

Methane and Nitrous Oxide

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:

<http://www2.atmos.umd.edu/~rjs/class/spr2022>

<https://myelms.umd.edu/courses/137772>

Goals :

- CH₄
 - sources and sinks
 - lifetime
 - human influences (mighty complicated!)
- N₂O
 - sources and sinks
 - human influence
 - connection to stratospheric O₃

Note:

1 Gt (gigaton) = 10⁹ tons, which also equals 10¹⁵ grams

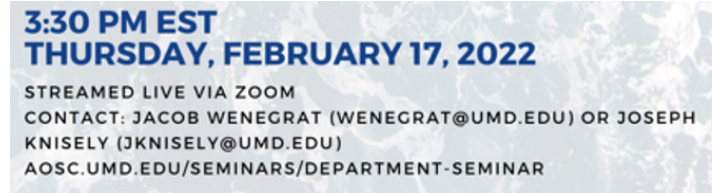
1 Mt (megaton) = 10⁶ tons, which also equals 10¹² grams , or 1 Tg (Terra gram)

Lecture 6

15 February 2022

Announcements

1) AOSC Weekly Seminar: Thursday, 3:30 pm



2) Problem Set #1 due today at 5 pm

3) 10 points per day late, unless there is a legitimate medical or extra-curricular circumstance brought to our attention prior to the due date!

3) Would like to hold problem set review during either a Mon or Wed evening

- How many interested in attending?
- Will review solutions, hence no credit for P Set #1 if not submitted by start of the review
- We'll circle back to P Set review on Thurs

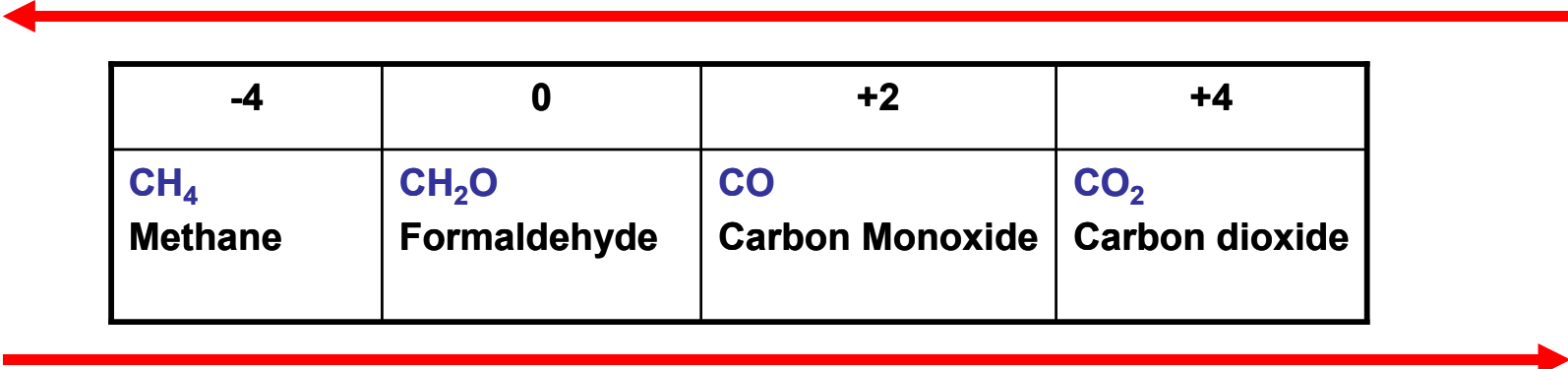
4) Problem Set #2 due Thurs, 24 Feb; will be posted by 17 Feb

5) First exam is Thurs, 3 Mar:

- If held in class, will be closed book / no notes
- Will focus on concepts much more than calculations, although a very simple calculation-type question could appear
- New exams every year; will review prior exam on Tues 1 Mar to help you prepare

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

Decreasing oxidation number (reduction reactions)

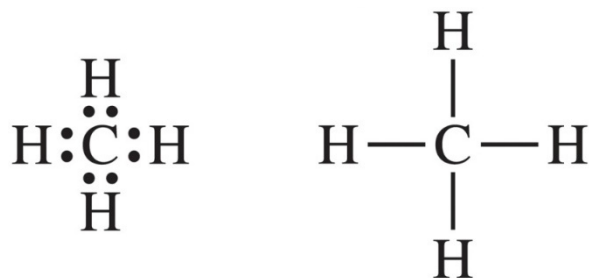


-4	0	+2	+4
CH_4 Methane	CH_2O Formaldehyde	CO Carbon Monoxide	CO_2 Carbon dioxide



Increasing oxidation number (oxidation reactions)

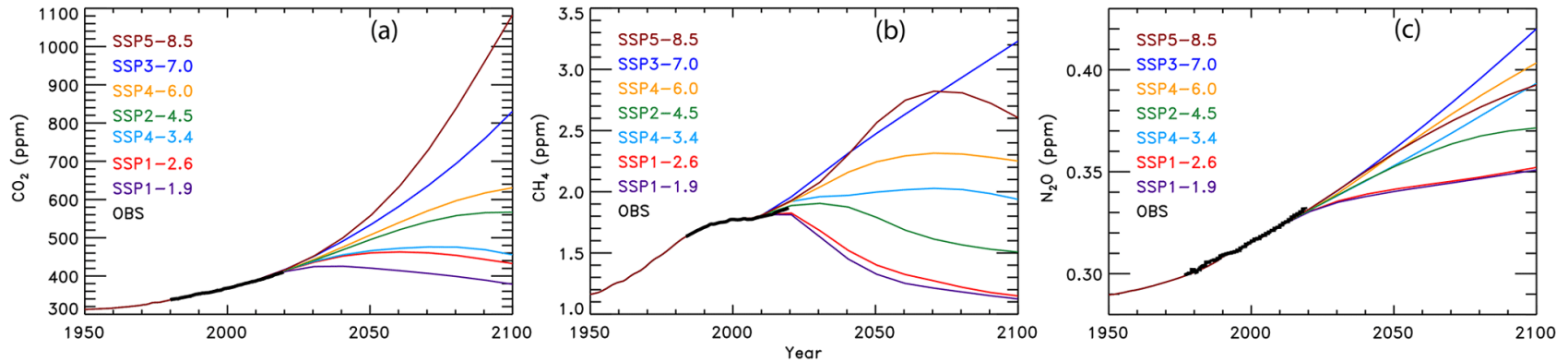
Oxidation state represents number of electrons:
added to an element (negative #) or removed from an element (positive #)



C in CH_4 : has received an electron from each H atom.

All electrons are paired and hence this compound
is relatively stable

Background



- SSP: Shared Socioeconomic Pathways (SSPs)
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 McBride et al., 2021: <https://esd.copernicus.org/articles/12/545/2021>

Atmospheric CH₄

AT6, Q1:

According to Table 3.2 of Chemistry in Context, what was pre-industrial atmospheric abundance of CH₄ **and** is this consistent with Figure 3.7 of the Houghton reading?

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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 ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl ₂ F ₂	0	0.56 ppb	102	Liquid coolants, foams	8100

*A single value for the atmospheric lifetime of CO₂ is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.

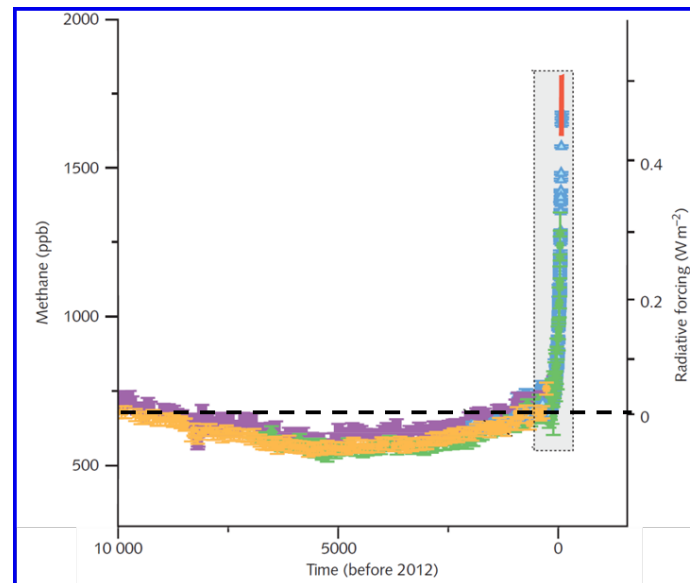
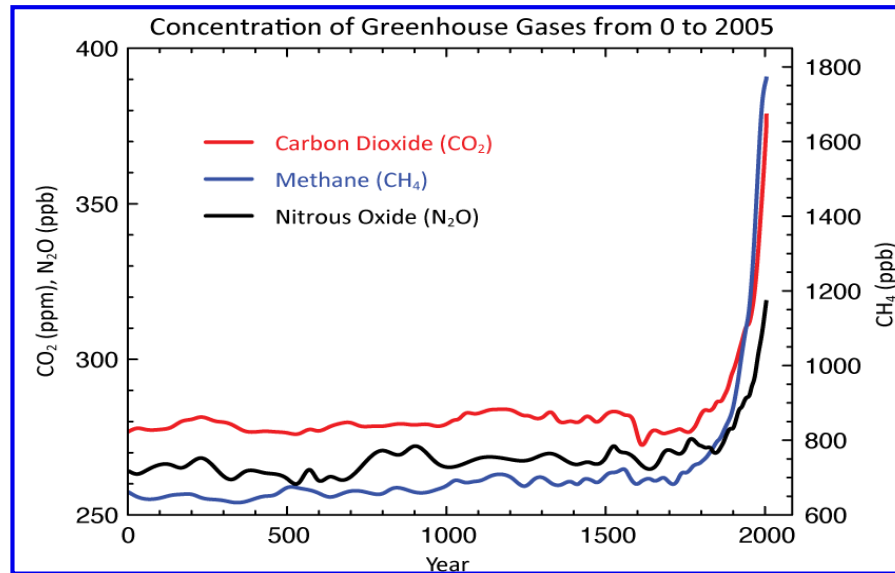
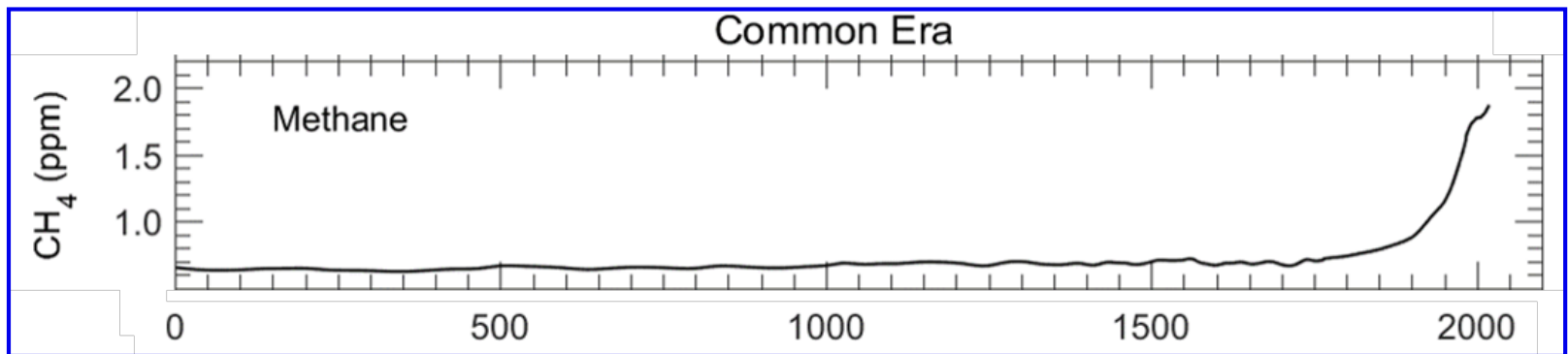


