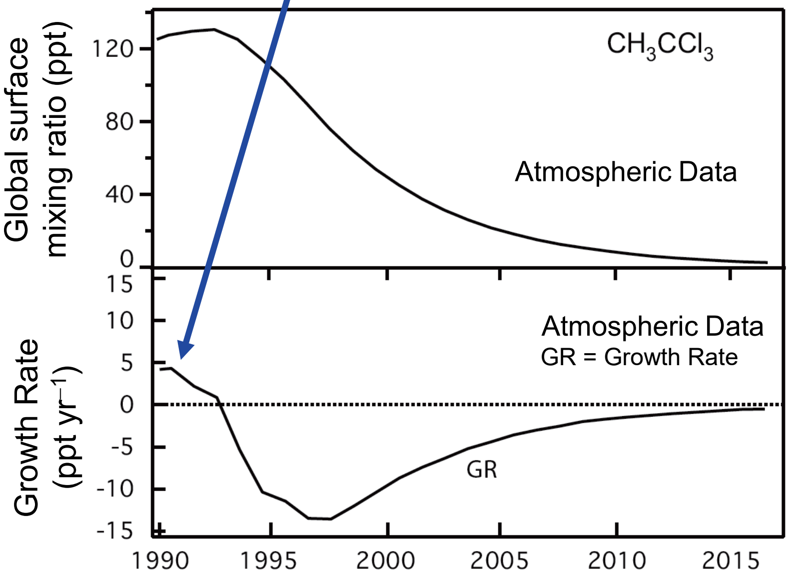

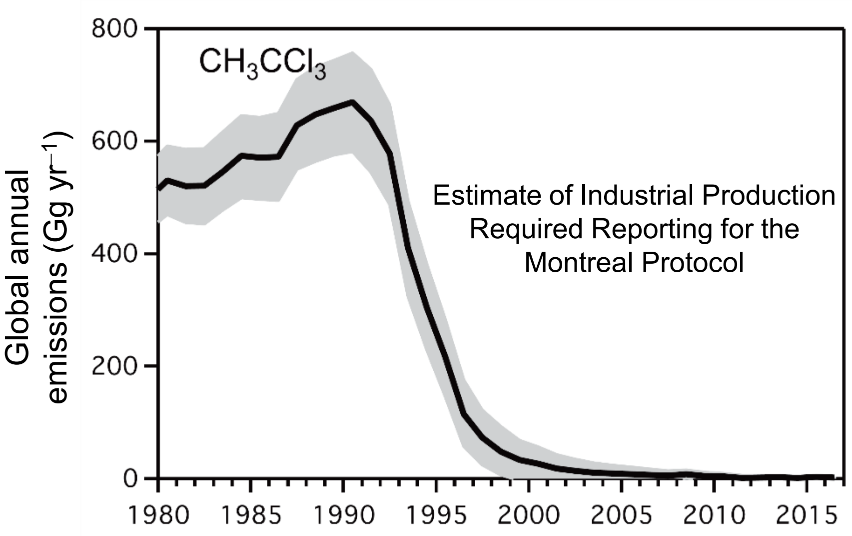

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$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$

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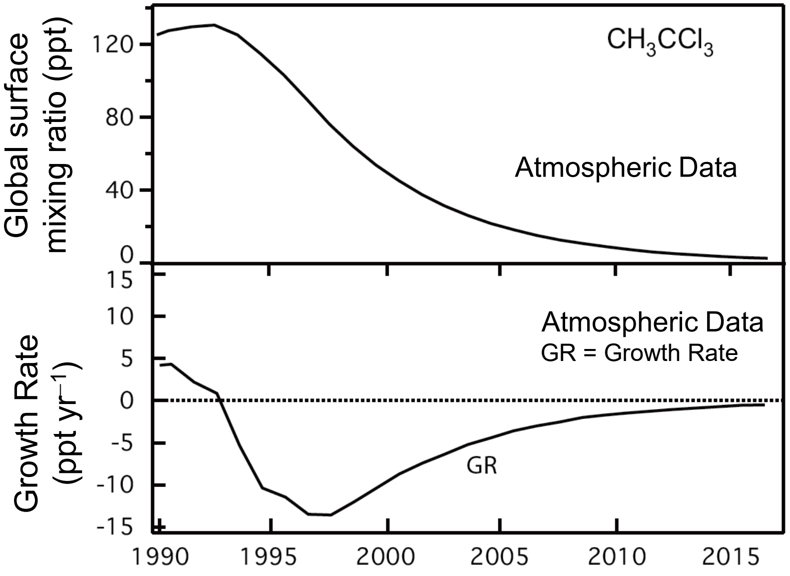
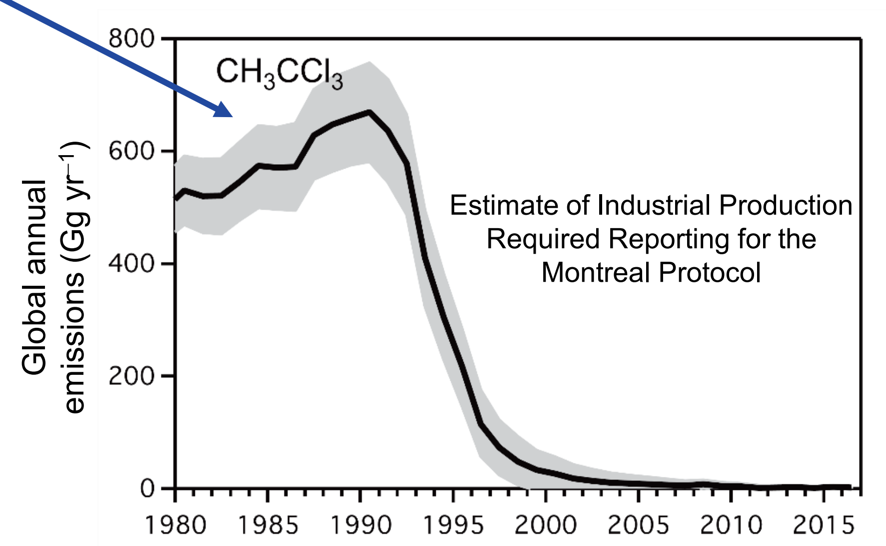




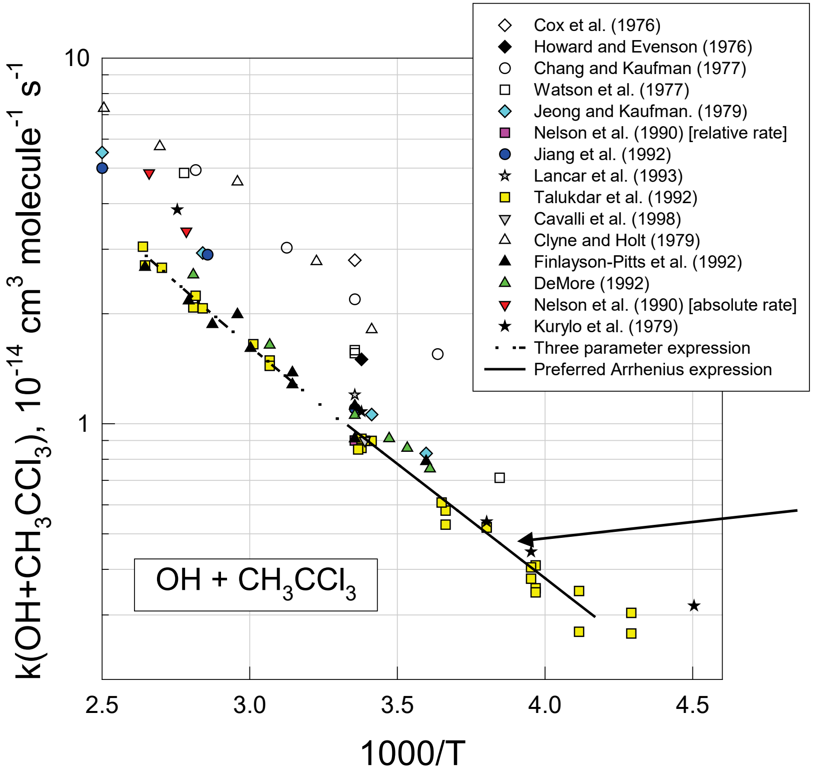
Estimate of Industrial Production
Required Reporting for the
Montreal Protocol

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

$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$

$$\frac{dCH_3CCl_3}{dt} = \text{Industrial Production} - k^{\text{CH3CCl3 + OH}}\,[CH_3CCl_3]\,[OH]$$

Even more **Laboratory Experiments**:
many PhDs, tenure-type research, etc.



$$k^{\text{CH3CCl3 + OH}} = 1.20\times10^{-12}\times e^{-1440/T}\ \text{cm}^3\ \text{sec}^{-1}$$

