

Biogeochemical Cycles of Methane and Nitrous Oxide

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2017>

Goals :

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

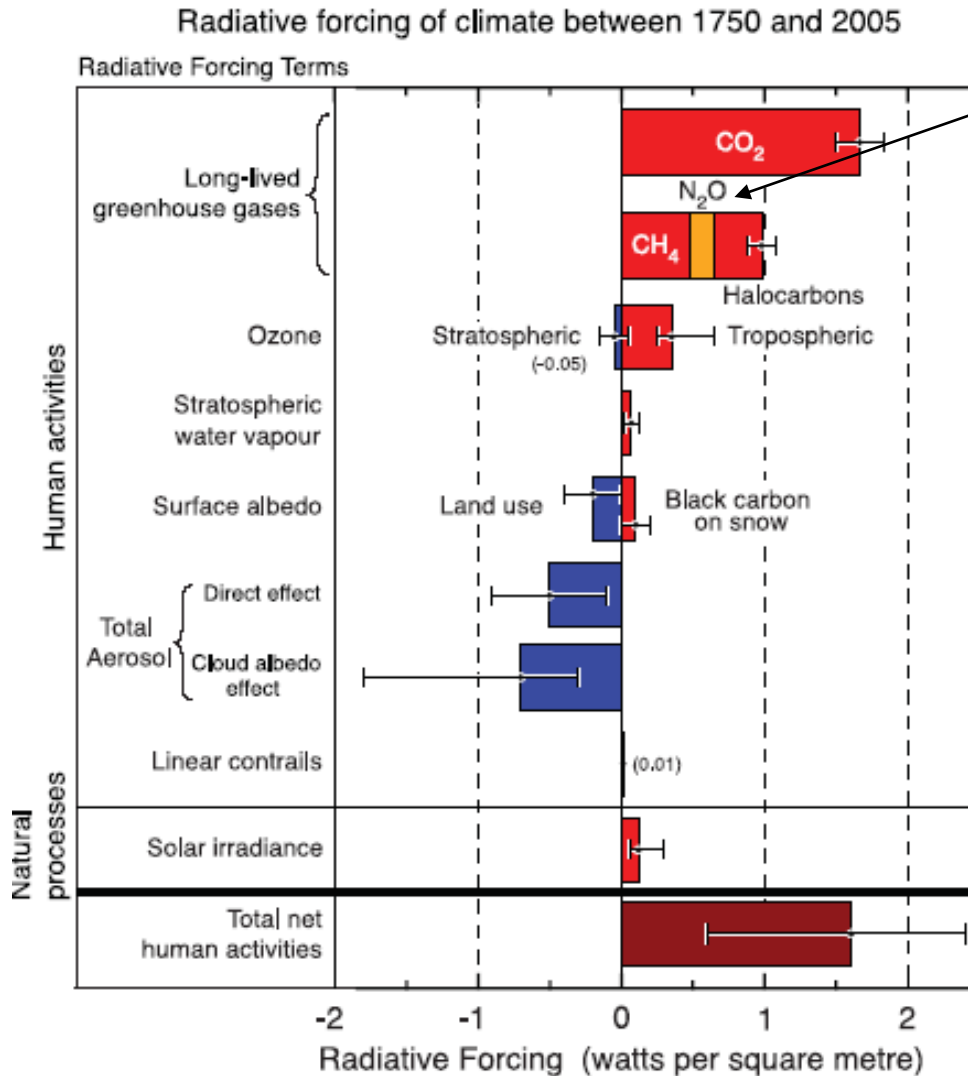
Lecture 06

14 February 2017

Announcements

- Problem Set #1 due today
- Pam will hold problem set reviews in this room during various evenings
 - Problem Set #1 review will be Monday, 20 Feb, at 6 pm
 - 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, 23 Feb; will review Mon, 27 Feb
- First exam is Tues, 28 Feb, 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, 23 Feb to help you prepare

Radiative Forcing of Climate, 1750 to 2005



CH₄ & N₂O have contributed about 38% of the RF of CO₂

FAQ 2.1, Figure 2. Summary of the principal components of the radiative forcing of climate change.