Figure 3.7, Houghton

Atmospheric CH₄



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



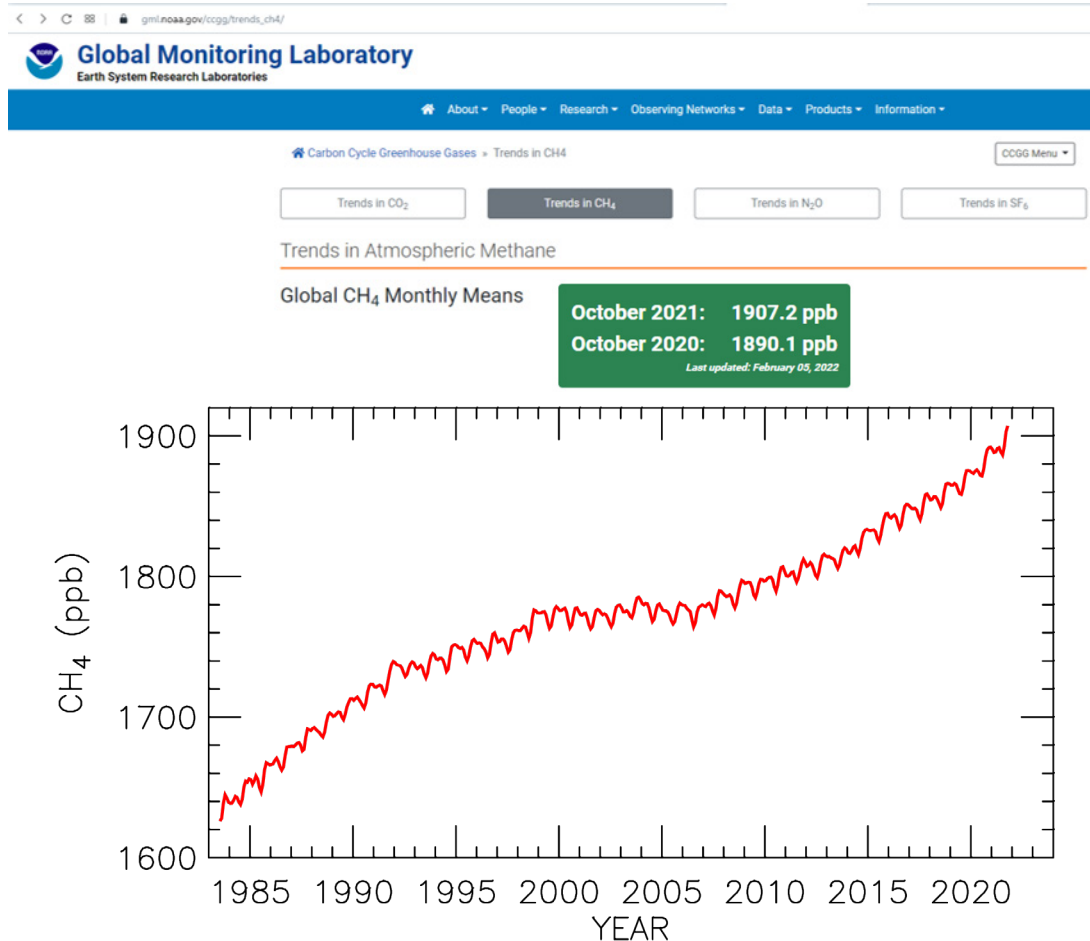
Atmospheric CH₄

AT6, Q2:

What is the approximate current atmospheric abundance of CH₄?

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

Latest data indicate CH₄ is over 1900 ppb and rising, and also that CH₄ exceeded 1760 ppb in late-1990s and exceeded 1.84 ppm in mid-2017.



Atmospheric CH₄

AT6, Q3:

What are the values given for:

- a) enhanced greenhouse effect caused by a molecule of CH₄ relative to that of a molecule of CO₂ given on pg 47 of Houghton
- b) the GWP for CH₄ given in Table 3.2 of *Chemistry in Context*
- c) the GWP for CH₄ over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

The ~10 year atmospheric lifetime for CH₄ has important policy implications. This is best illustrated by comparing the human release of CH₄ to that of CO₂. Throughout the world, humans presently release about 335 Tg of CH₄ and 39 Gt of CO₂ per year. Since 1000 Tg = 1 Gt, these sources are 0.335 Gt of CH₄ and 39 Gt of CO₂ per year: i.e., the mass of CO₂ released to the atmosphere each year by human society is about 116 times more than the mass of CH₄. The impact on climate is entirely dependent on the time scale of interest. Nearly all of the CH₄ released to the atmosphere in year 2015 will be gone by the end of this century. The **CO₂-equivalent** emission of CH₄, found by multiplying the current release by the GWP for CH₄ for a 100-year time horizon, is 28 × 0.335 Gt of CH₄ or 9.4 Gt per year. If our concern is global warming over the next century, then we would conclude the human release of CO₂ in year 2015 was about four times more harmful for climate (39 ÷ 9.4 = 4.1) than the release of CH₄. However, if our concern is the next two decades, we must consider the GWP of CH₄ over a 20-year time horizon. In this case, the CO₂-equivalent emission of CH₄ is 84 × 0.335 Gt or 28.1 Gt per year, and we would conclude the present human release of CH₄ is nearly as harmful for climate (28.1 versus 39) as the release of CO₂.

Atmospheric CH₄

AT6, Q3:

What are the values given for:

- a) enhanced greenhouse effect caused by a molecule of CH₄ relative to that of a molecule of CO₂ given on pg 47 of Houghton
- b) the GWP for CH₄ given in Table 3.2 of *Chemistry in Context*
- c) the GWP for CH₄ over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

Table 1.1 *Paris, Beacon of Hope*

Global Warming Potentials				
GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
<i>100 Year Time Horizon</i>				
CH ₄	21	23	25	28
N ₂ O	310	296	298	265
<i>20 Year Time Horizon</i>				
CH ₄	56	62	72	84
N ₂ O	280	275	289	264

Atmospheric CH₄

AT6, Q3:

What are the values given for:

- enhanced greenhouse effect caused by a molecule of CH₄ relative to that of CO₂ given on pg 47 of Houghton
- the GWP for CH₄ given in Table 3.2 of *Chemistry in Context*
- the GWP for CH₄ over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

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

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.

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 CO₂ with atomic mass of 44 weighs 2.75 times a molecule of CH₄ (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 **CH₄ is 28 times more potent than CO₂ on a per mass basis** and, *at the same time*, is **10.2** (28 ÷ 2.75) **times more potent than CO₂ on a per molecule basis.**

Atmospheric CH₄

Scientific utility of quantifying the human and natural sources of CH₄

CH₄ Sources:

Human: 335 Tg yr⁻¹

Natural: 218 Tg yr⁻¹

Total: 553 Tg yr⁻¹

Human ≈ 60% of total

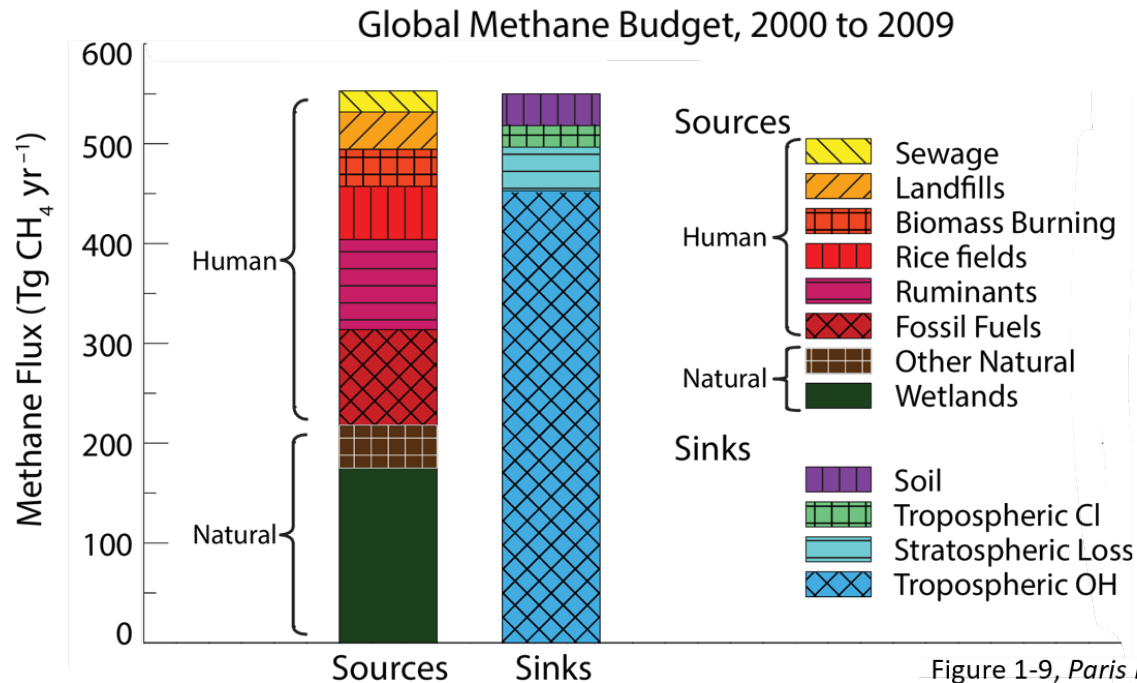


Figure 1-9, *Paris Beacon of Hope*

If:

Production of CH₄ = Loss of CH₄ and if the loss involves a chemical reaction of CH₄ with a Gas, then

Production of CH₄ = $k [\text{CH}_4] [\text{Gas}]$, where k is the rate of a chemical reaction and $[]$ denotes abundance

Assuming k and $[\text{Gas}]$ are constant over time, we can write:

Production^{Preindustrial} = $k [\text{CH}_4]^{\text{Preindustrial}} [\text{Gas}]$ & Production^{Present} = $k [\text{CH}_4]^{\text{Present}} [\text{Gas}]$

which can be re-arranged to yield:

$k [\text{Gas}] = \text{Production}^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Preindustrial}}$ & $k [\text{Gas}] = \text{Production}^{\text{Present}} / [\text{CH}_4]^{\text{Present}}$

Atmospheric CH₄

Scientific utility of quantifying the human and natural sources of CH₄

If:

$$k [\text{Gas}] = \text{Production}^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Preindustrial}} \quad \& \quad k [\text{Gas}] = \text{Production}^{\text{Present}} / [\text{CH}_4]^{\text{Present}}$$

Then:

$$\text{Production}^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Preindustrial}} = \text{Production}^{\text{Present}} / [\text{CH}_4]^{\text{Present}}$$

Or:

$$[\text{CH}_4]^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Present}} = \text{Production}^{\text{Preindustrial}} / \text{Production}^{\text{Total}}$$

Or:

$$[\text{CH}_4]^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Present}} = \text{Source}^{\text{Preindustrial}} / \text{Source}^{\text{Present}}$$

From prior slide:

$$[\text{CH}_4]^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Present}} = \text{Source}^{\text{Preindustrial}} / \text{Source}^{\text{Present}}$$

Presumably:

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

If so, then top equation can be written as:

$$\begin{aligned} [\text{CH}_4]^{\text{Preindustrial}} / [\text{CH}_4]^{\text{Present}} &= (\text{Source}^{\text{Present}} - \text{Source}^{\text{Human}}) / \text{Source}^{\text{Present}} \\ &= 1 - \text{Source}^{\text{Human}} / \text{Source}^{\text{Present}} = 1 - (335 \text{ Tg yr}^{-1}) / (553 \text{ Tg yr}^{-1}) \\ &= 1 - 0.61 = 0.39 \end{aligned}$$

AT6, Q1:

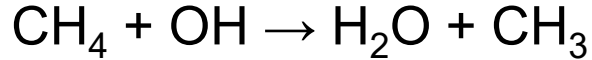
According to Table 3.2 of Chemistry in Context what was pre-industrial atmospheric abundance of CH₄? $\Rightarrow$ 700 ppb

AT6, Q2:

What is the approximate current atmospheric abundance of CH₄? $\Rightarrow$ 1800 ppb

$$\text{ppb} / \text{ppb} = !!!$$

CH₄ is in fact lost by reaction with OH, the hydroxyl radical



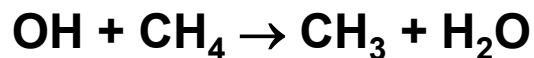
$$\frac{d\text{CH}_4}{dt} = \text{Production} - \text{Loss} = \text{Production} - k^{\text{CH}_4 + \text{OH}} [\text{CH}_4] [\text{OH}]$$

Rate constant (speed at which CH₄ reactions with OH):

$$k^{\text{CH}_4 + \text{OH}} = 1.85 \times 10^{-20} \times T^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

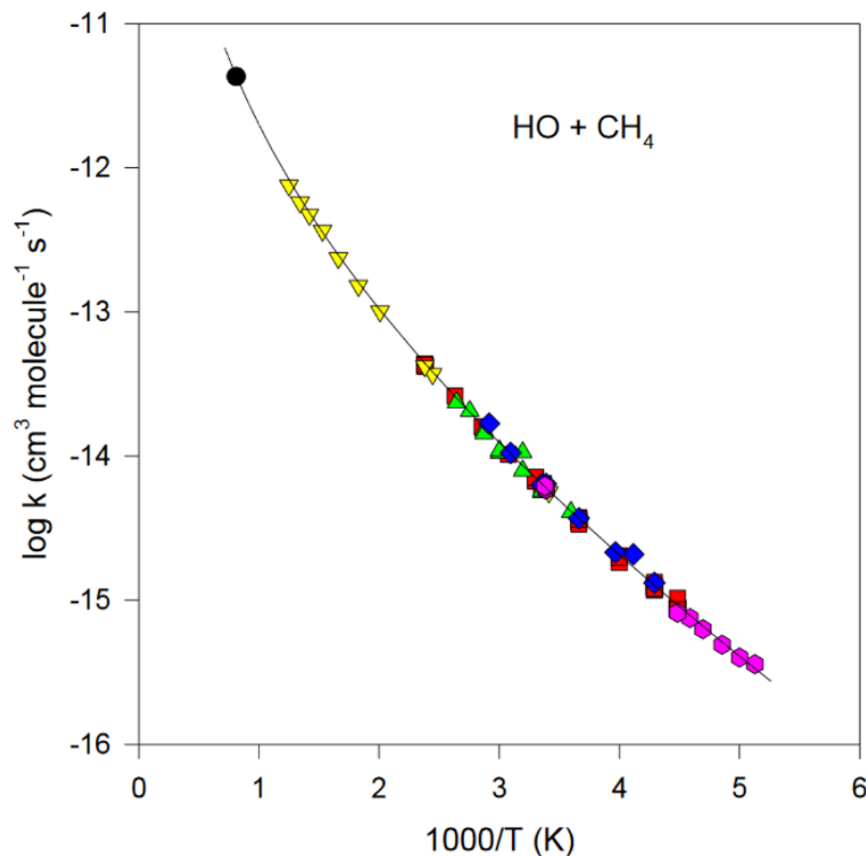
which is obtained from analysis of laboratory measurements

Bimolecular Gas Phase Reactions



Rate constant recommended by IUPAC

$$k^{\text{OH}+\text{CH}_4} = 1.85 \times 10^{-20} \times T^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

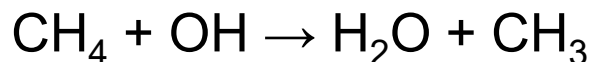


Various **Laboratory Experiments**:
many PhDs, tenure-type research, etc.

- Bott and Cohen (1989)
- Vaghjiani and Ravishankara (1991)
- ▲ Finlayson-Pitts et al. (1992)
- ▼ Dunlop and Tully (1993)
- ◆ Mellouki et al. (1994)
- ◆ Gierczak et al. (1997)
- Recommendation

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

CH₄ is in fact lost by reaction with OH, the hydroxyl radical



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

Arrhenius Expression for rate constant: i.e., speed at which CH₄ reactions with OH:

$$k^{\text{CH}_4 + \text{OH}} = 1.85 \times 10^{-12} \times e^{-1690/T} \text{ cm}^3 \text{ sec}^{-1}$$

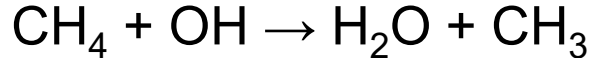
which is obtained from analysis of laboratory measurements

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

Commonly T = 272 K and **[OH] = 1 × 10⁶ molec cm⁻³** are used, yielding:

$$\begin{aligned} \text{Lifetime of CH}_4 &= \frac{1}{k^{\text{CH}_4 + \text{OH}} [\text{OH}]} = \frac{1}{3.71 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}} \\ &= 2.70 \times 10^8 \text{ sec} = \text{yr} \end{aligned}$$

CH₄ is in fact lost by reaction with OH, the hydroxyl radical



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

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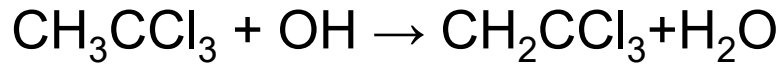
which is obtained from analysis of laboratory measurements

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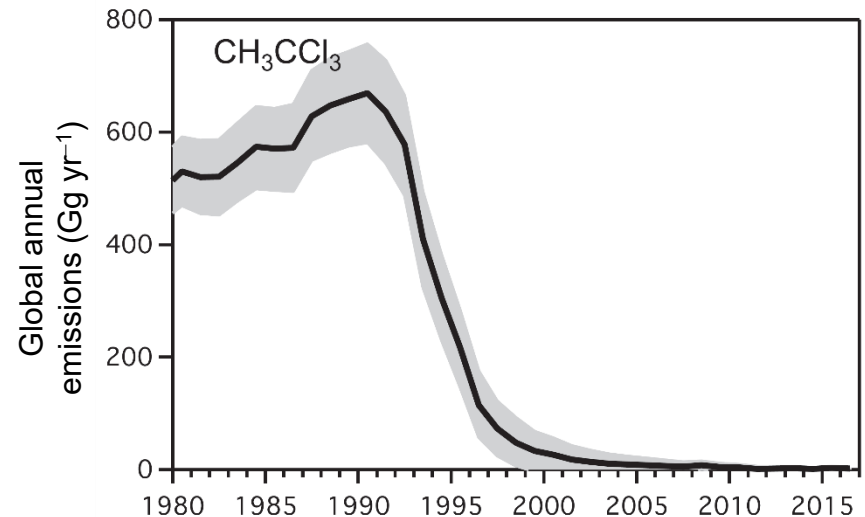
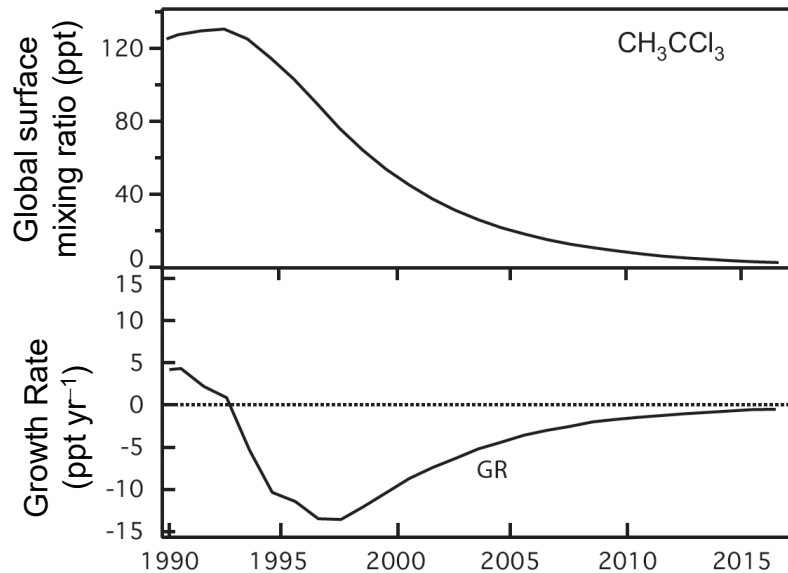
Commonly T = 272 K and **[OH] = 1 × 10⁶ molec cm⁻³** are used, yielding:

$$\begin{aligned} \text{Lifetime of CH}_4 &= \frac{1}{k^{\text{CH}_4 + \text{OH}} [\text{OH}]} = \frac{1}{3.60 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}} \\ &= \end{aligned}$$