“Arrhenius” Rate Constant expression
(i.e., pre-exponential multiplied by exp(something/temperature)
defines the line on the plot to the left

http://iupac.pole-ether.fr/htdocs/datasheets/doc/oClOx50_HO_CH3CCl3.doc

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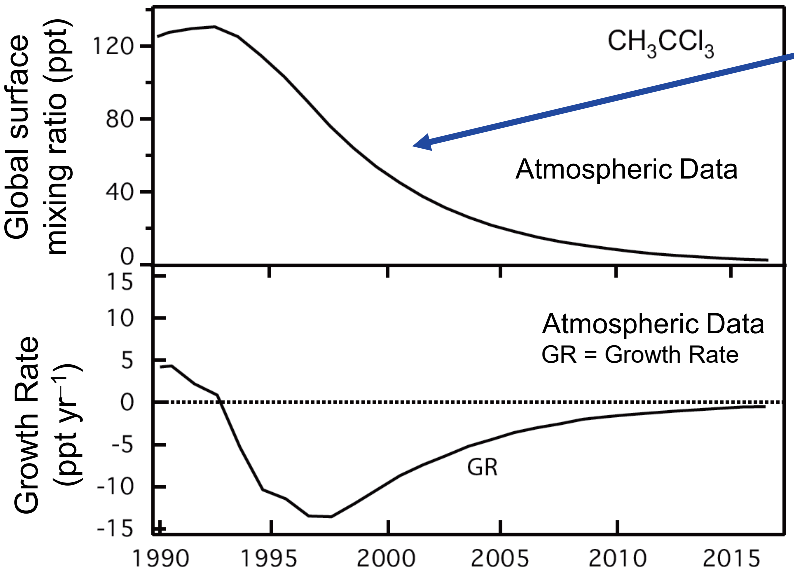
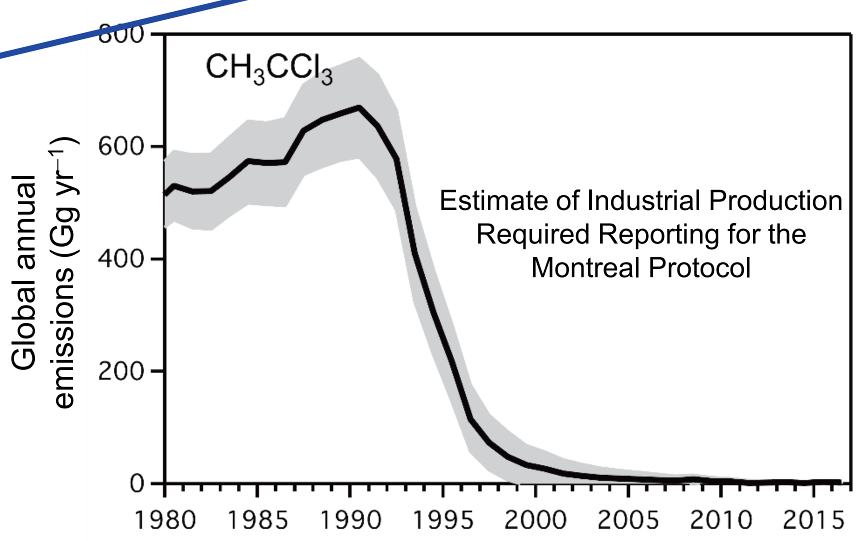


Atmospheric Data

Atmospheric Data
GR = Growth Rate

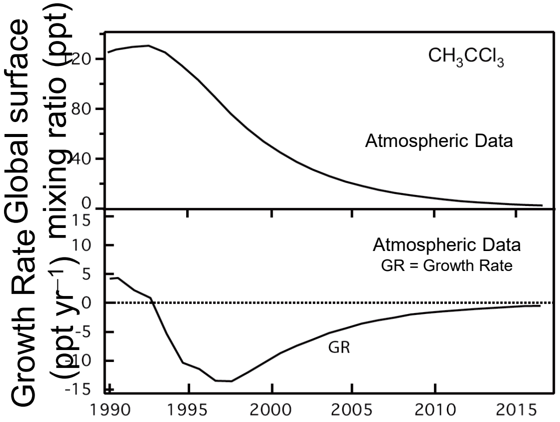


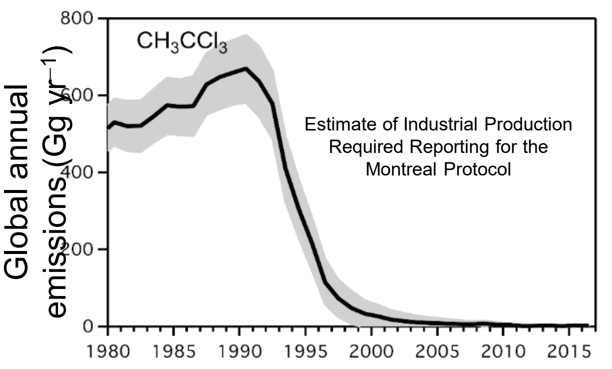
Estimate of Industrial Production
Required Reporting for the
Montreal Protocol

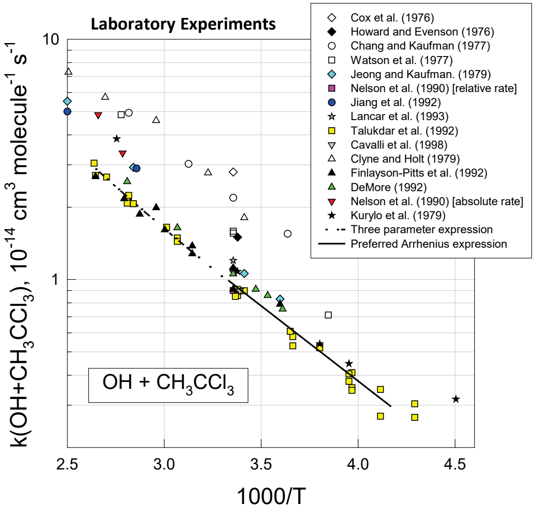
CH_3CCl_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

We can find [OH] by re-arranging terms:

$$[\mathrm{OH}]\,(\mathrm{time}) = \frac{\left(\text{Industrial Production of } CH_3CCl_3\,(\mathrm{time}) - \dfrac{d\,CH_3CCl_3^{\;\mathrm{ATMOS}}}{dt}\,(\mathrm{time})\right)}{k^{\mathrm{CH3CCl3+OH}}_{\mathrm{LAB}} \times [CH_3CCl_3]^{\mathrm{ATMOS}}\,(\mathrm{time})}$$







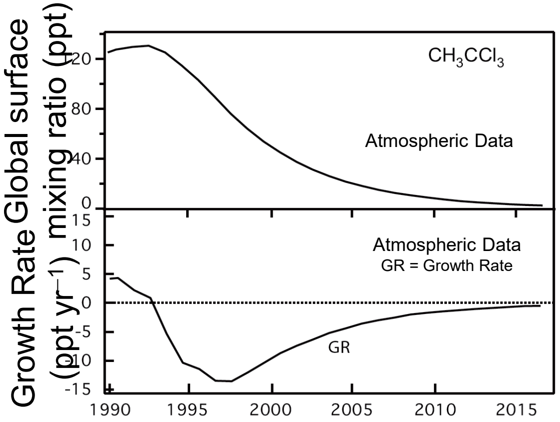
The global average OH concentration, **$9.4 \pm 1.3 \times 10^5$ molec cm^{-3}**, for observations obtained from 1978 to 2000, does not vary statistically from that derived by us earlier for the 1978 to 1994 period **$9.7 \pm 1.3 \times 10^5$ molec cm^{-3}**

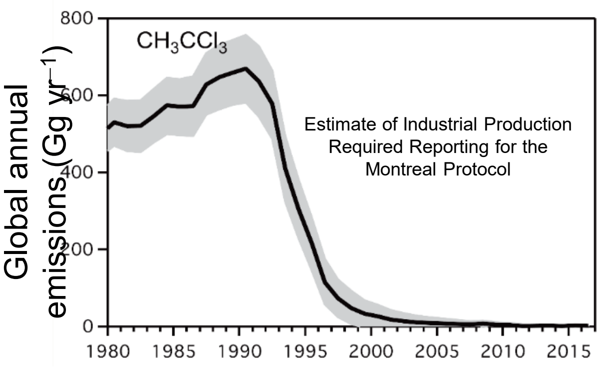
Prinn et al., *Science*, 2001

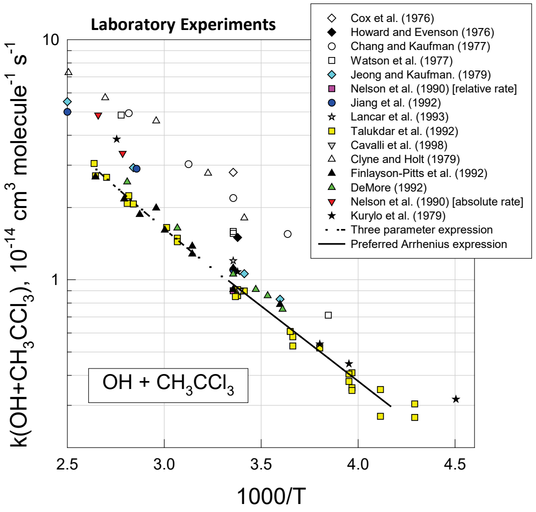
CH_3CCl_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

We can find [OH] by re-arranging terms:

$$[OH]\ (time) = \frac{\left(\text{Industrial Production of CH3Cl3 (time)} - \frac{d\,CH_3CCl_3^{\,ATMOS}}{dt}\,(time)\right)}{k^{CH3CCl3\,+\,OH}_{\qquad\qquad LAB} \times [CH_3CCl_3]^{ATMOS}\,(time)}$$







The global average OH concentration, **9.4 ± 1.3 × 10^5 molec cm^{-3}**, for observations obtained from 1978 to 2000, does not vary statistically from that derived by us earlier for the 1978 to 1994 period **9.7 ± 1.3 × 10^5 molec cm^{-3}**

Prinn et al., *Science*, 2001

Use of [OH] = 1.0 × 10^6 molec cm^{-3} in the formula for the **lifetime of CH_4** gives a value of **8.8 years**
Use of [OH] = 9.7 × 10^5 molec cm^{-3} in the formula for the **lifetime of CH_4** gives a value of **9.1 years**
Use of [OH] = 9.4 × 10^5 molec cm^{-3} in the formula for the **lifetime of CH_4** gives a value of **9.4 years**

Houghton & *Chemistry in Context* give a Lifetime for CH_4 of 12 Years
What's up with the 12 year lifetime?