Radiative Forcing of Climate, 1750 to 2011

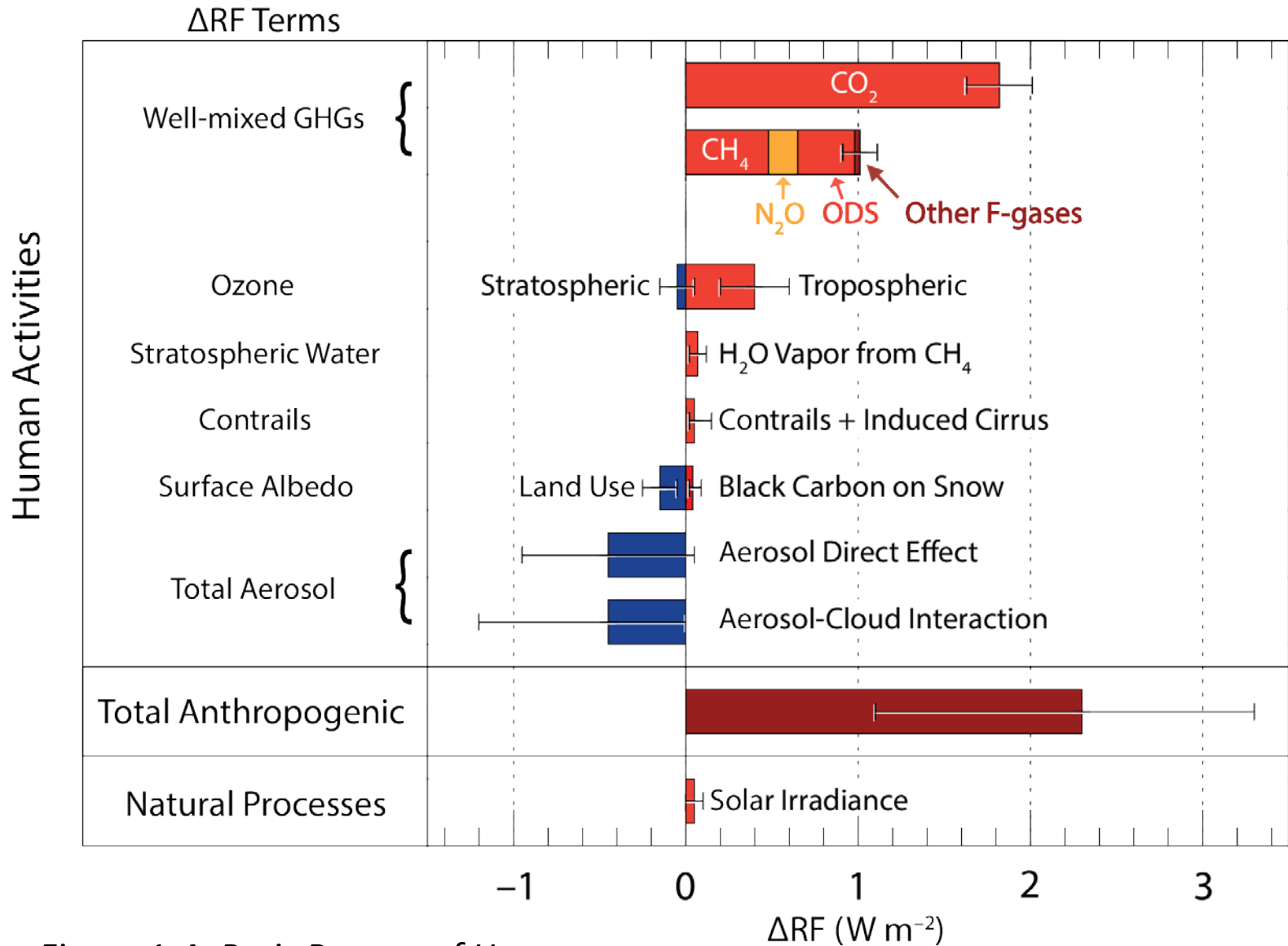


Figure 1-4, *Paris Beacon of Hope*

CO₂, CH₄ & N₂O time series

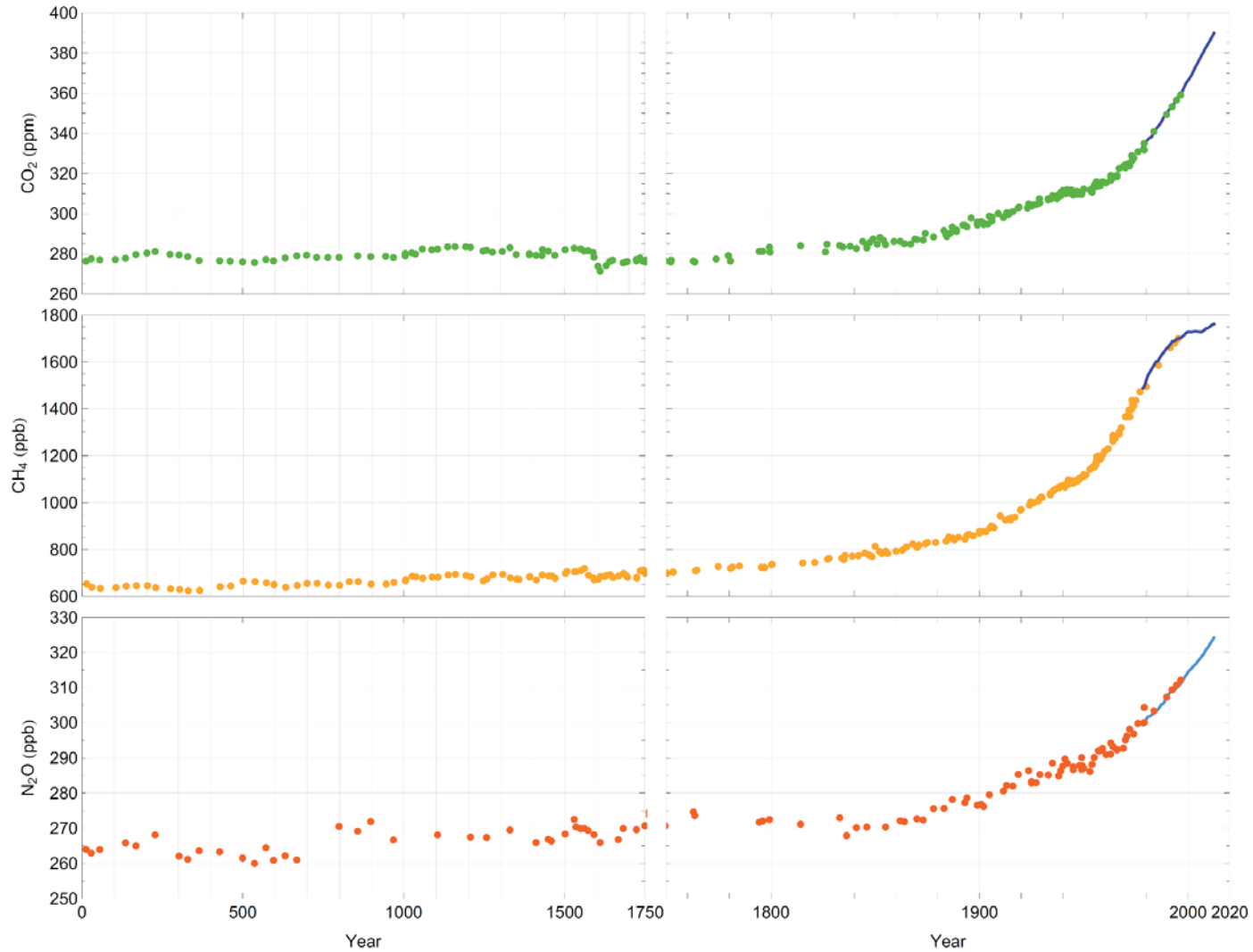
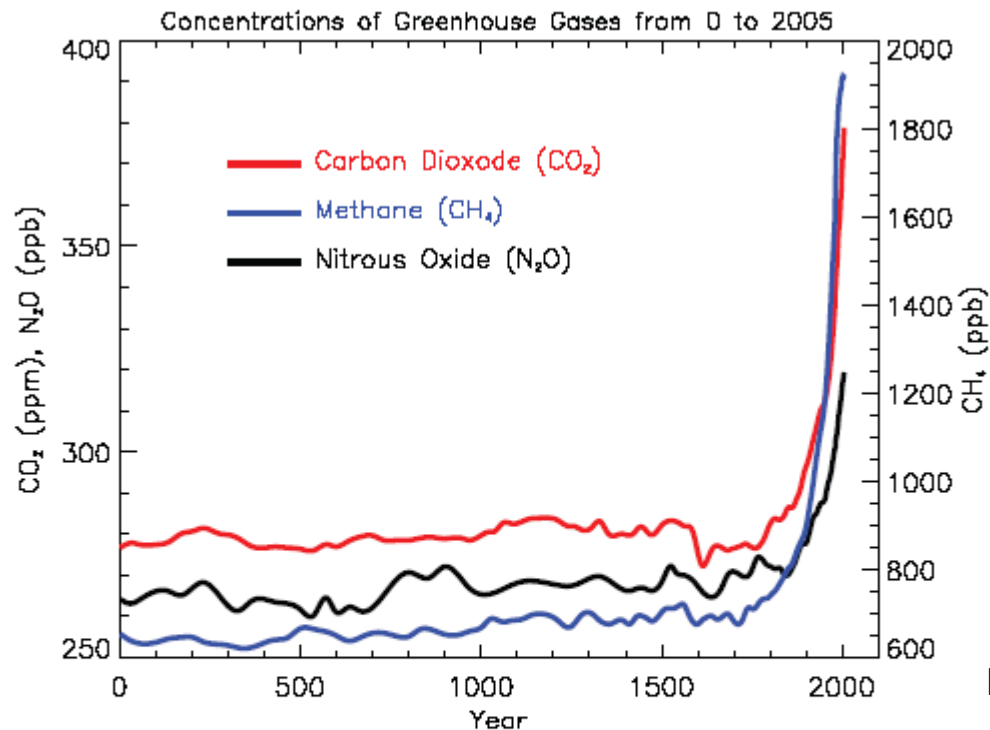