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



$$\frac{d\text{CH}_3\text{CCl}_3}{dt} = \text{Production} - \text{Loss} = \text{Production} - k^{\text{CH}_3\text{CCl}_3 + \text{OH}} [\text{CH}_3\text{CCl}_3] [\text{OH}]$$



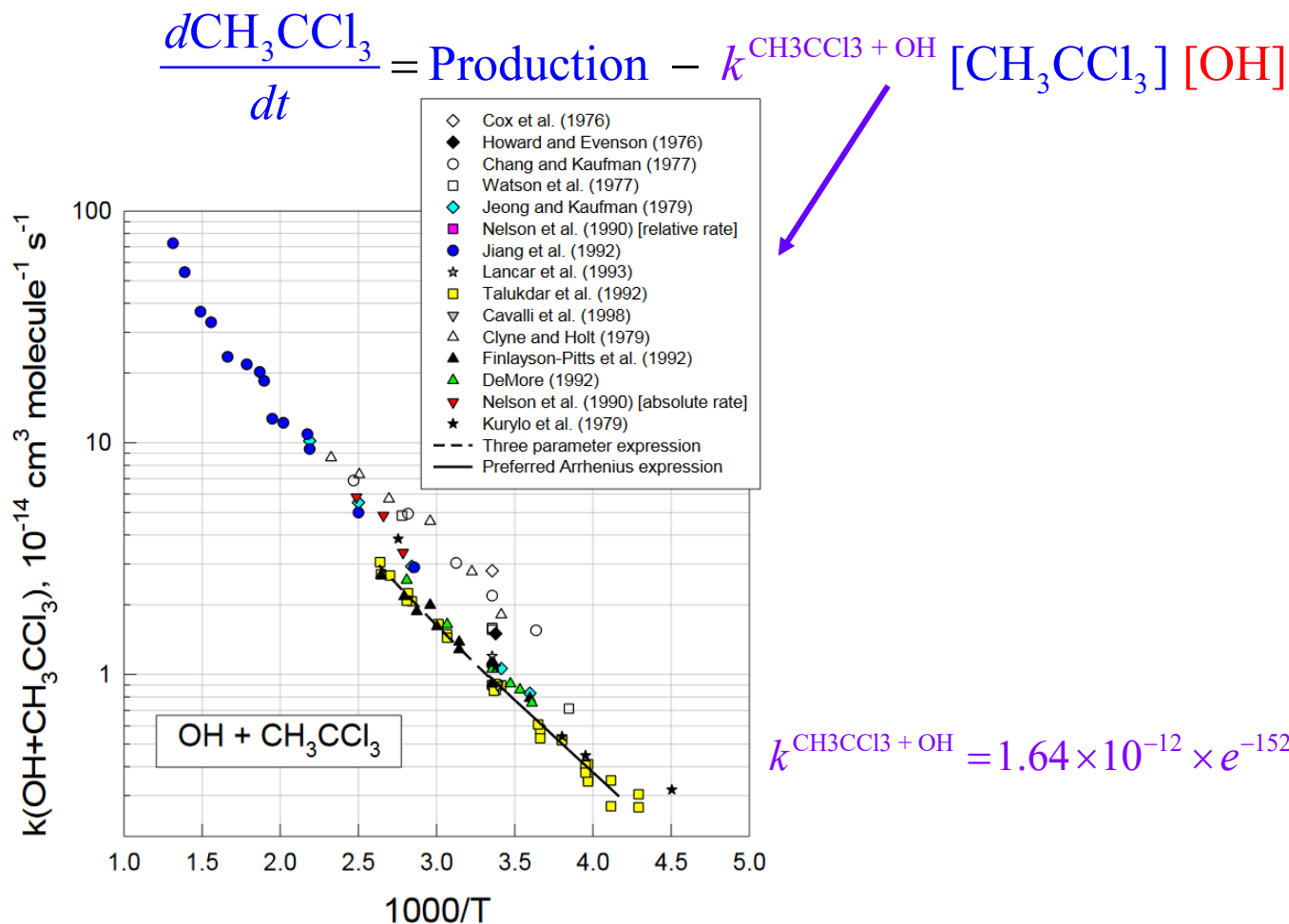
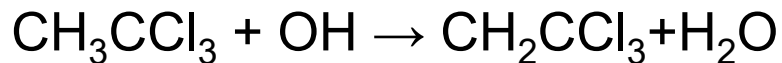
https://www.esrl.noaa.gov/csd/assessments/ozone/2018/report/Chapter1_2018OzoneAssessment.pdf

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.

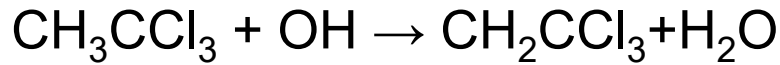
Montreal Protocol banned the use of methyl chloroform and it was rapidly phased out, throughout the world.

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

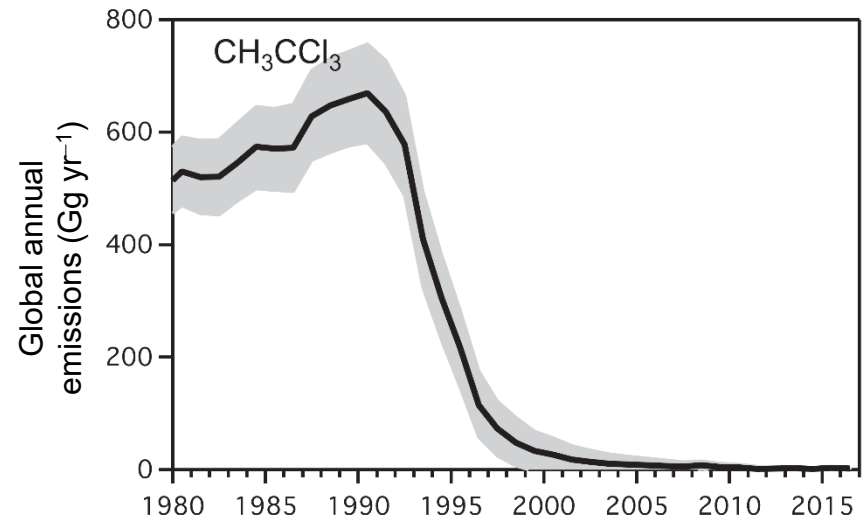
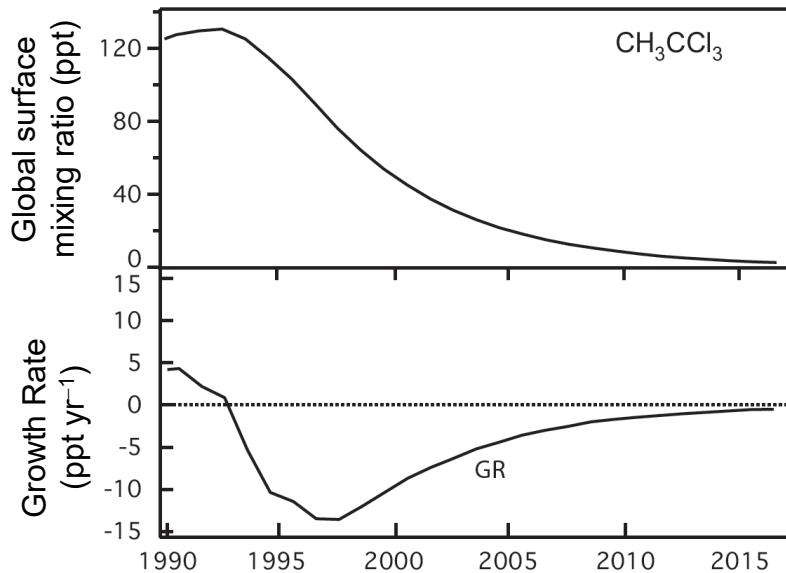
CH_3CCl_3 (methyl chloroform) is lost by reaction with OH
& its atmospheric abundance / industrial production are well known



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



$$\frac{d\text{CH}_3\text{CCl}_3}{dt} = \text{Production} - k^{\text{CH}_3\text{CCl}_3 + \text{OH}} [\text{CH}_3\text{CCl}_3] [\text{OH}]$$



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

Prinn et al., *Science*, 2001

Houghton & *Chemistry in Context* give a Lifetime for CH₄ of 12 Years

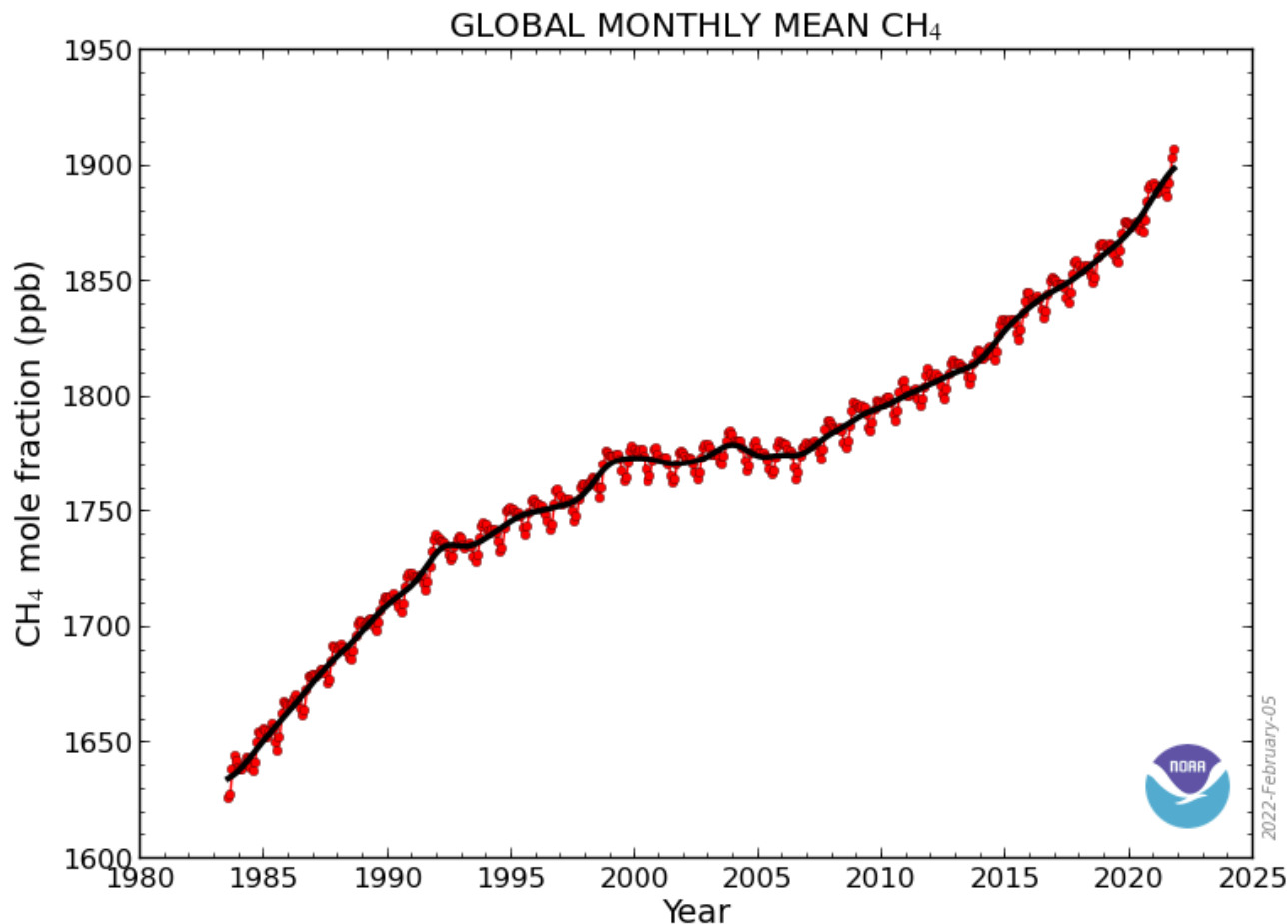
What's up with the 12 year lifetime?