From prior slides:

$$\text{Lifetime of } CH_4 \text{ with respect to loss by raction with OH} \approx 9 \text{ years}$$

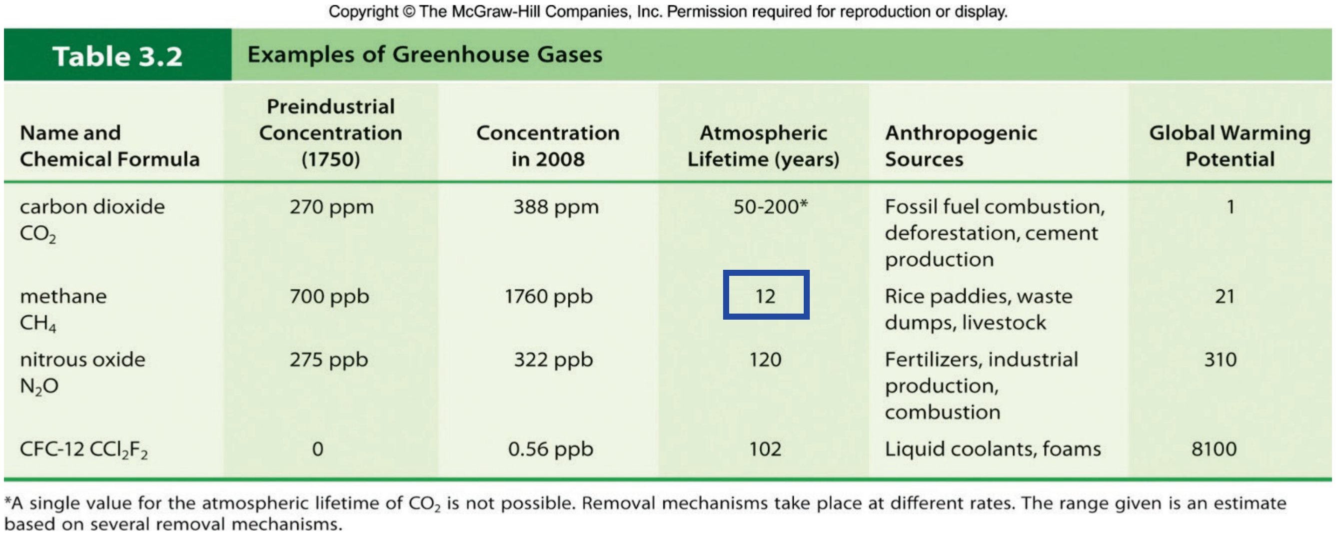


Table 3.2 Examples of Greenhouse Gases

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*

Houghton & *Chemistry in Context* give a Lifetime for CH_4 of 12 Years What's up with the 12 year lifetime?

From prior slides:

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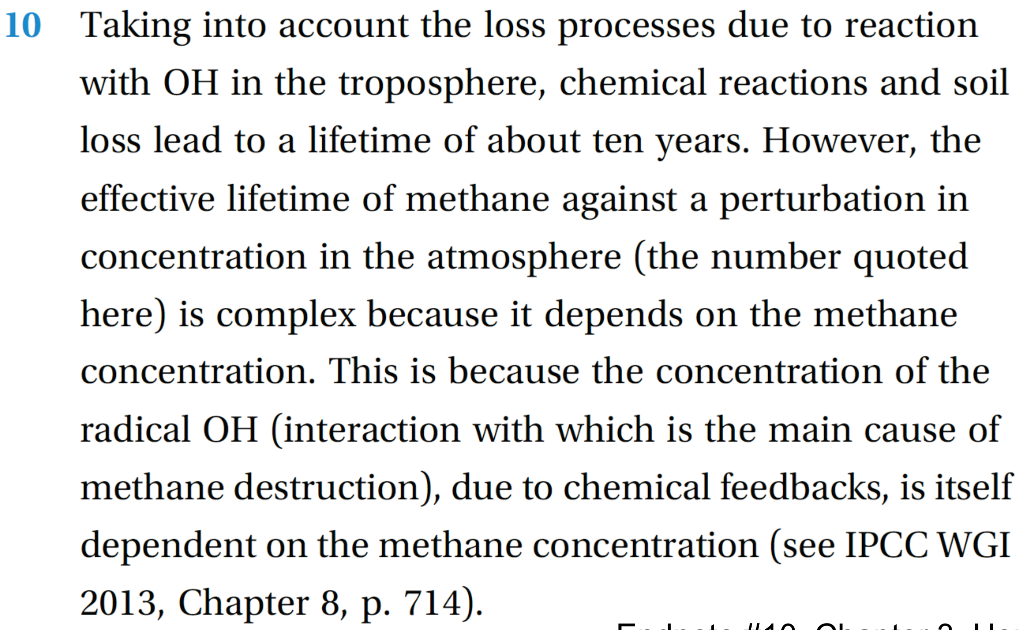
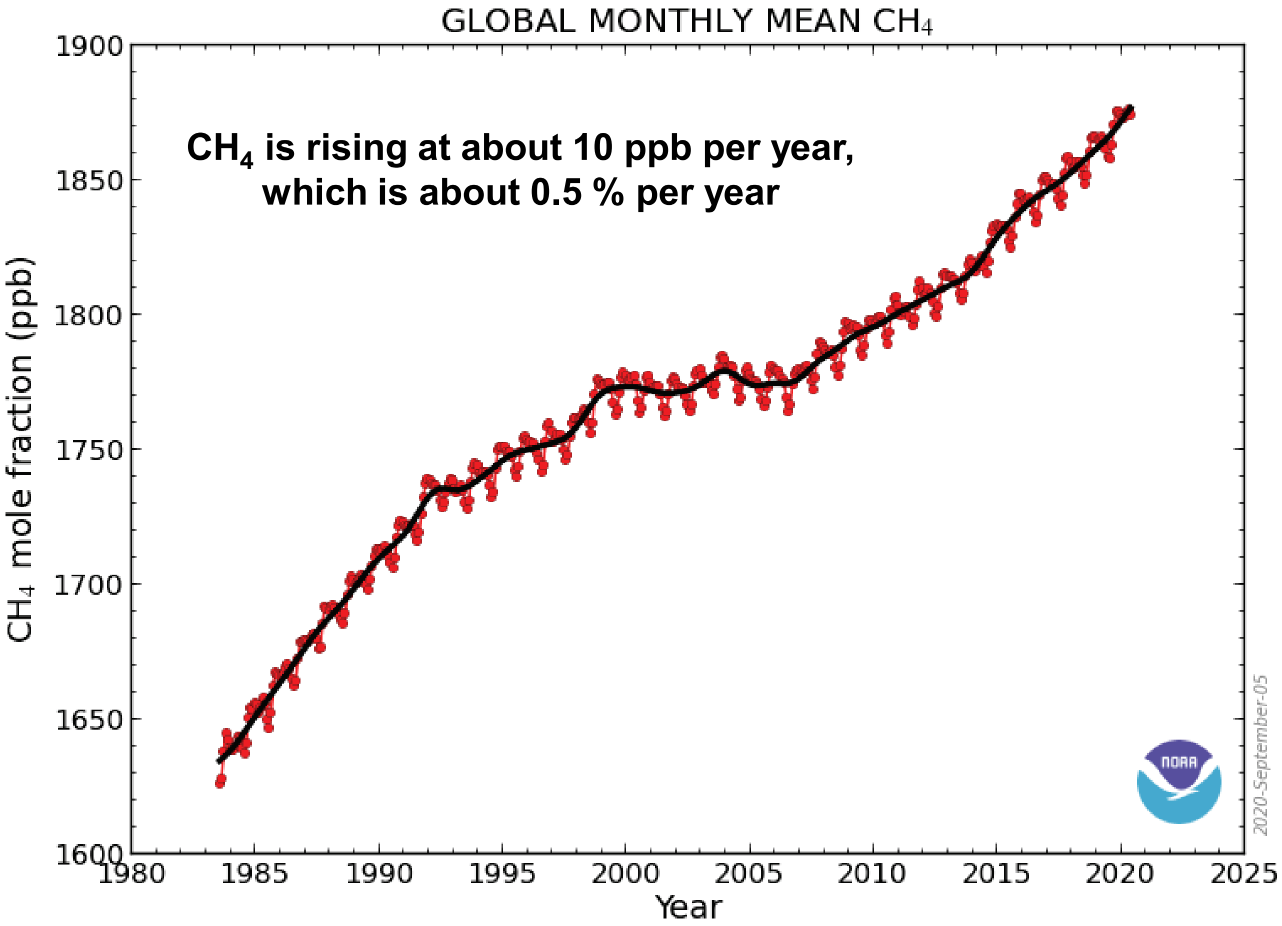


10 Taking into account the loss processes due to reaction with OH in the troposphere, chemical reactions and soil loss lead to a lifetime of about ten years. However, the effective lifetime of methane against a perturbation in concentration in the atmosphere (the number quoted here) is complex because 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