Figure 6.11 | Atmospheric CO₂, CH₄, and N₂O concentrations history over the industrial era (right) and from year 0 to the year 1750 (left), determined from air enclosed in ice cores and firn air (colour symbols) and from direct atmospheric measurements (blue lines, measurements from the Cape Grim observatory) (MacFarling-Meure et al., 2006).

CO₂, CH₄ & N₂O time series



IPCC 2007 FAQ

FAQ 2.1, Figure 1. Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion air molecules, respectively, in an atmospheric sample. (Data combined and simplified from Chapters 6 and 2 of this report.)

CO₂, CH₄ & N₂O time series

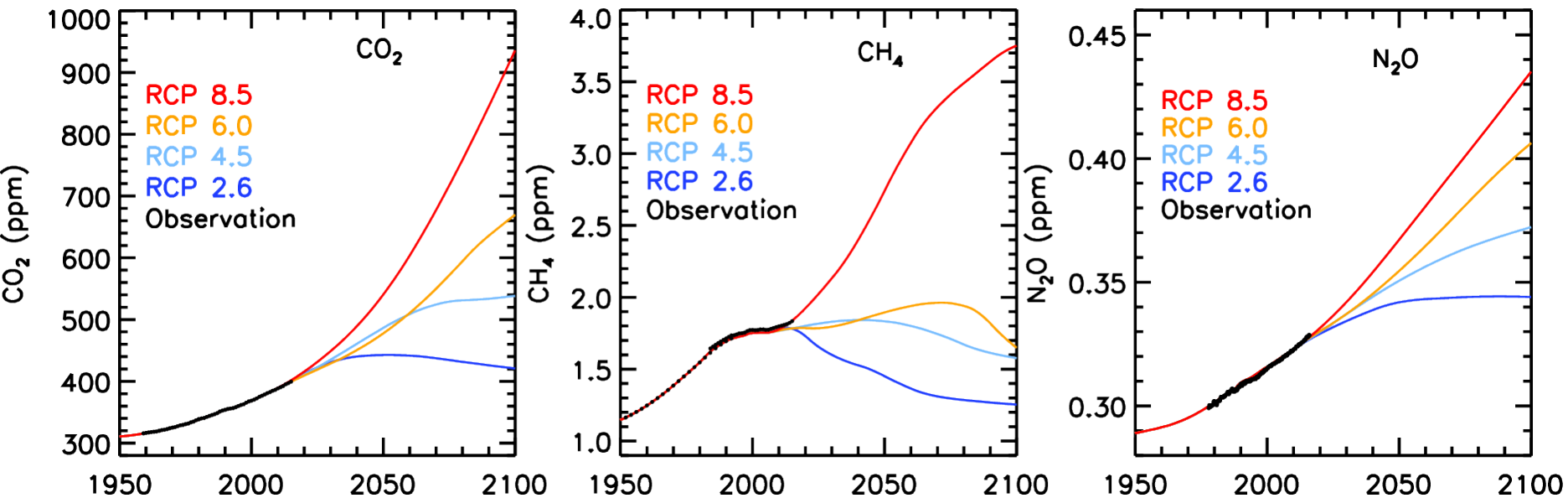


Figure 2-1, *Paris Beacon of Hope*

- RCP: Representative Concentration Pathway
Number represents RF of climate, units $W m^{-2}$, at the end of this century
- GHG mixing ratio time series for CO₂, CH₄, N₂O, as well as CFCs, HCFCs, and HFCs provided to all of the climate model groups

CO₂, CH₄, N₂O, & CFC-12

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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.