$$\begin{aligned}\text{Lifetime of CH}_4 &= \frac{1}{k^{\text{CH}_4 + \text{OH}} [\text{OH}]} = \frac{1}{3.59 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}} \\ &= 2.79 \times 10^8 \text{ sec} = 8.8 \text{ yr}\end{aligned}$$

- 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

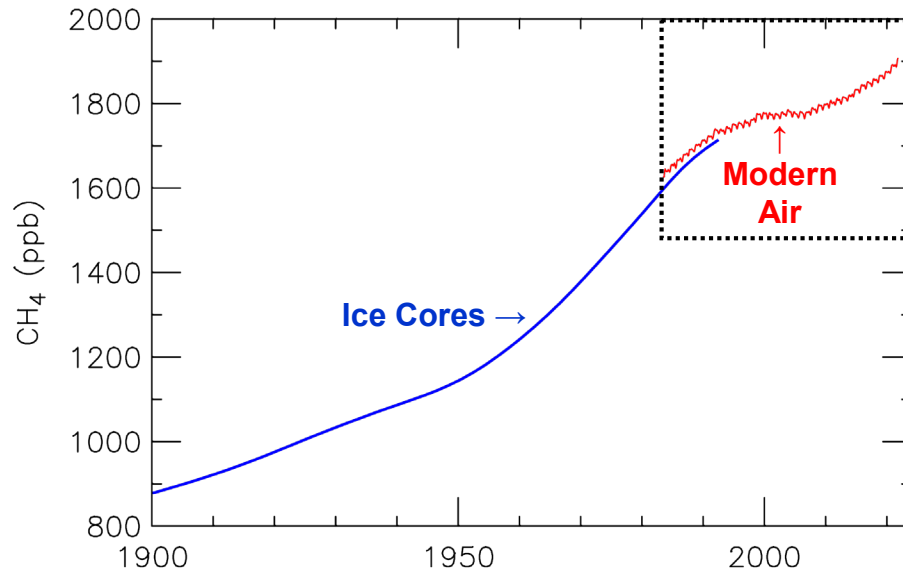
Understanding the observed time series of CH₄ is a “hot ticket item” in modern atmospheric chemistry



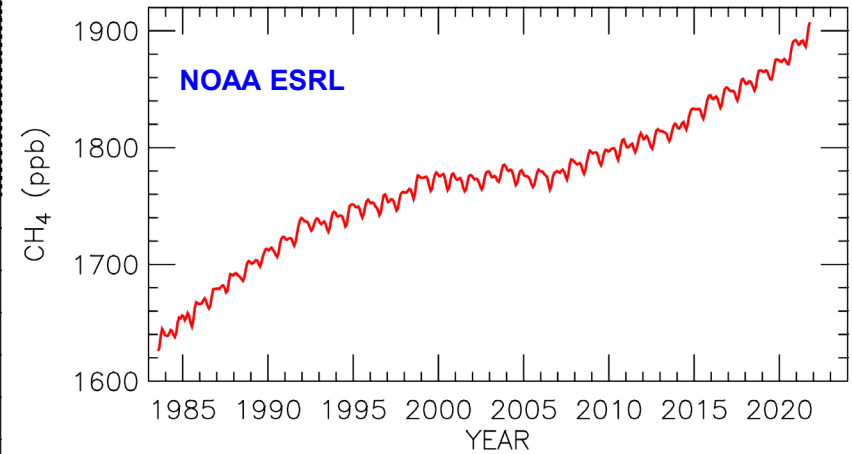
https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4

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

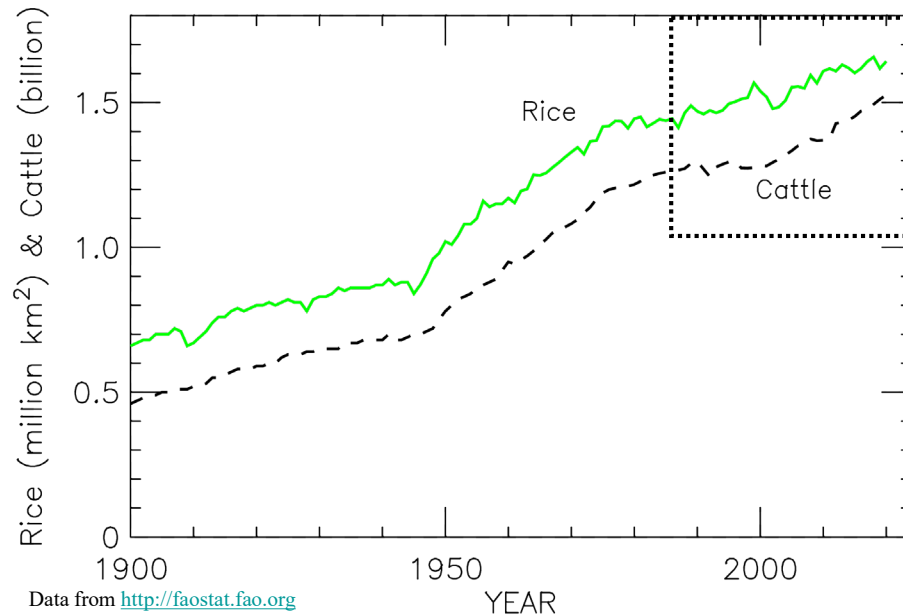
Atmospheric CH₄ and Energy from Gas, Rice, Cattle Trends



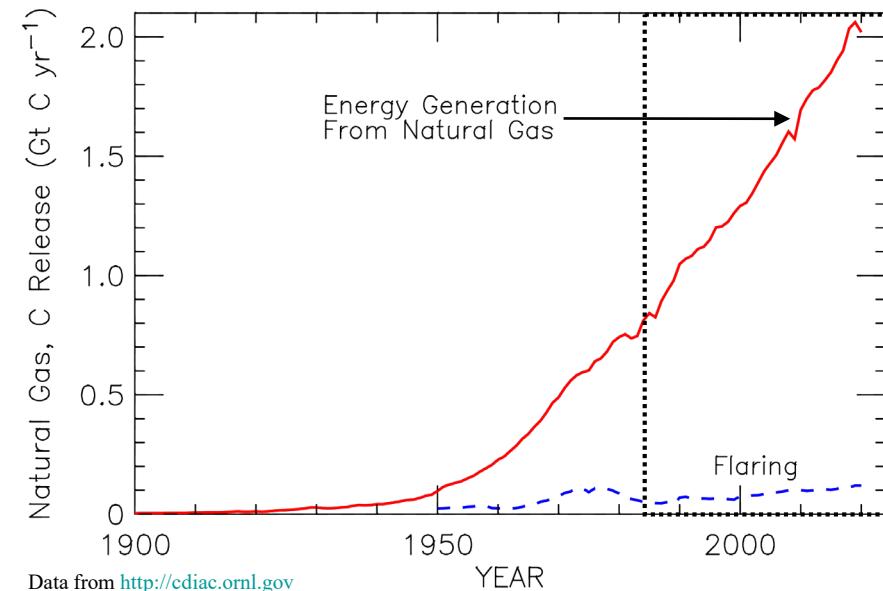
Data from http://cdiac.ornl.gov/ftp/trends/atm_meth



<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>

Recent trends in CH₄

These papers offer conflicting views on the cause of the recent rise in CH₄

- 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 CH₄

These papers offer conflicting views on the cause of the recent rise in CH₄

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

Between 1999 and 2006, a plateau interrupted the otherwise continuous increase of atmospheric methane concentration [CH₄] since preindustrial times. Causes could be sink variability or a temporary reduction in industrial or climate-sensitive sources. We reconstructed the global history of [CH₄] 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 CH₄ sink caused the [CH₄] plateau. Thermogenic emissions did not resume to cause the renewed [CH₄] 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 CH₄ emissions 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 CH₄ 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 CH₄ per year from the 2001–2007 to the 2008–2014 time periods using satellite measurements of CO and CH₄, 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 CH₄ 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 CH₄

These papers offer conflicting views on the cause of the recent rise in CH₄

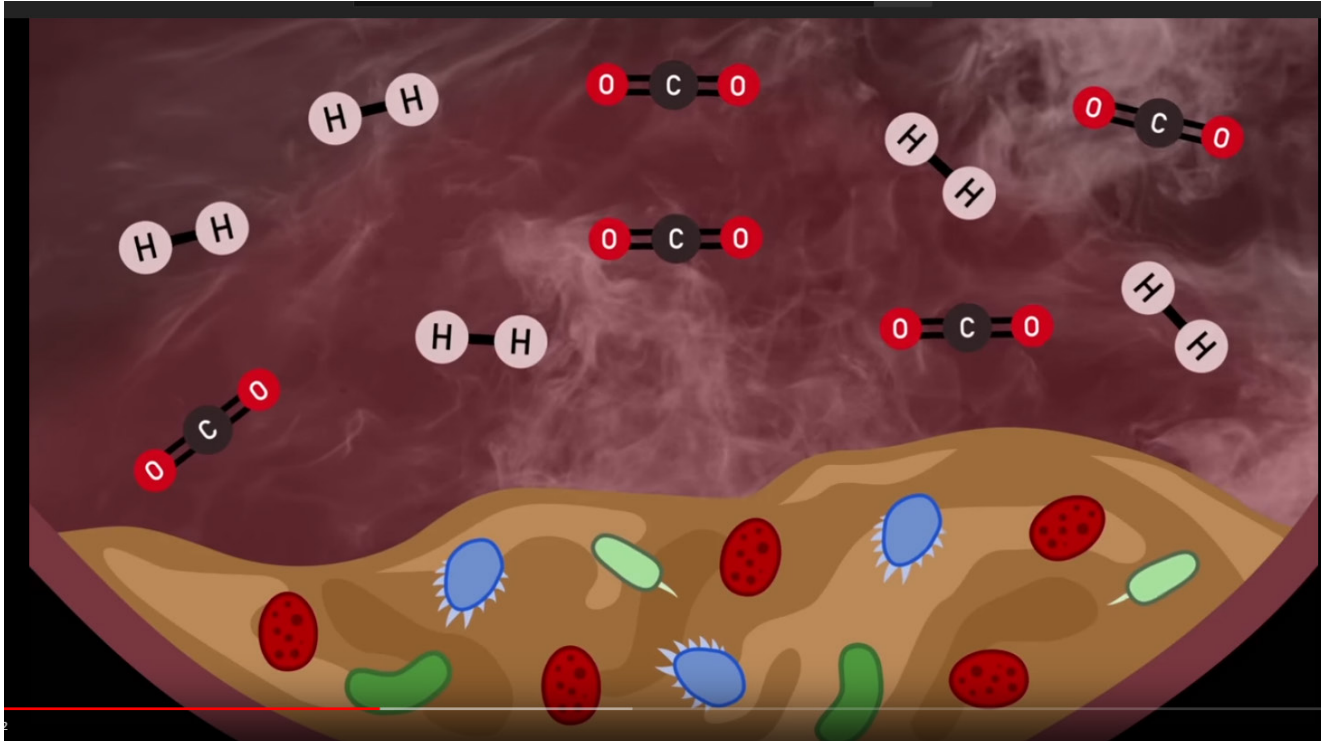
- Wolf *et al.*, *Carbon Balance and Management*, 2017:

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

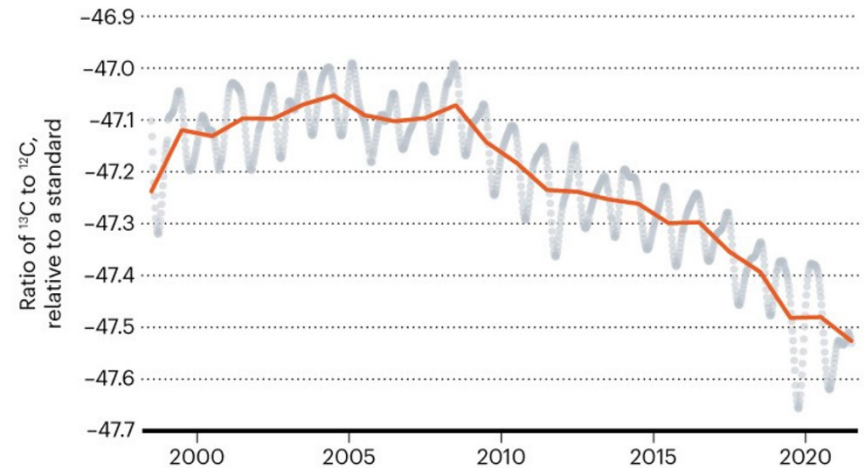
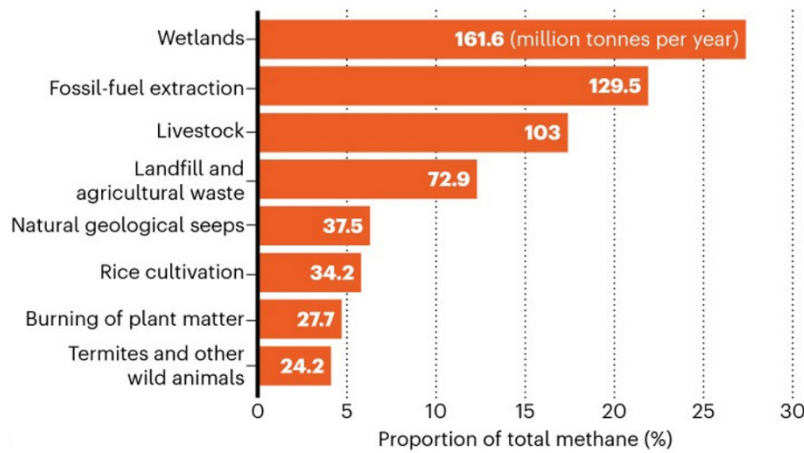


https://www.youtube.com/watch?v=MnRFUSGz_ZM

Recent trends in CH₄

These papers offer conflicting views on the cause of the recent rise in CH₄

- Tollefson *et al.*, *Nature*, 2022:
 - Tropical wetlands such as those pictured (Brazil) major source of CH₄ emissions
 - Isotopic signature seems to indicate most of the rise in the emissions of CH₄ are [recent] biological in origin, rather than extraction of fossil fuels [ancient biological]



Wetter-gets-Wetter, Dry-gets-Drier (WWDD) Paradigm

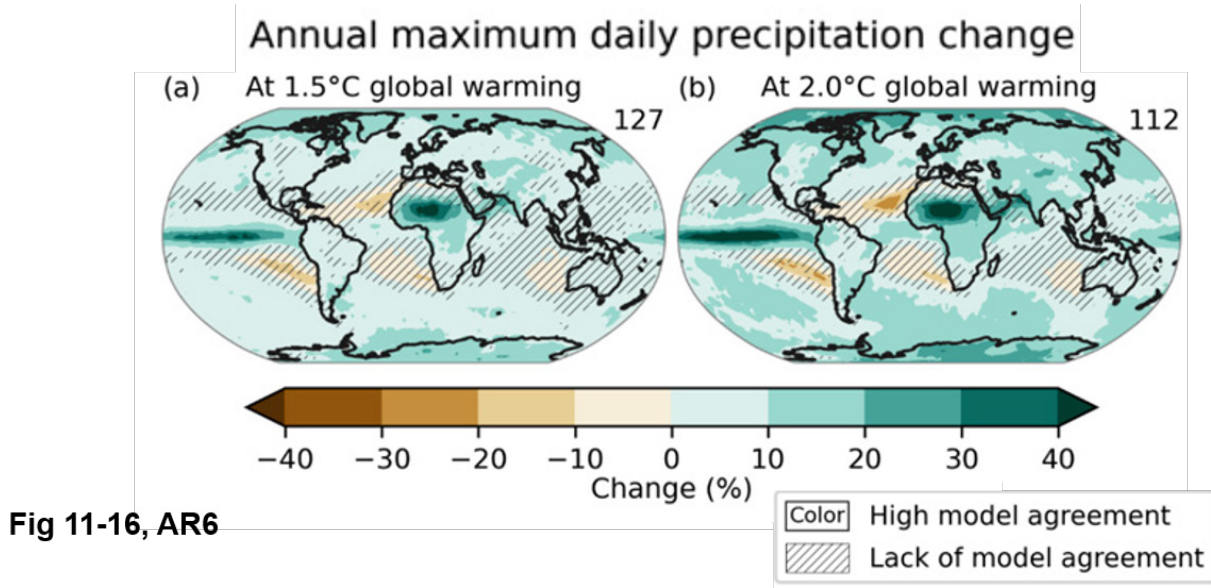
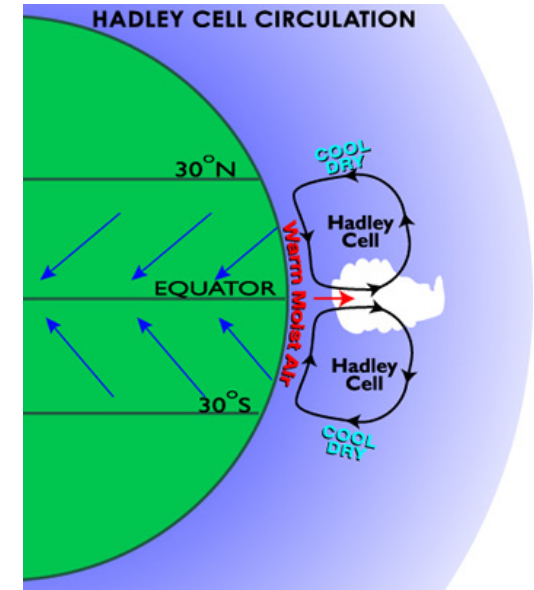


Fig 11-16, AR6



Projected changes in annual maximum daily precipitation at (a) 1.5°C, (b) 2°C warming compared to the 1851-1900 baseline.

Results are based on simulations from the CMIP6 multi6 model ensemble under the SSP1-1.9, SSP1-2.6, SSP2-4.5, SSP3-7.0, and SSP5-8.5 scenarios. The numbers on the top right indicate the number of simulations included. Uncertainty is represented as follows: no overlay indicates regions with high model agreement, where $\geq 80\%$ of models agree on sign of change; diagonal lines indicate regions with low model agreement, where $< 80\%$ of models agree on sign of change

https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC_AR6_WGI_Chapter_11.pdf

See also <https://www.preventionweb.net/news/explainer-what-new-ipcc-report-says-about-extreme-weather-and-climate-change>

Hadley Cell Circulation: http://www.windows2universe.org/vocals/images/HadleyCell_small.jpg

Nitrous Oxide: N₂O

Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

Chapter 3, Chemistry in Context

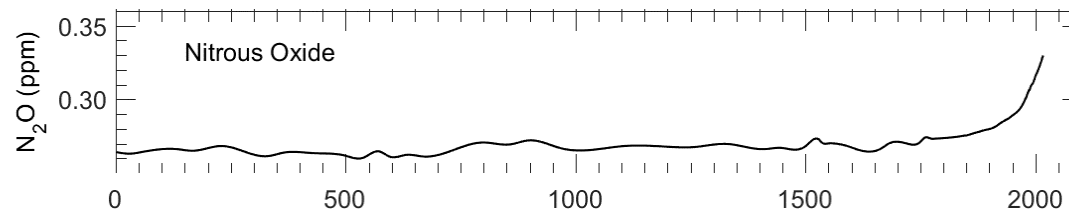
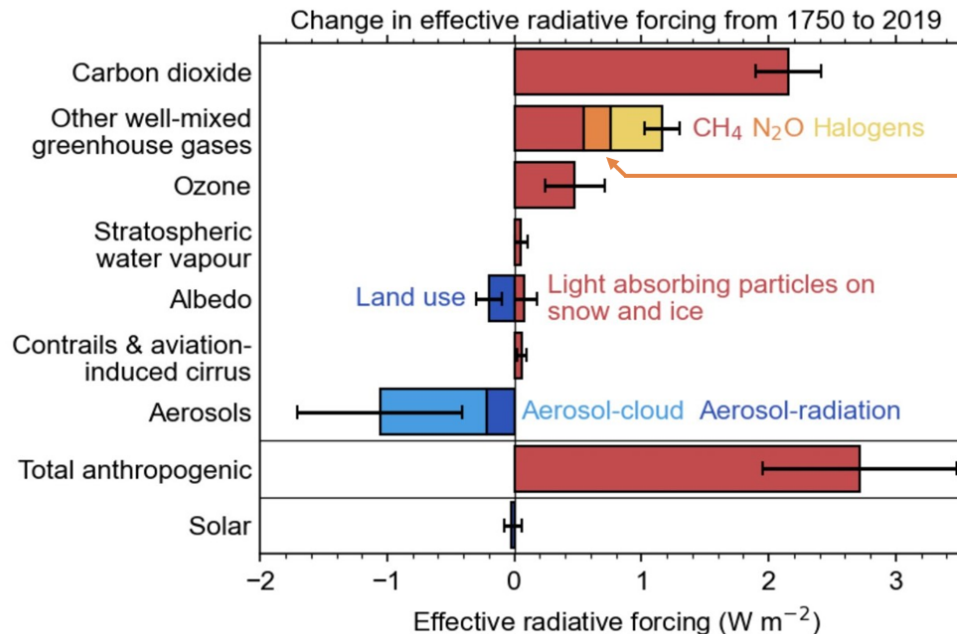


Figure 1.2, Paris, Beacon of Hope



Nitrous oxide (N₂O) is commonly identified as the third most important anthropogenic GHG.