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

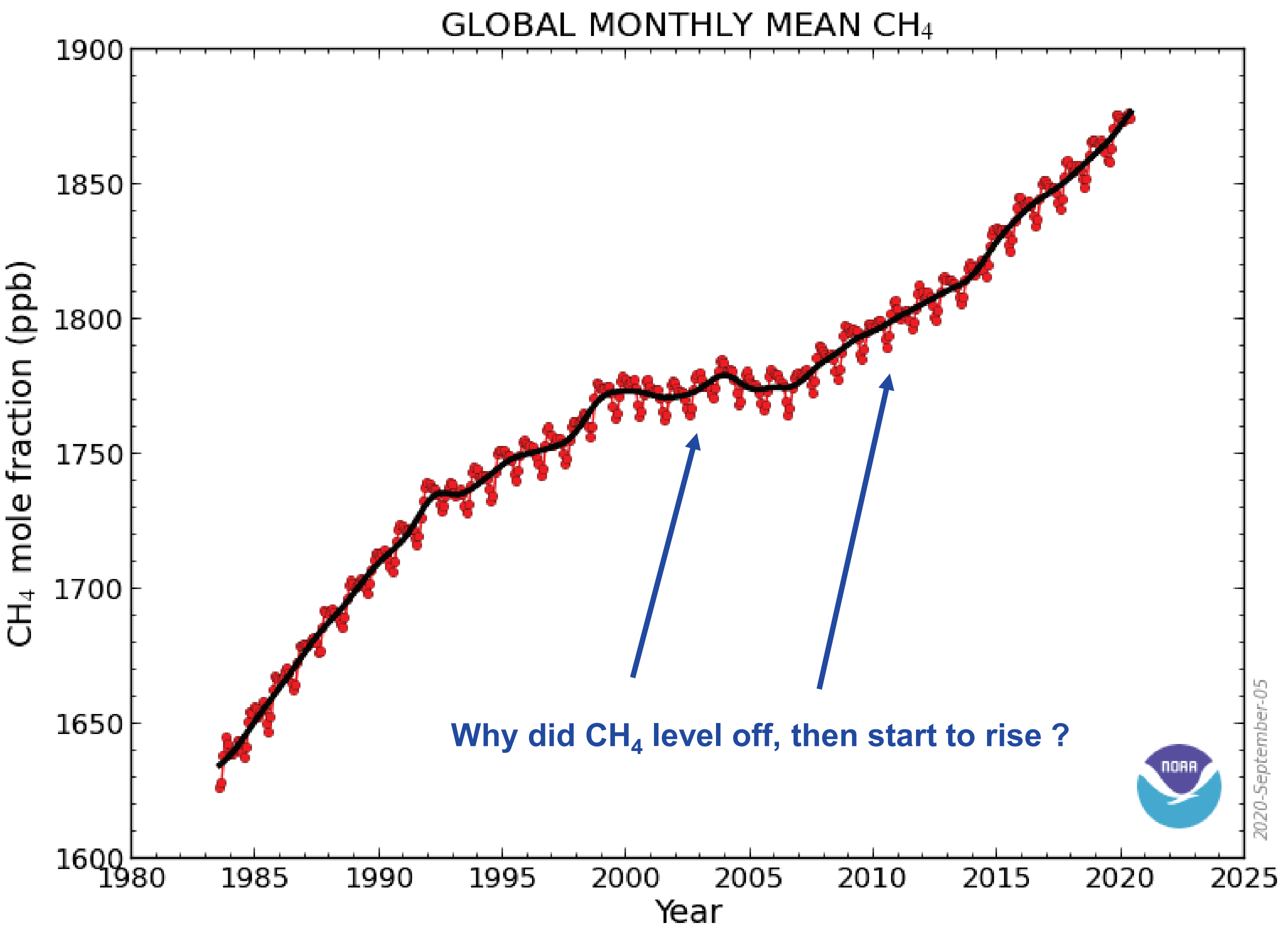


CH_4 is rising at about 10 ppb per year, which is about 0.5 % per year

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

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

Understanding the observed time series of CH_4 is a "hot ticket item" in modern atmospheric chemistry

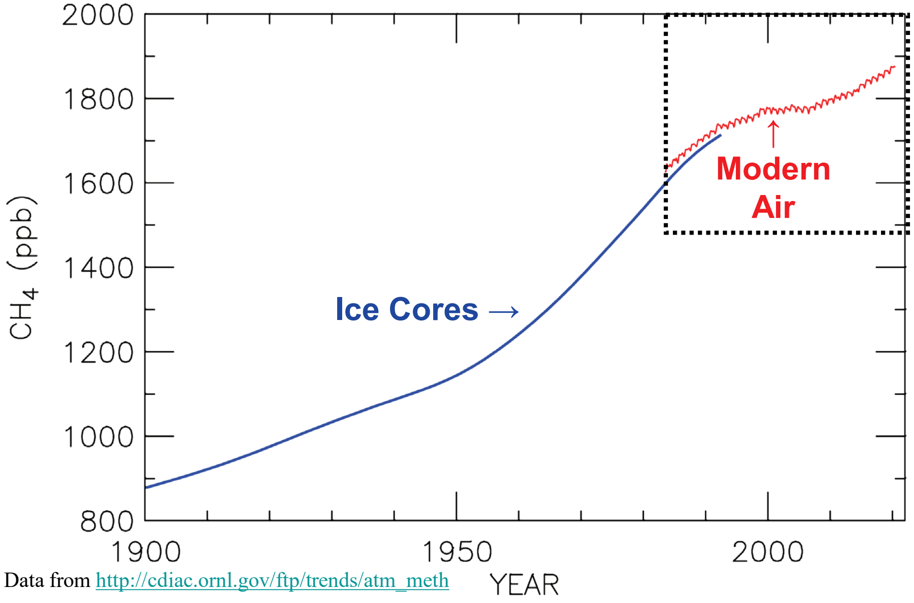


Why did CH_4 level off, then start to rise ?

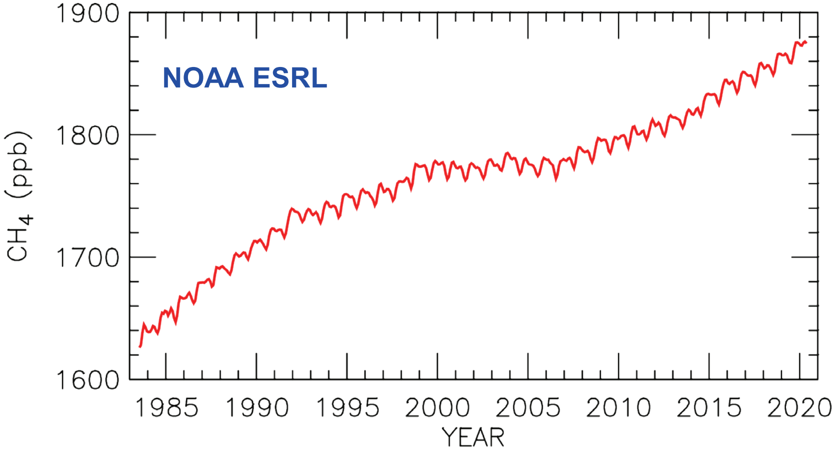
https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4

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

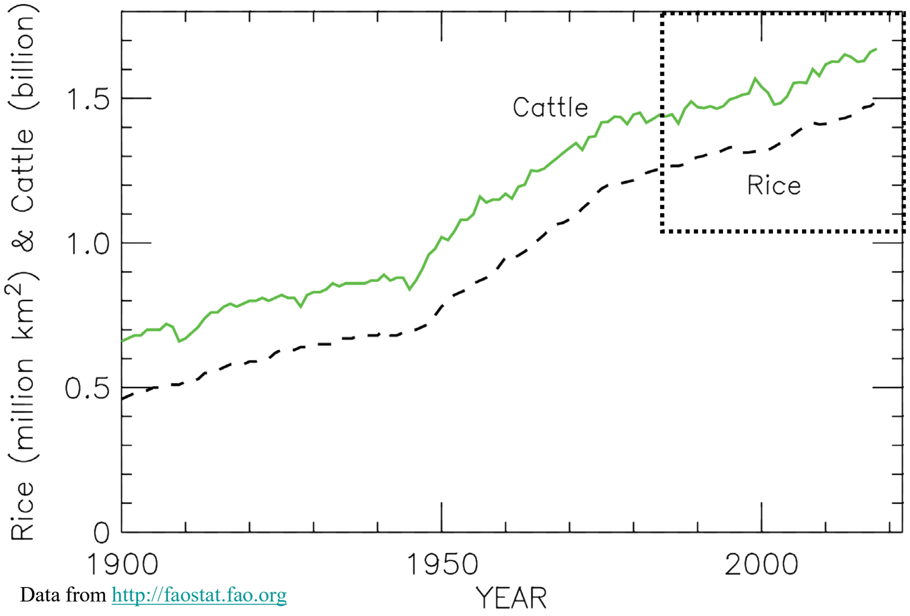
Atmospheric CH_4 and Energy from Gas, Rice, Cattle Trends