Chapter 3, Chemistry in Context

$$\text{GWP}(\text{CH}_4) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\text{CH}_4} \times [\text{CH}_4(t)] dt}{\int_{\text{time initial}}^{\text{time final}} a_{\text{CO}_2} \times [\text{CO}_2(t)] dt}$$

where:

a_{CH_4} = Radiative Efficiency (W m⁻² kg⁻¹) due to an increase in CH₄

a_{CO_2} = Radiative Efficiency (W m⁻² kg⁻¹) due to an increase in CO₂

CH₄(t) = time-dependent response to an instantaneous release of a pulse of CH₄

CO₂(t) = time-dependent response to an instantaneous release of a pulse of CO₂

CH₄ & N₂O

IPCC (2013) raises GWP of CH₄, lowers GWP of N₂O, and adds complexity of another GWP found upon consideration of Carbon Cycle Feedback

Table 8.7, IPCC (2013)

	Lifetime (years)		GWP ₂₀	GWP ₁₀₀
CH ₄	12.4	No cc fb	84	28
		With cc fb	86	34
N ₂ O	121.0	No cc fb	264	265
		With cc fb	268	298

cc fb ⇒ Carbon Cycle Feedback

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH₄) global warming potentials (GWP) relative to CO₂. {Table 2.14}

Industrial Designation or Common Name (years)	Chemical Formula	Lifetime (years)	Radiative Efficiency (W m ⁻² ppb ⁻¹)	Global Warming Potential for Given Time Horizon			
				SAR [‡] (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO ₂	See below ^a	^b 1.4x10 ⁻⁵	1	1	1	1
Methane ^c	CH ₄	12 ^c	3.7x10 ⁻⁴	21	72	25	7.6
Nitrous oxide	N ₂ O	114	3.03x10 ⁻³	310	289	298	153

IPCC (2007)

Global Warming Potentials of CH₄ & N₂O

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
<i>100 Year Time Horizon</i>				
CH ₄	21	23	25	28, 34*
N ₂ O	310	296	298	265, 298*
<i>20 Year Time Horizon</i>				
CH ₄	56	62	72	84, 86*
N ₂ O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

Table 1.1 *Paris, Beacon of Hope*

Page 42 of Houghton states “the enhanced greenhouse effect caused by a molecule of methane is about eight times that of a molecule of carbon dioxide”.

What, prey tell, is going on?

CO₂ – equivalent emissions:

$$\text{CO}_2^{\text{FF+LUC}}: 10.6 \text{ Gt C / year or } (44/12) \times 10.6 \text{ Gt CO}_2 / \text{year} = 39 \text{ Gt CO}_2 / \text{yr}$$