On either a per molecule or a per mass basis, N₂O causes 264 times more warming than CO₂ over a 20-yr time horizon.

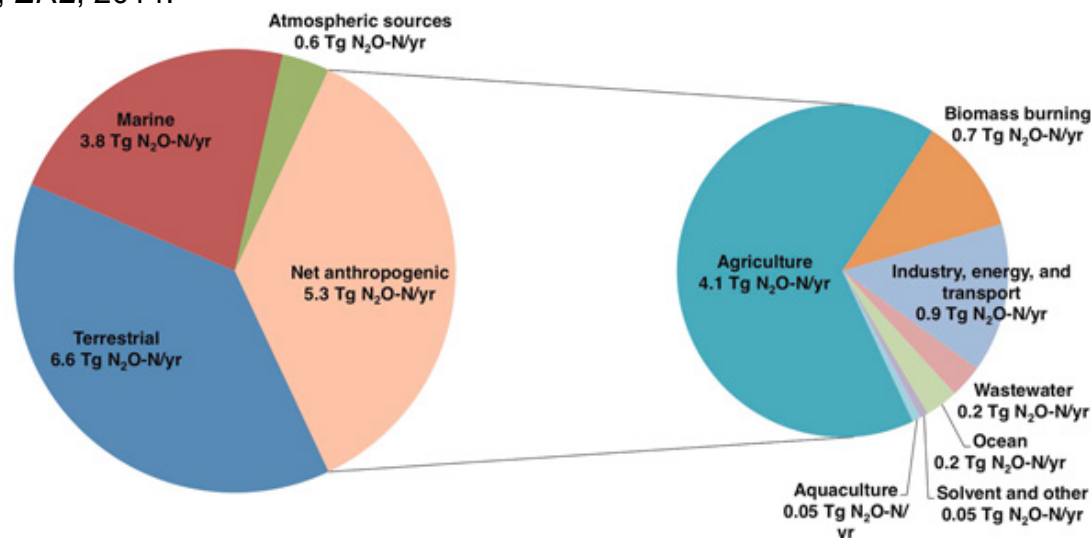
Between 1750 and 2011, the rise in atmospheric N₂O caused RF of climate to rise by 0.21 W m⁻²

Nitrous Oxide: N₂O

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 ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

Chapter 3, *Chemistry in Context*

Davidson and Kanter, *ERL*, 2014:



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

$$\begin{aligned}
 [\text{N}_2\text{O}]^{\text{Preindustrial}} / [\text{N}_2\text{O}]^{\text{Present}} &= 1 - \text{Source}^{\text{Human}} / \text{Source}^{\text{Total}} = 1 - (5.3 \text{ Tg yr}^{-1}) / (16.3 \text{ Tg yr}^{-1}) \\
 &= 1 - 0.32 = 0.67
 \end{aligned}$$

$$\text{From above, } [\text{N}_2\text{O}]^{\text{Preindustrial}} / [\text{N}_2\text{O}]^{\text{Present}} = (275 \text{ ppb}) / (322 \text{ ppb}) = 0.85$$

Difference between these two values could reflect a short-coming in our understanding of the net anthropogenic source of N₂O, but more likely is due to the fact that with a 120 year lifetime, the fundamental assumption of Production = Loss is not true for N₂O

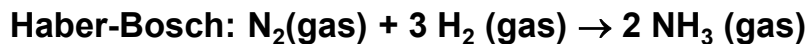
Sources and Sinks of N₂O

Table 6.9, IPCC 2013

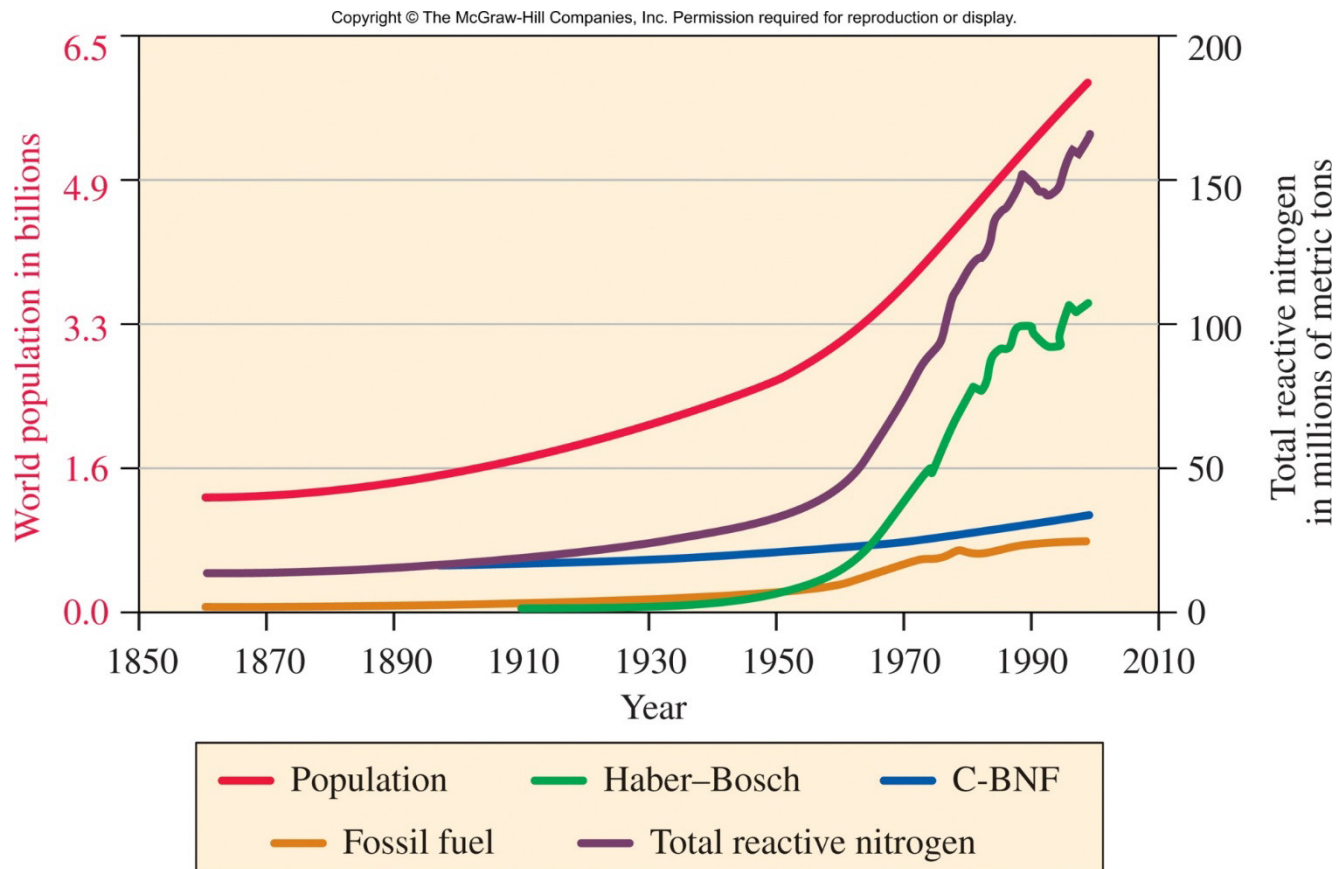
SECTION 2 (N ₂ O)		All units for N ₂ O fluxes are in Tg N yr ⁻¹
		AR5 (2006/2011)
Anthropogenic sources		
Fossil fuel combustion and industrial processes		0.7 (0.2–1.8) ^a
Agriculture		4.1 (1.7–4.8) ^b
Biomass and biofuel burning		0.7(0.2–1.0) ^a
Human excreta		0.2 (0.1–0.3) ^a
Rivers, estuaries, coastal 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)

The Nitrogen Cycle



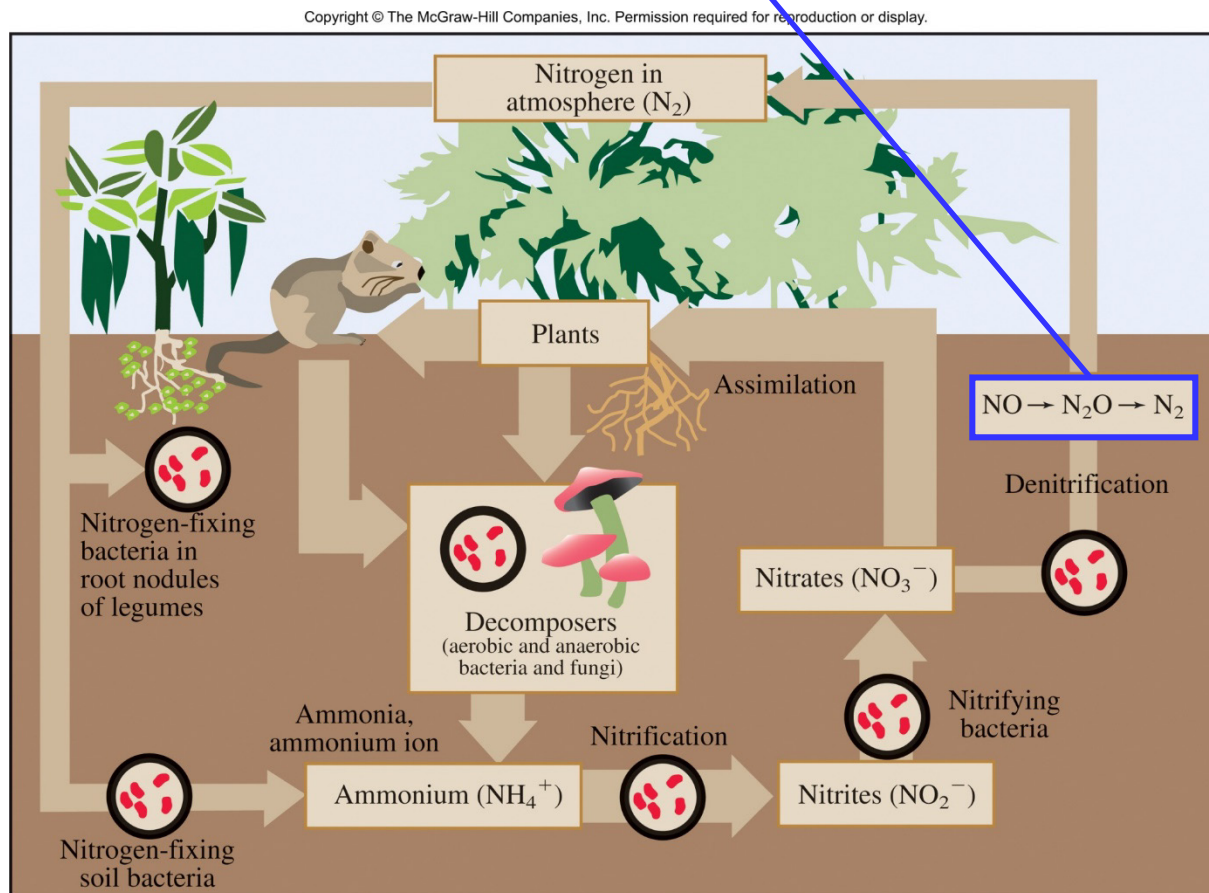
Led to large scale, economical production of ammonia based fertilizer