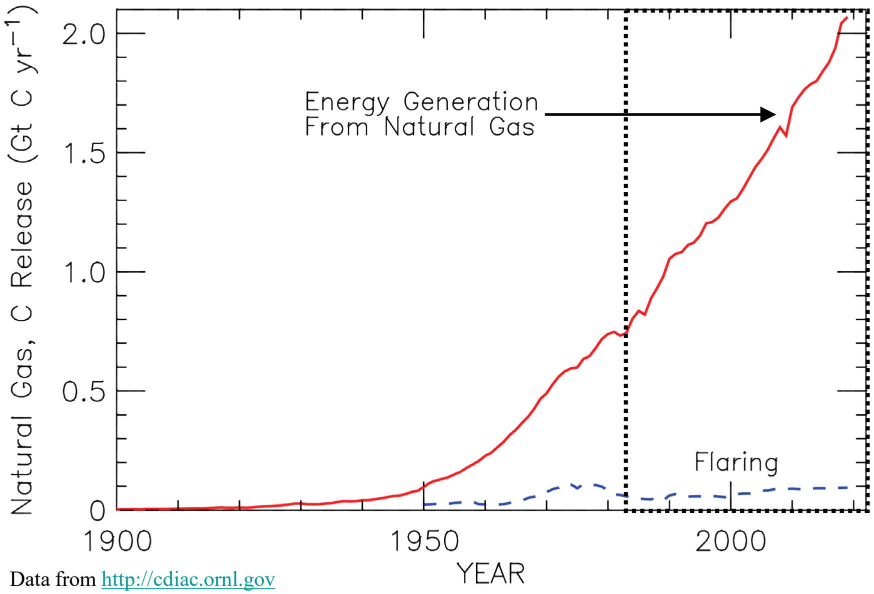
Data from http://cdiac.ornl.gov/ftp/trends/atm_meth



http://www.esrl.noaa.gov/gmd/obop/mlo/programs/esrl/methane/methane.html

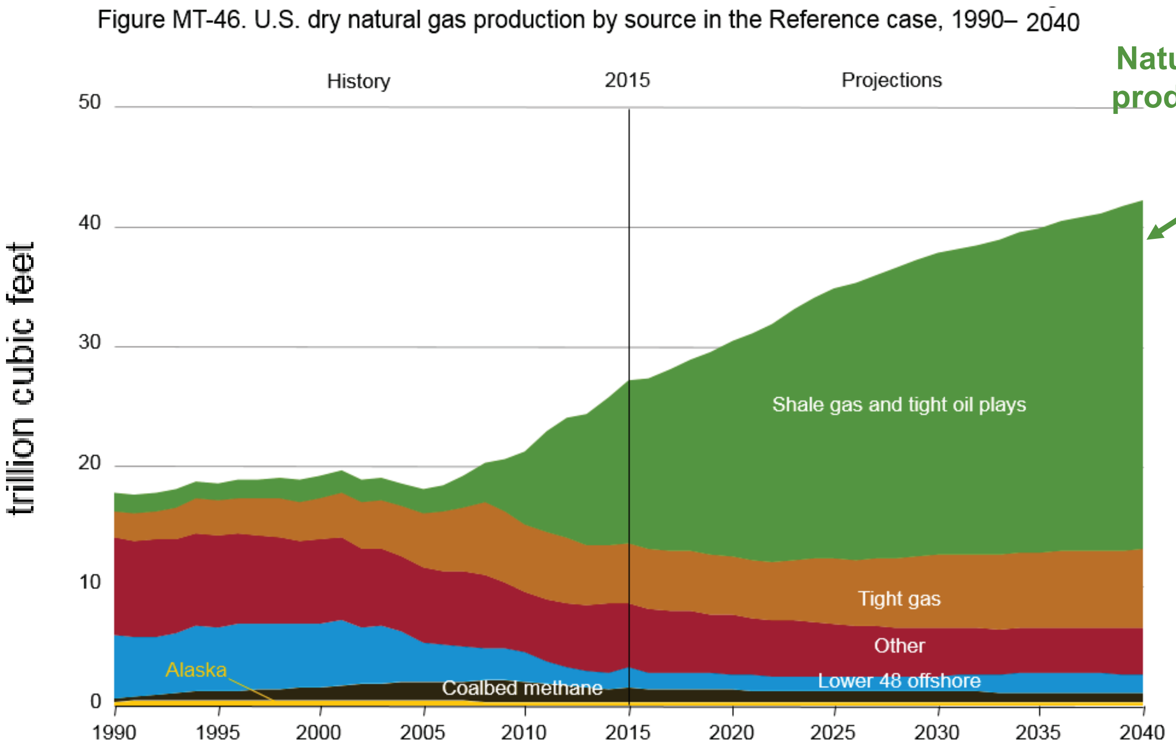


Data from http://faostat.fao.org



Data from http://cdiac.ornl.gov

Fracking



Natural gas (mainly CH_4) production from fracking

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

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*

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

- 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

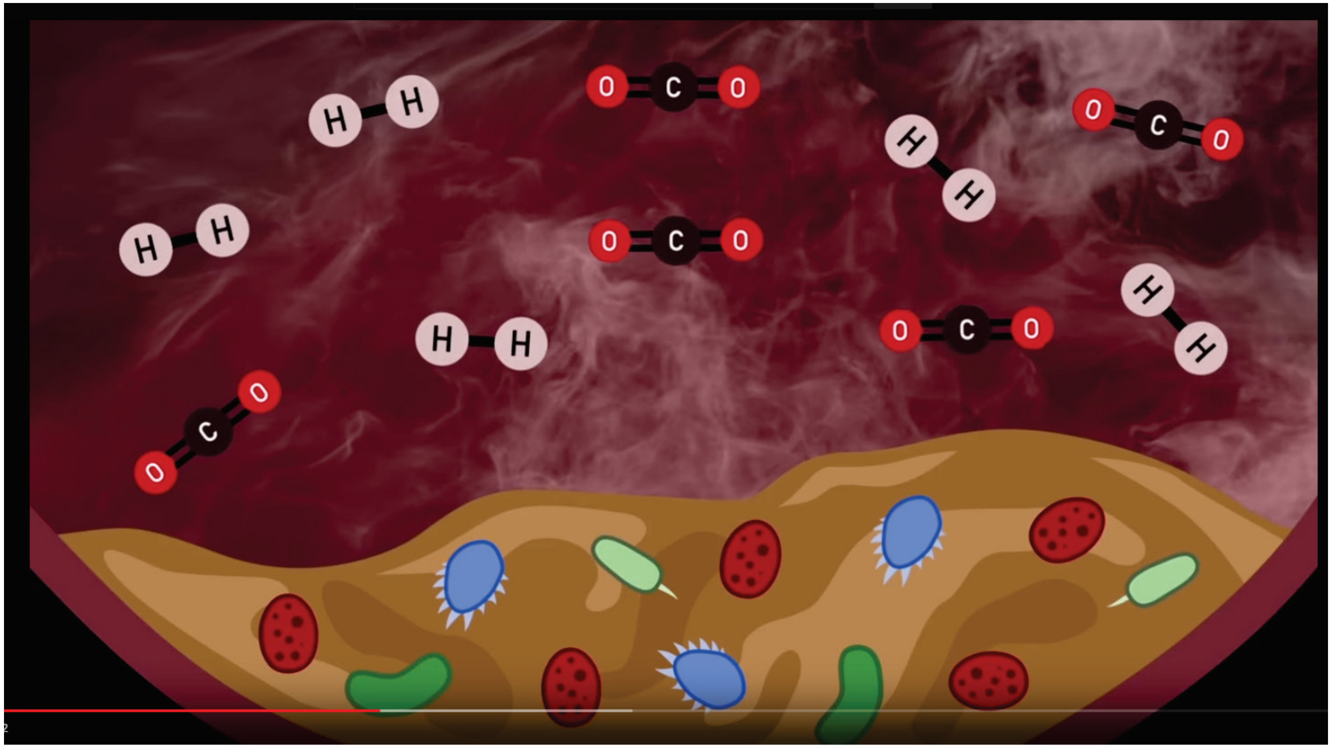
Recent trends in CH_4

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

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

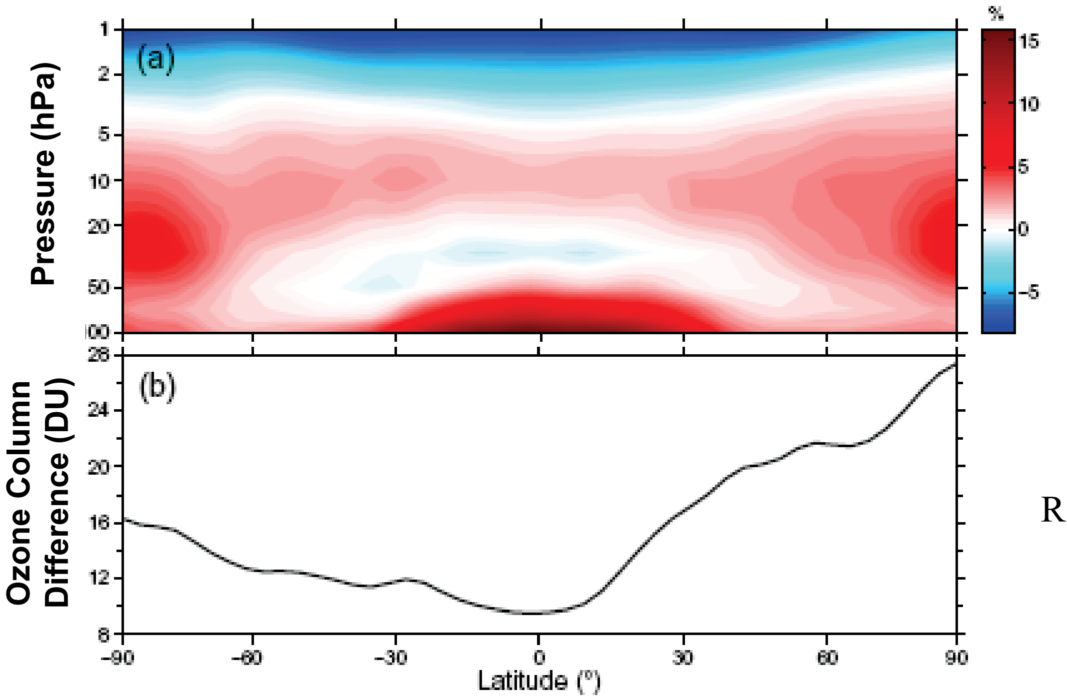
> Livestock play an important role in carbon cycling through consumption of biomass and emissions of methane. Recent research suggests that existing bottom-up inventories of livestock methane emissions in the US, such as those made using 2006 IPCC Tier 1 livestock emissions factors, are too low. This 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.