CH₄ versus time, past millennia

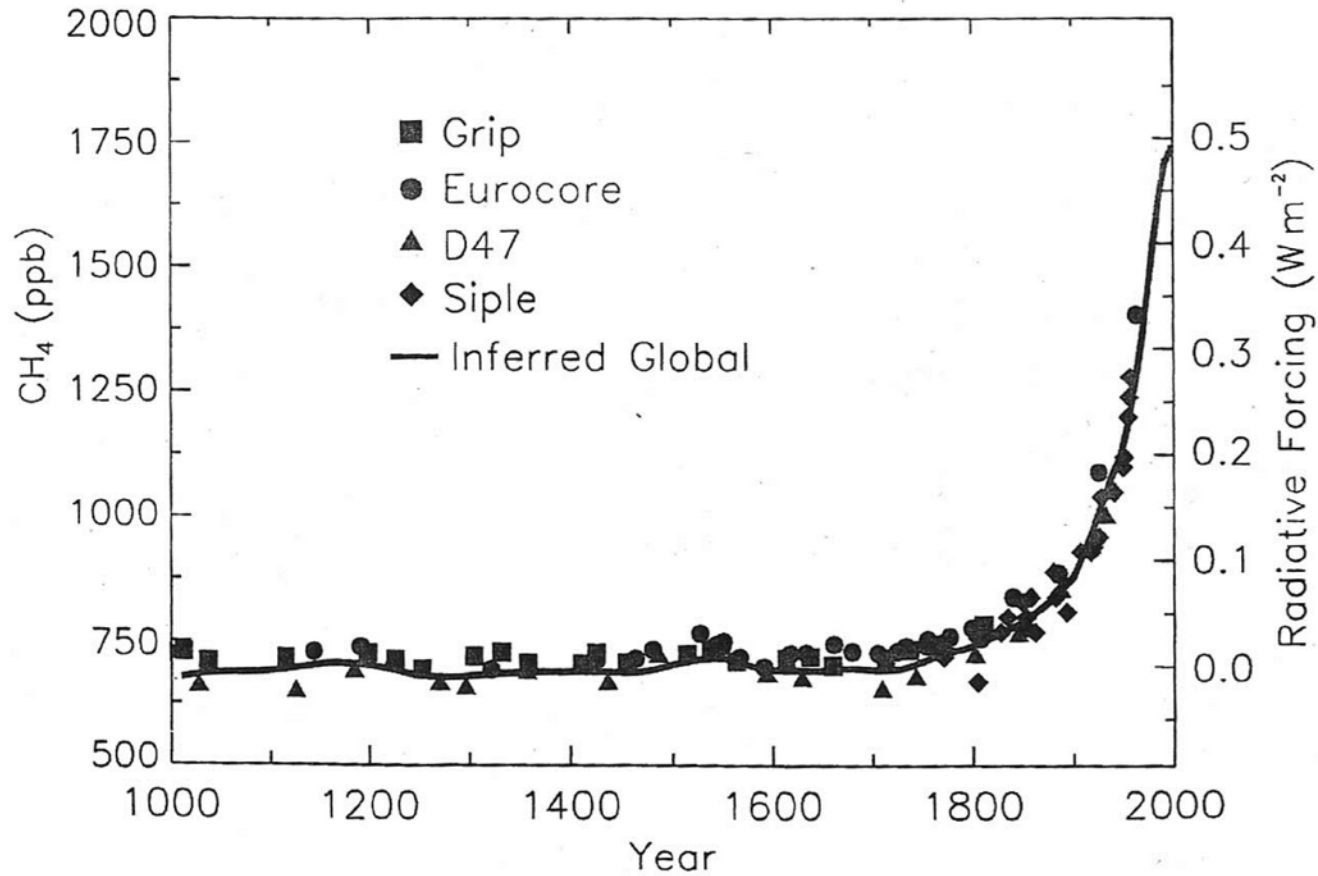


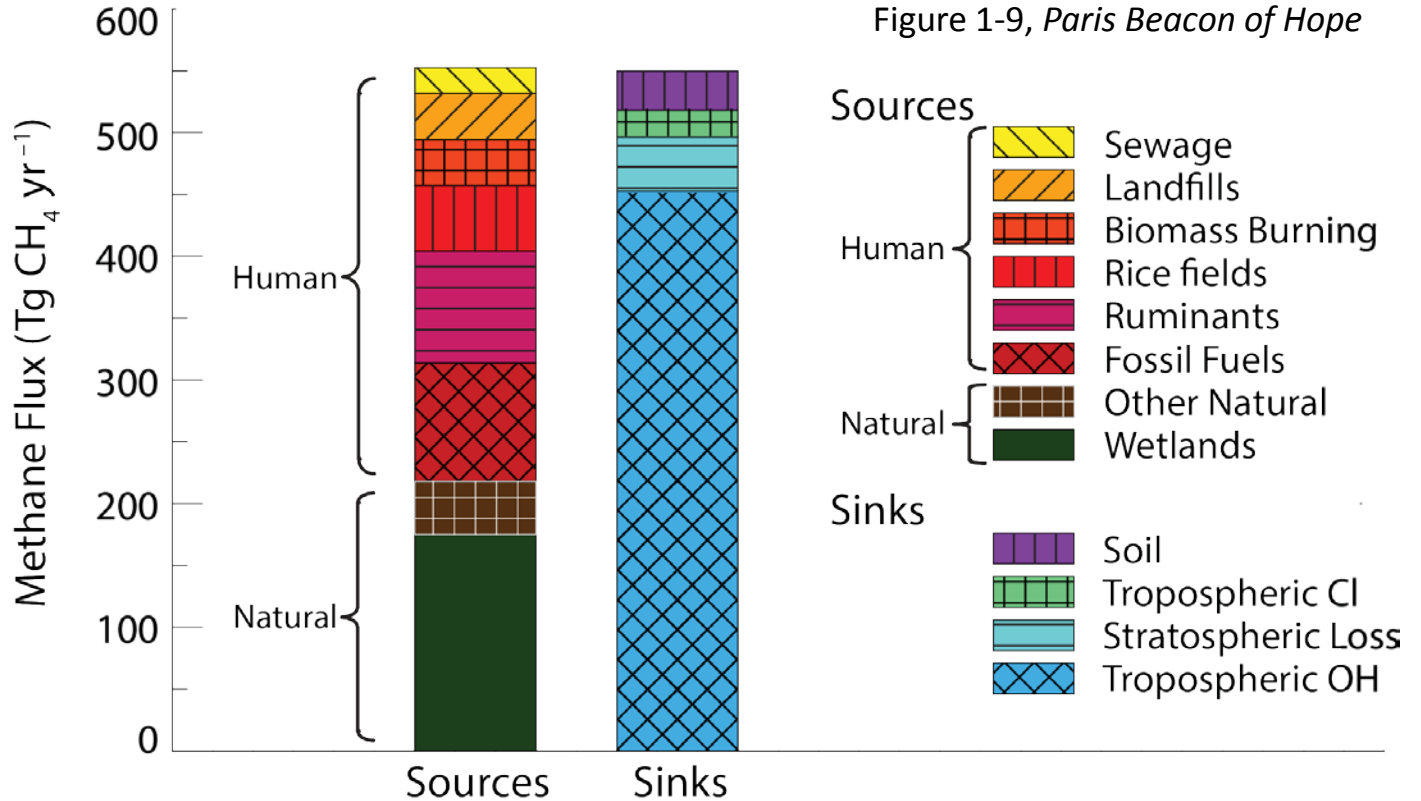
Fig 3.6, Houghton

What was the mixing ratio of CH₄ about 1000 years ago?

Source and Sinks of CH₄

Figure 1-9, Paris Beacon of Hope

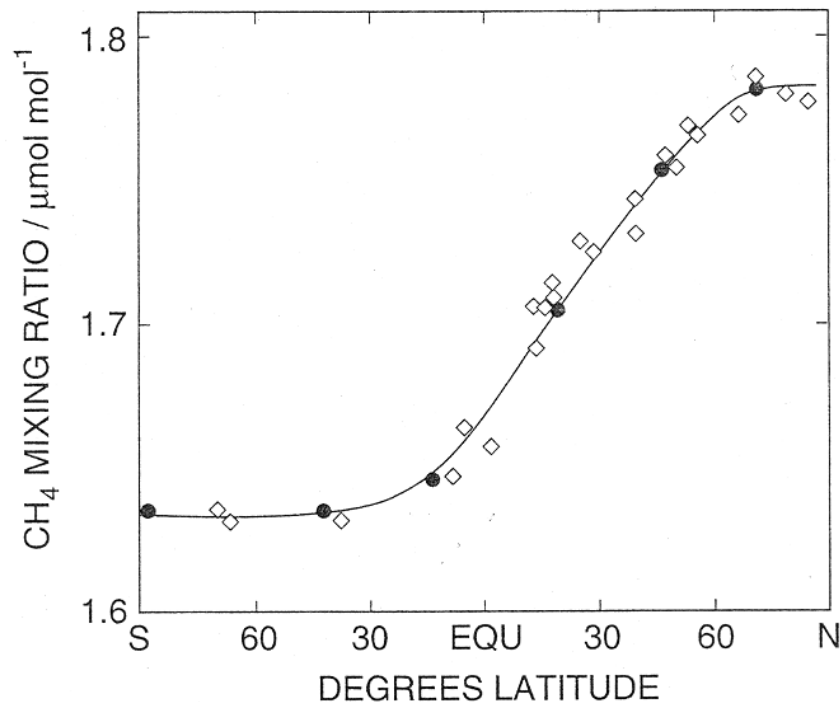
Human sources:
335 Tg per year
 Total, all sources:
 553 Tg per year
 Human ≈ 60% of total