Chapter 6, *Chemistry in Context*

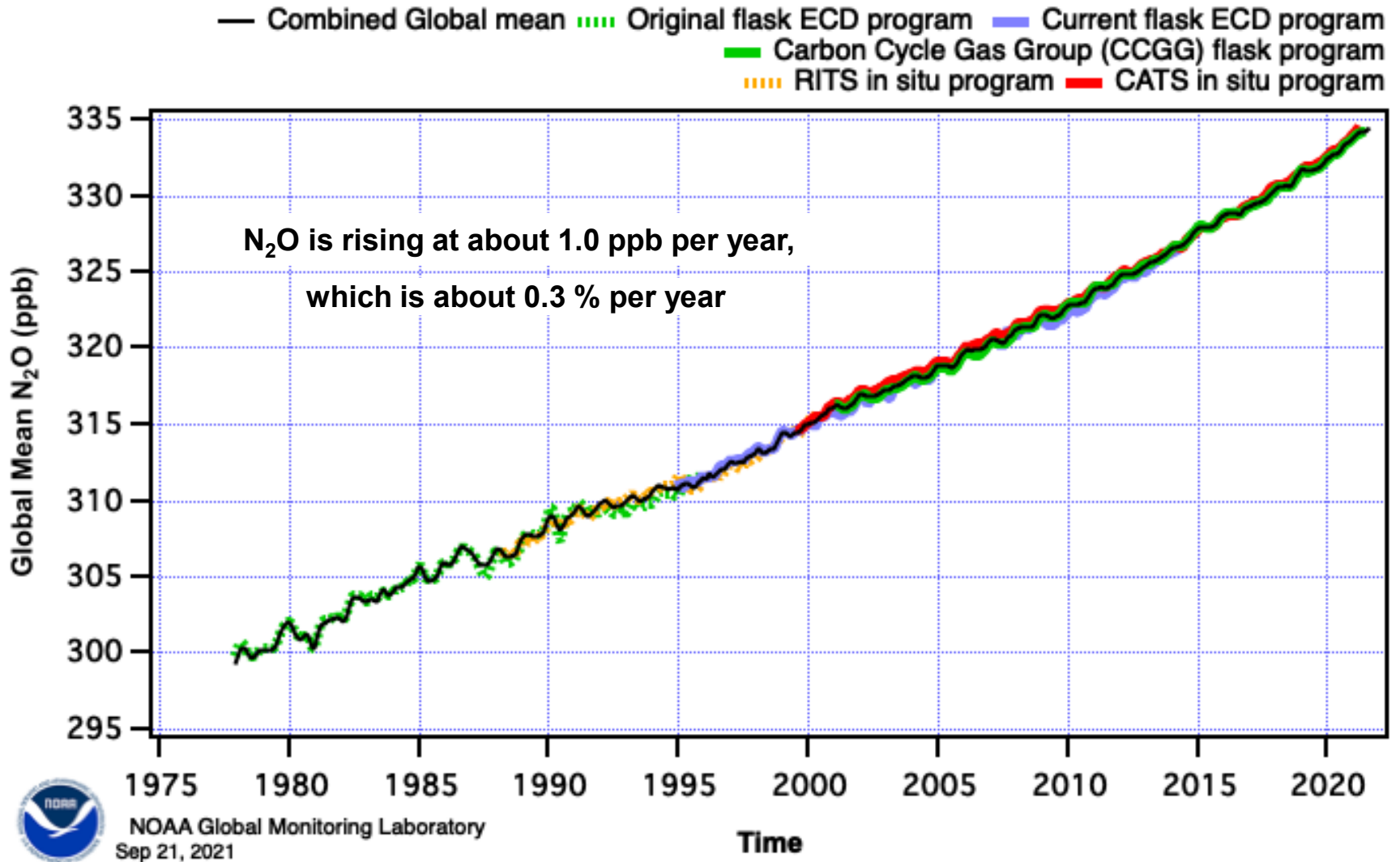
The Nitrogen Cycle

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*

N₂O Time Series



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

N₂O and NO_y

Loss of N₂O occurs mainly in the stratosphere due to:
photolysis – main sink
reaction with vibrationally excited O(¹D) – minor sink

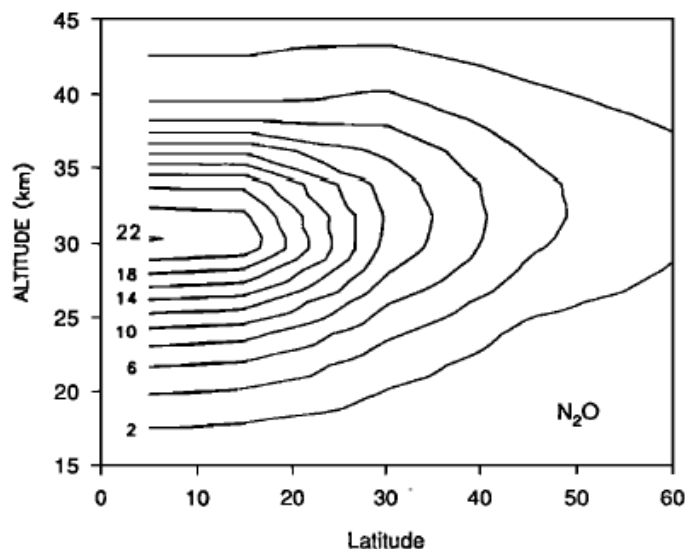
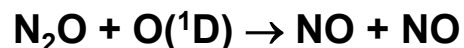


Fig. 11. Diurnally averaged loss rate for N₂O (10² molecules cm⁻³ s⁻¹) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N₂O by reaction with O(¹D) as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

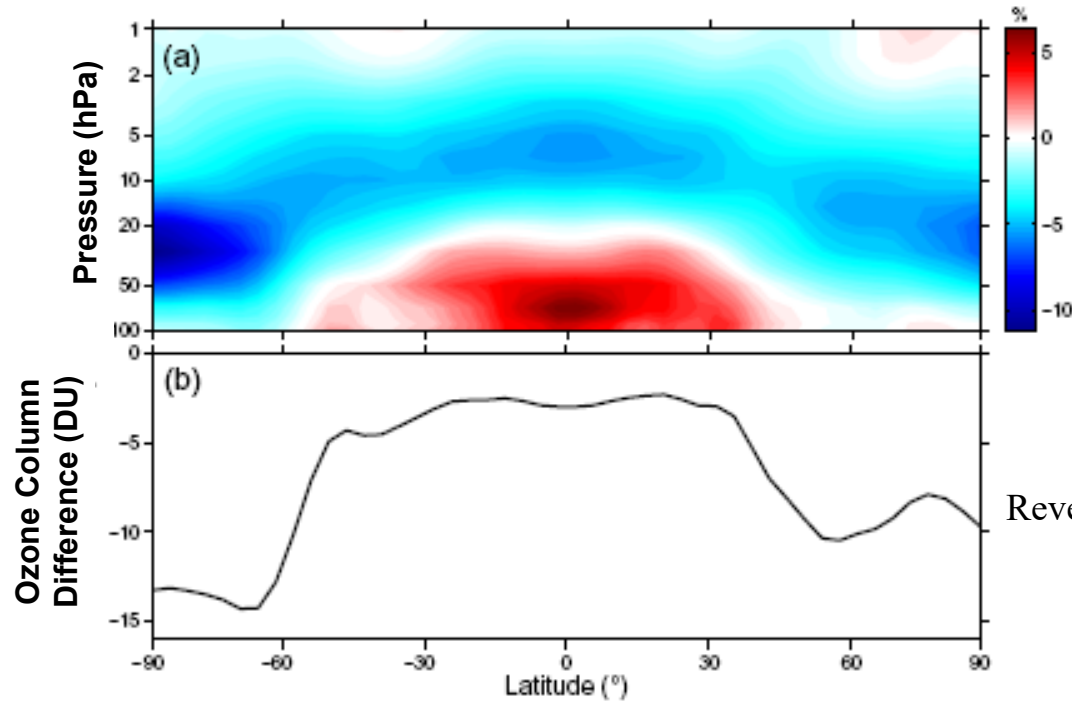
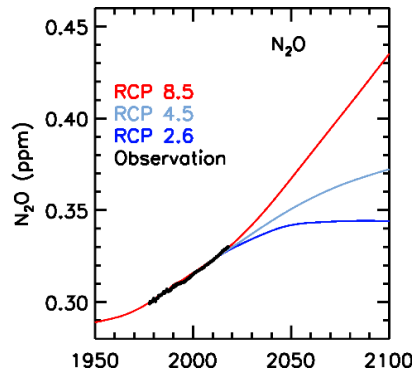
The minor sink for N₂O loss has a path that results in “fixed nitrogen”:



Fixed nitrogen (NO_y) is crucial to stratospheric chemistry

Oxides of nitrogen catalyze loss of stratospheric O₃ & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.

N₂O and Stratospheric Ozone



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

Difference of stratospheric O₃ in the 2090s for a computer simulation run using N₂O from RCP 8.5 minus that of a simulation using N₂O from RCP 2.6

Rising N₂O leads to:

- a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO₂ mediated loss cycles.
- b) speeds up the rate of OH+NO₂+M→HNO₃ & ClO+NO₂+M→ClONO₂+M in the lowermost stratosphere, leading to slower ozone loss by these cycles & less O₃ where these cycles dominate total loss of O₃

Computer models project stratospheric column O₃ will decline as N₂O rises