Time for Another YouTube Video



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

CH_4 and Stratospheric Ozone



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

Stratospheric O_3 difference in the 2090s found for a computer simulation run using CH_4 from RCP 8.5 minus that of a simulation using CH_4 from RCP 2.6

Rising CH_4 leads to:
- a) ozone loss in the upper stratosphere by increasing the speed of OH and HO_2 (HO_x) mediated loss cycles.
- b) a cooler stratosphere, slowing the rate of all ozone loss cycles.
- c) speeds up the rate of $Cl+CH_4$, shifting chlorine from ClO into HCl
- d) more HO_2 in the lowermost stratosphere where there is sufficient CO to result in O3 production by smog chemistry

Computer models project stratospheric column O_3 will increase as CH_4 rises

Nitrous Oxide: N_2O

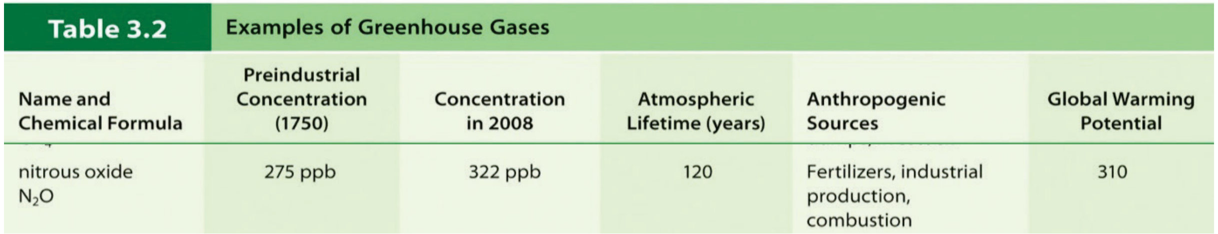


Table 3.2 **Examples of Greenhouse Gases**

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*

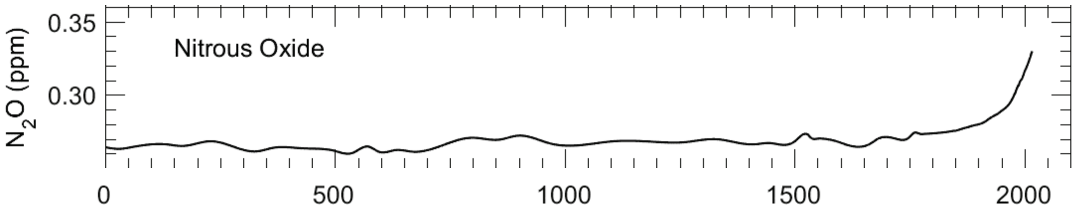


Figure 1.2, *Paris, Beacon of Hope*

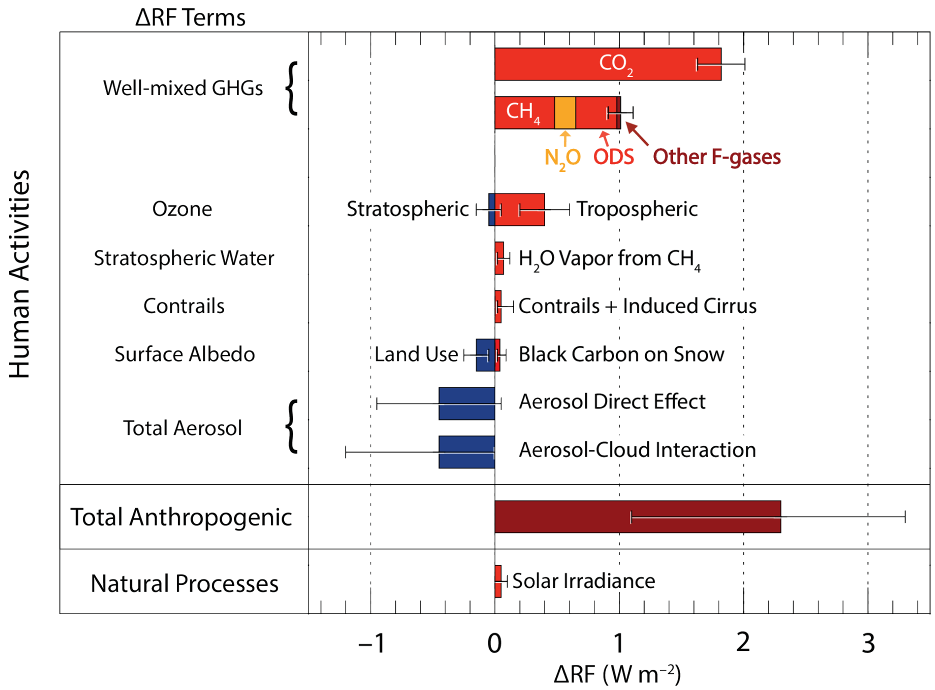
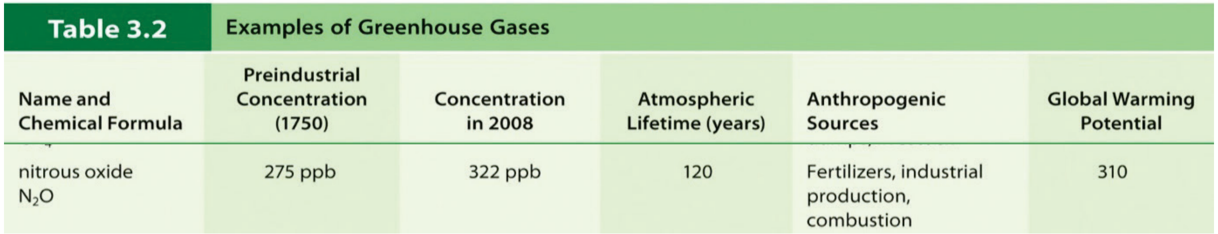


Figure 1.4, *Paris, Beacon of Hope*

Nitrous Oxide: N_2O



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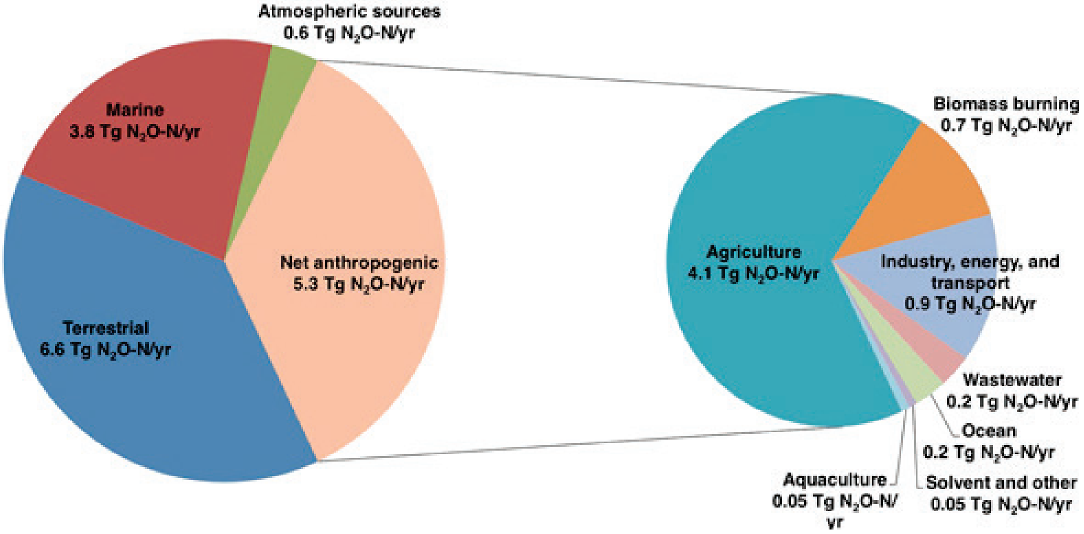
Chapter 3, *Chemistry in Context*

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})