Global Methane Budget, 2000 to 2009



Latitudinal Distribution of CH₄



Warneck, Chemistry of the Natural Atmosphere, 2000

FIGURE 4.4 Latitudinal distribution of methane in the troposphere in 1988. Solid points indicate stations at Point Barrow, Alaska; Cape Meares, Oregon; Mauna Loa, Hawaii; Cape Matatula, Samoa; Cape Grim, Tasmania; and the South Pole. The open points are from the National Oceanic and Atmospheric Administration flask sampling program at various marine background locations. (Adapted from Khalil *et al.* (1993a).)

A nice animation of CH₄ vs latitude, as time evolves, is at http://www.esrl.noaa.gov/gmd/ccgg/globalview/ch4/ch4_intro.html

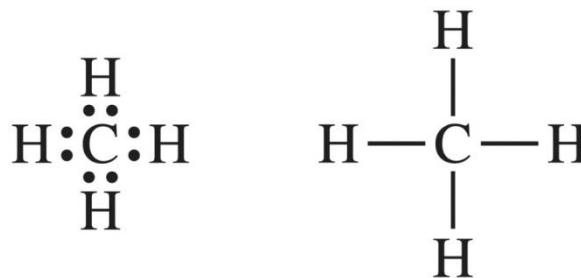
CH₄ is the most reduced form of carbon

Decreasing oxidation number (reduction reactions)

-4	0	+2	+4
CH₄ Methane	CH₂O Formaldehyde	CO Carbon Monoxide	CO₂ Carbon dioxide

Increasing oxidation number (oxidation reactions)

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

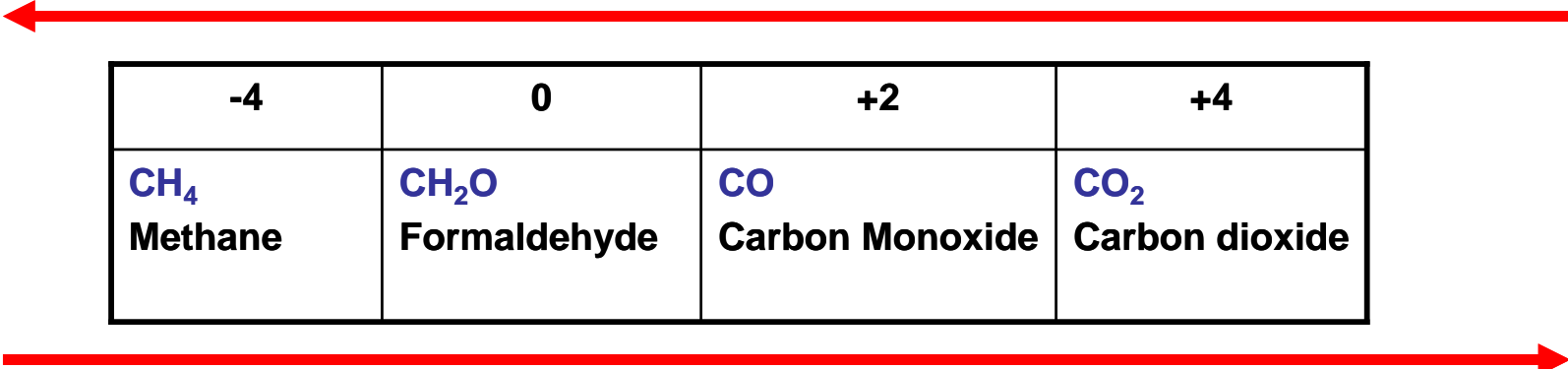


C in CH₄: has received an electron from each H atom.

All electrons are paired and hence this compound
is relatively stable

CH₄ is the most reduced form of carbon

Decreasing oxidation number (reduction reactions)



-4	0	+2	+4
CH₄ Methane	CH₂O Formaldehyde	CO Carbon Monoxide	CO₂ 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 CO₂: has donated two electrons to each oxygen atom,
completing the L shell of electrons & resulting
in an electron configuration analogous to helium

Biological Production of CH₄

CH₄ produced by “methanogenic” bacteria:

- grow only in low O₂ environments
- fermentation of cellulose and other organic material
- swamps, marshes, rice paddy fields
- rumina of cows and sheep.

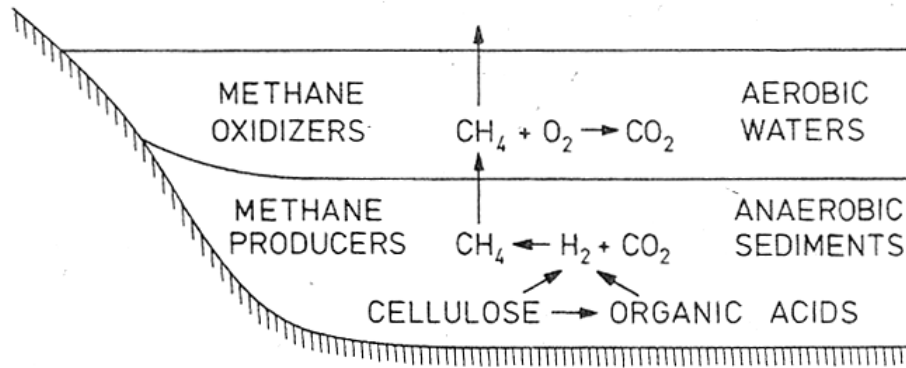
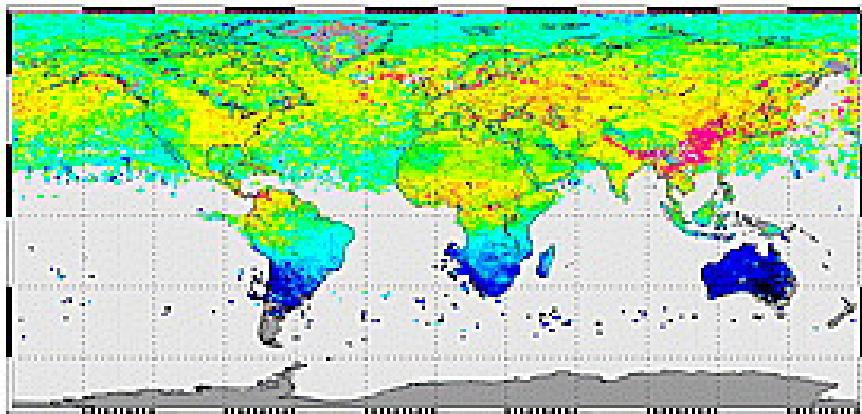