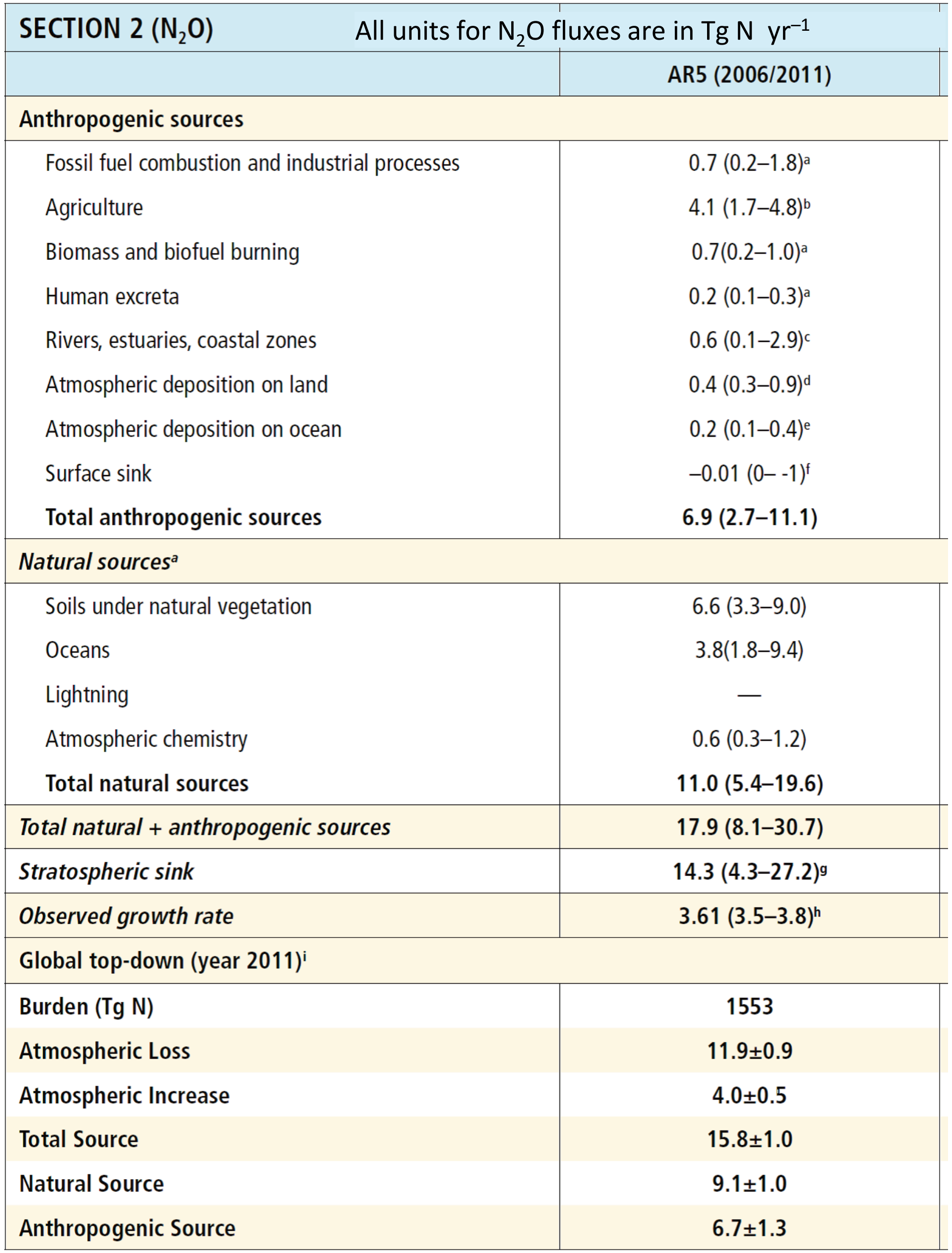
= 1 – 0.32 = 0.67

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).

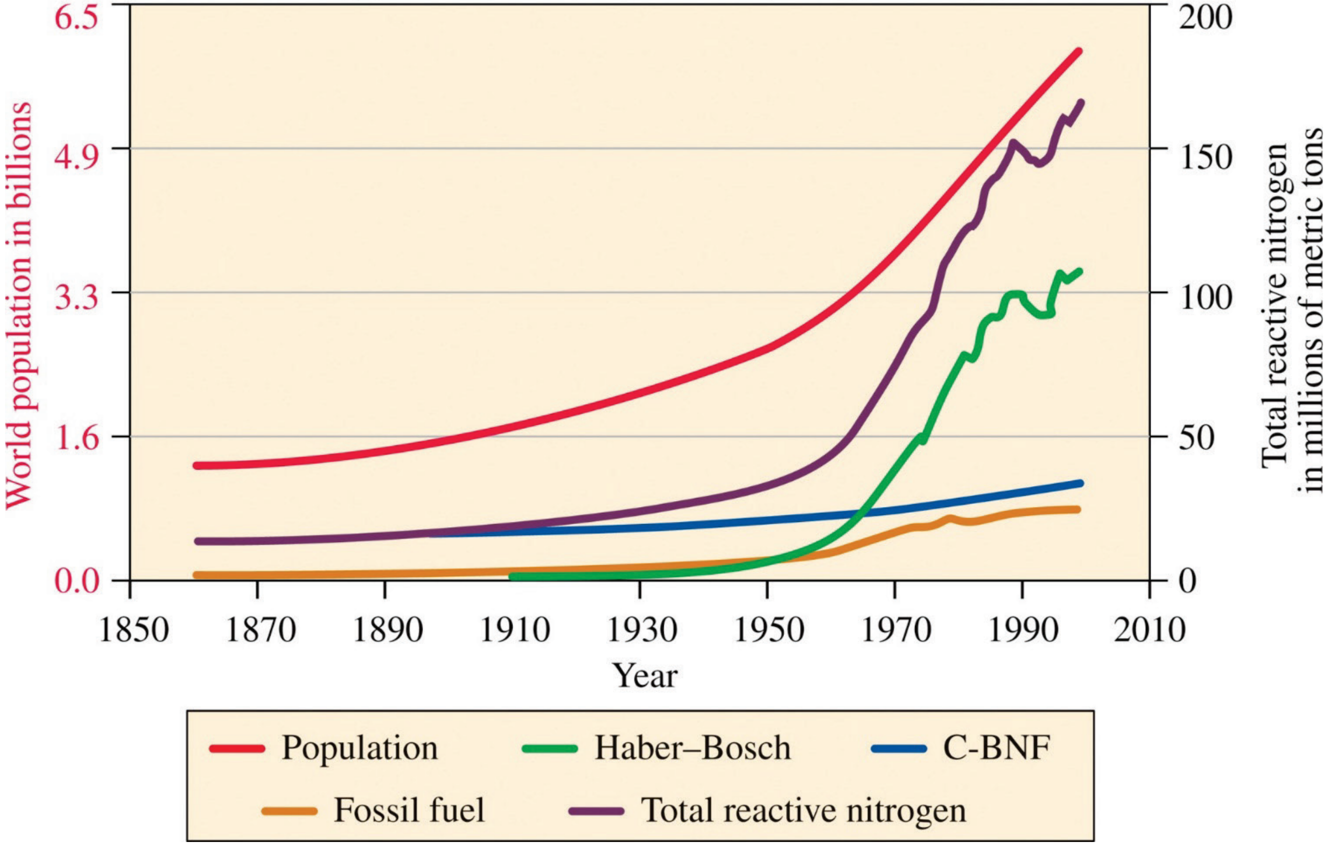
g *The stratospheric sink regroups losses via photolysis and reaction with O(^{1}D) that account for 90% and 10% of the sink, respectively (Minschwaner et al., 1993).* The global magnitude of the stratospheric sink was adjusted in order to be equal to the difference between the total sources and the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

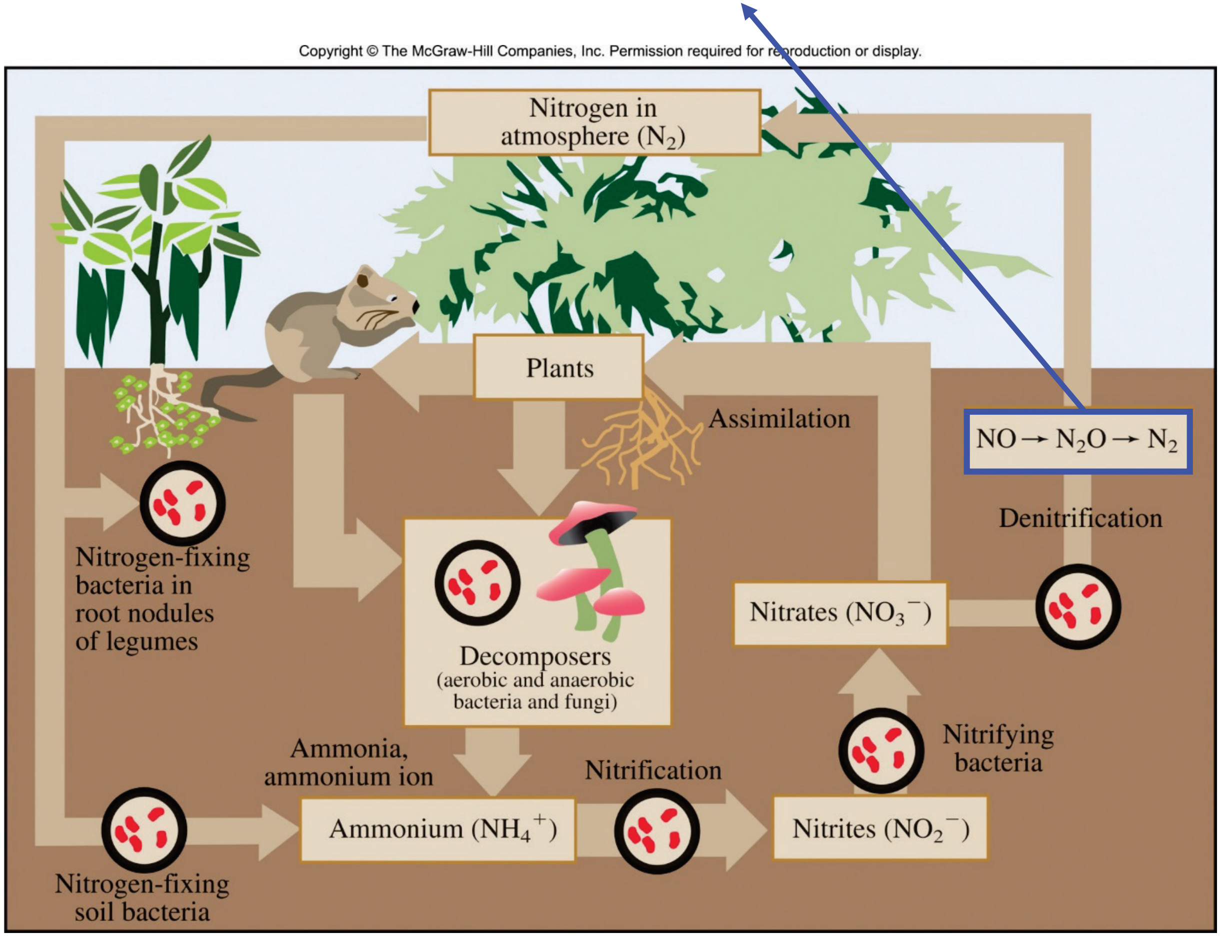
Haber-Bosch: N_2(gas) + 3 H_2 (gas) → 2 NH_3 (gas)
Led to large scale, economical production of ammonia based fertilizer