FIGURE 4.6 Production and consumption of methane at the bottom of a lake. (Adapted from Schlegel (1974).)

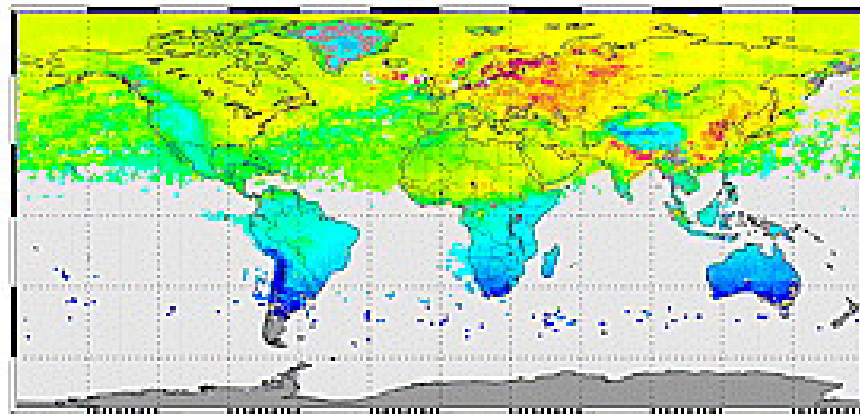
Warneck, Chemistry of the Natural Atmosphere, 2000

Biological Production of CH₄

(C) MAM SCIAMACHY



(D) MAM TM4



MAM: March, April, & May

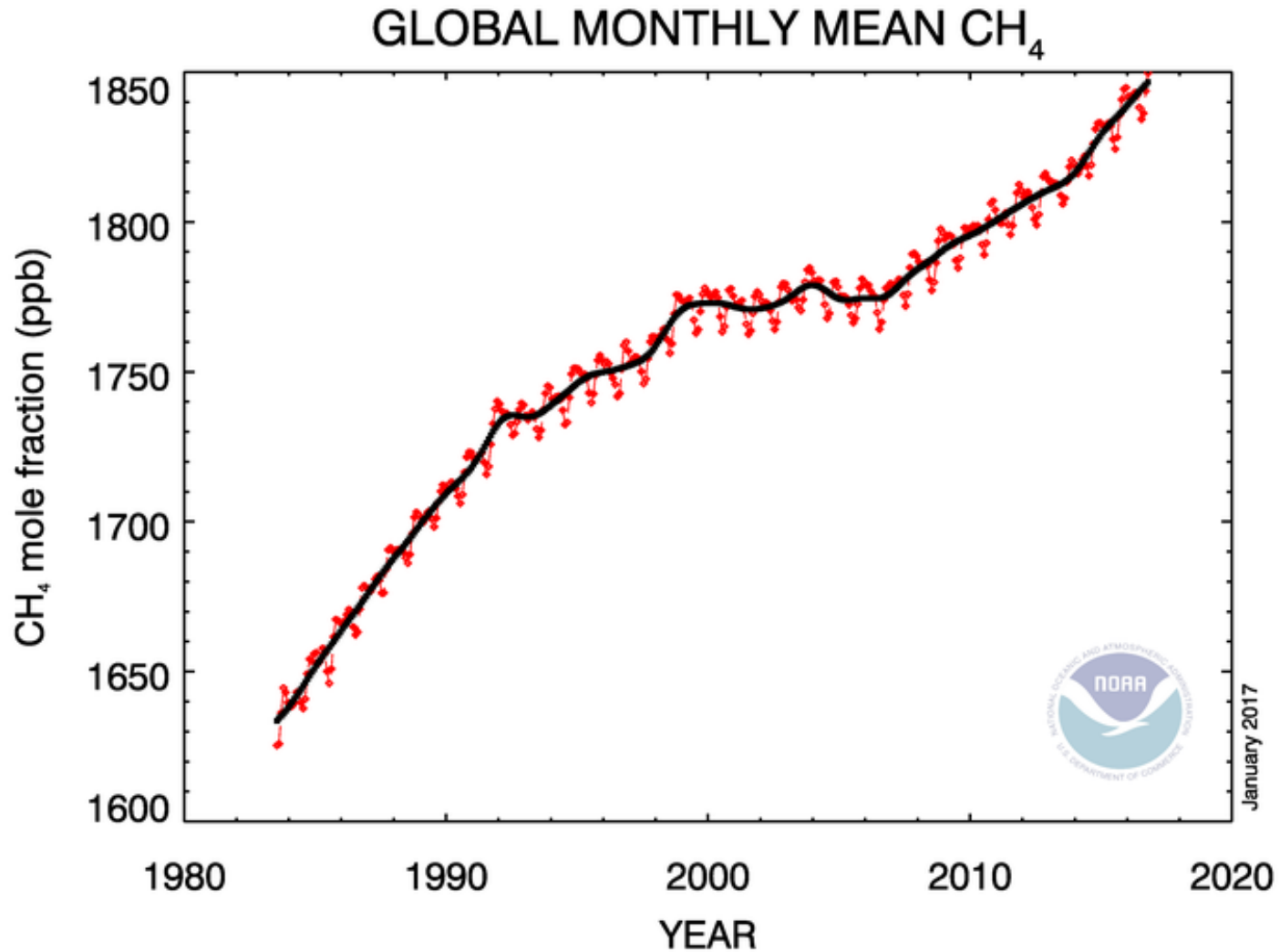
SCIAMACHY: SCanning Imaging Absorption spectroMeter for Atmospheric CHartography
European satellite instrument, operated from March 2002 to April 2012.