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*

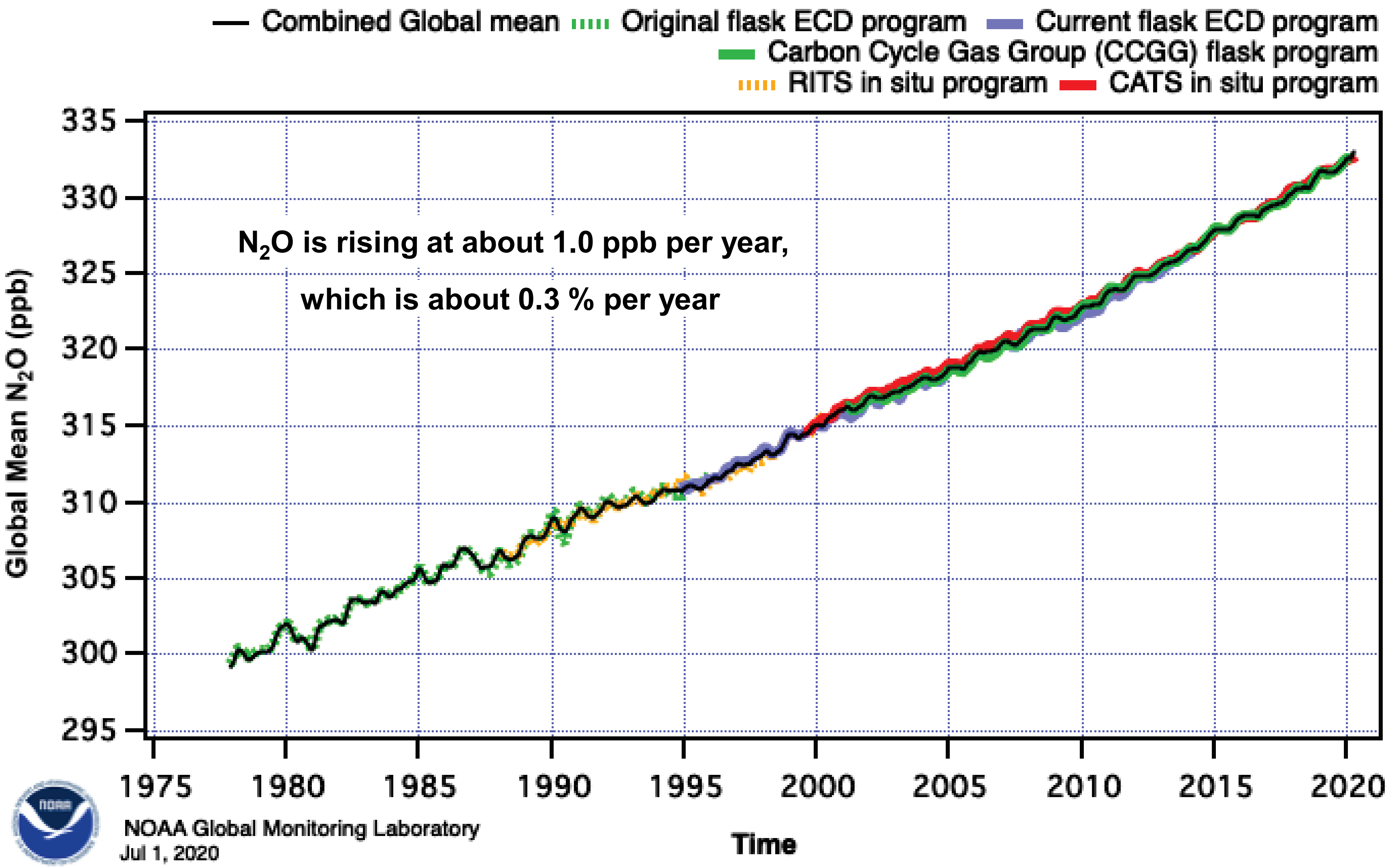
Atmospheric N_2O

AT6, Q4:
According to *Paris Climate Agreement, Beacon of Hope,* why has the atmospheric abundance of N_2O been rising over time ***and*** how is N_2O connected with possible, expanded future use of biofuels as a replacement for fossil fuels?

Text from Section 1.2.3.4 of *Paris, Beacon of Hope*:

> **Agriculture is the dominant activity responsible for human release of N_2O: use of nitrogen fertilizers results in release of N_2O to the atmosphere due to microbial processes in soils** (Smith *et al*. 1997).
>
> The possible increase in atmospheric N_2O due to expanded use of biofuels will receive considerable attention in the next few decades. **There is considerable interest in the development of biofuels as a replacement for fossil fuels because, in theory, biofuels could be close to carbon neutral.** The notion of carbon neutrality is predicated on the fact that the carbon in a hydrocarbon fuel produced by recent photosynthesis has been drawn out of the atmosphere just prior to combustion: i.e., the carbon is recycled. ***One of the many concerns regarding the modern biofuel industry is that the associated increase in production of atmospheric N_2O due to the need for additional fertilizer will offset the climate benefit from the supposed car-bon neutrality of this new fuel source*** (Crutzen *et al*. 2016).

N_2O Time Series



N_2O is rising at about 1.0 ppb per year, which is about 0.3 % per year

NOAA Global Monitoring Laboratory
Jul 1, 2020

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

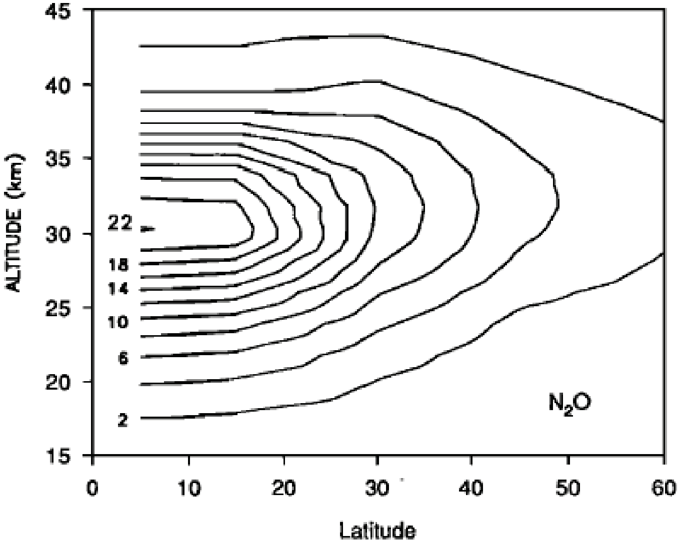


Fig. 11. Diurnally averaged loss rate for N_2O (10^2 molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N_2O by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

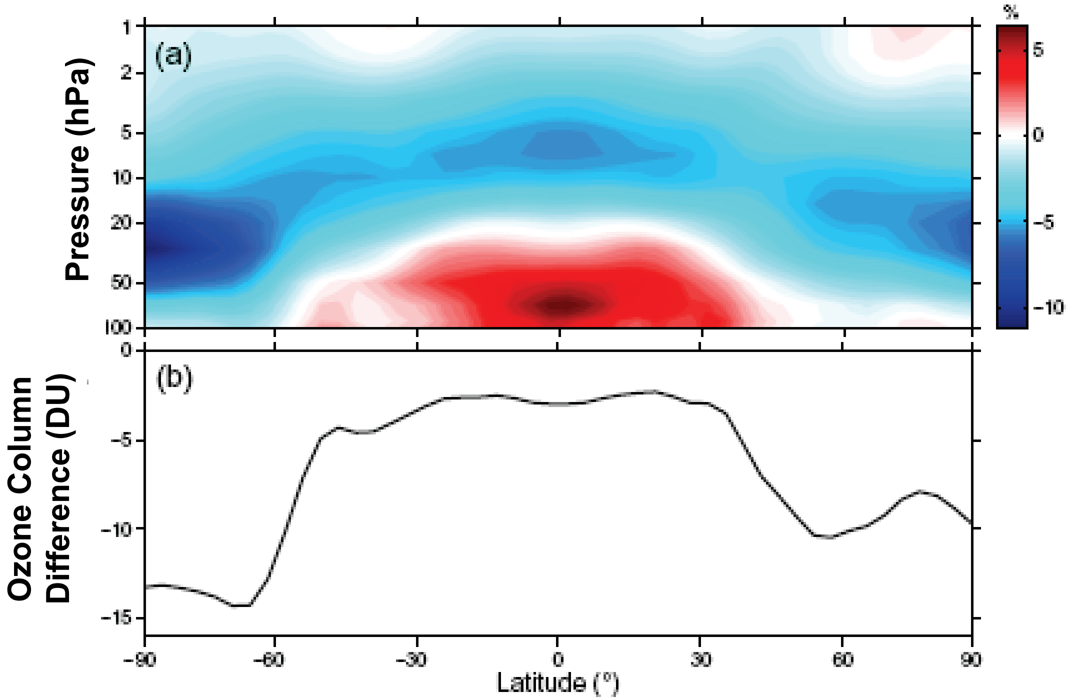
The minor sink for N_2O loss has a path that results in "fixed nitrogen":

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

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