TM4: Global chemistry–transport model driven by observed winds, precipitation, and EDGAR version 3.2 emissions inventory

The most pronounced feature we observe is due to the temporal variation of methane emissions from rice paddies in Southeast Asia with typical maxima from August through October, resulting in higher VMRs in the periods June–August and September–November ... In Africa, the highest methane abundances are situated towards the south in Dec/Jan/Feb, while they are strongest and situated further northward in Sep/Oct/Nov. This, on the whole, corresponds well to the temporal evolution and spatial distribution of wetland emissions

Frankenberg *et al.*, *JGR*, 2006

Atmospheric Time Series of CH₄ – Recent Data



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

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

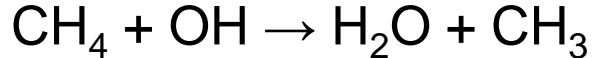
CH₄ Lifetime

Chemistry in Context (Table 3.2) and Houghton (page 44) give 12 years for the lifetime of CH₄

What is the removal process for CH₄?

How is the lifetime found?

CH₄ is lost by reaction with OH



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

Arrhenius Expression for rate constant:

$$k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1}$$

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

Commonly T = 272 K and **[OH] = 1 × 10⁶ molec cm⁻³** are used (see Box 1-3 of

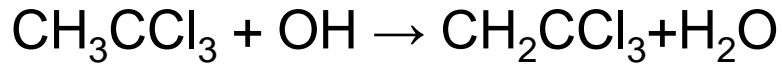
http://www.unep.ch/ozone/Assessment_Panels/SAP/Scientific_Assessment_2010/03-Chapter_1.pdf)

yielding :

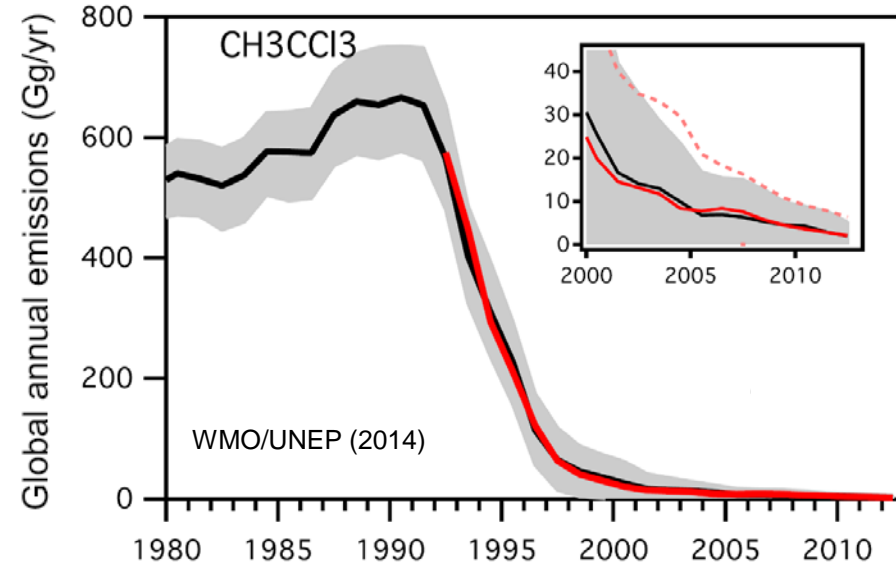
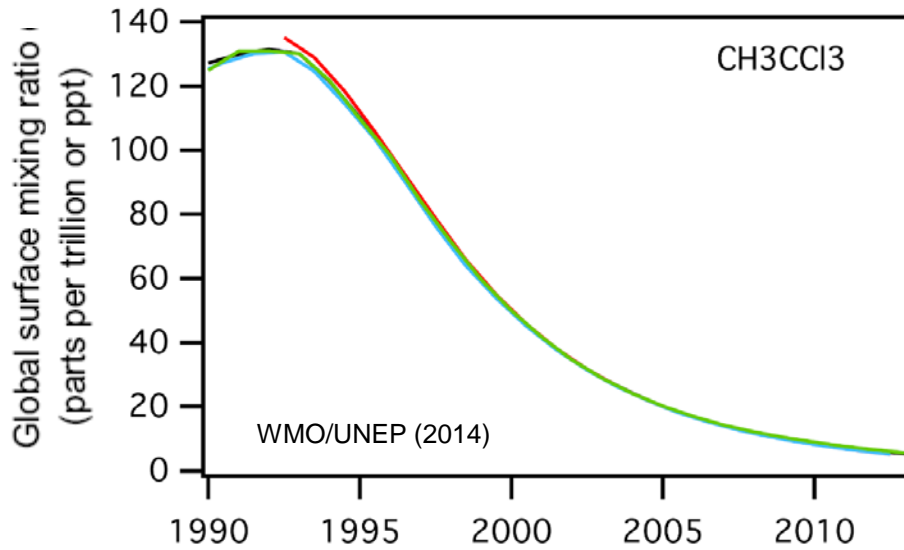
Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP) ^c
Halogen source gases		
<i>Chlorine gases</i>		
CFC-11	45	1
CFC-12	100	0.82
CFC-113	85	0.85
Carbon tetrachloride (CCl ₄)	26	0.82
HCFCs	1–17	0.01–0.12
Methyl chloroform (CH ₃ CCl ₃)	5	0.16
Methyl chloride (CH ₃ Cl)	1	0.02
<i>Bromine gases</i>		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH ₃ Br)	0.8	0.66
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

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



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



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

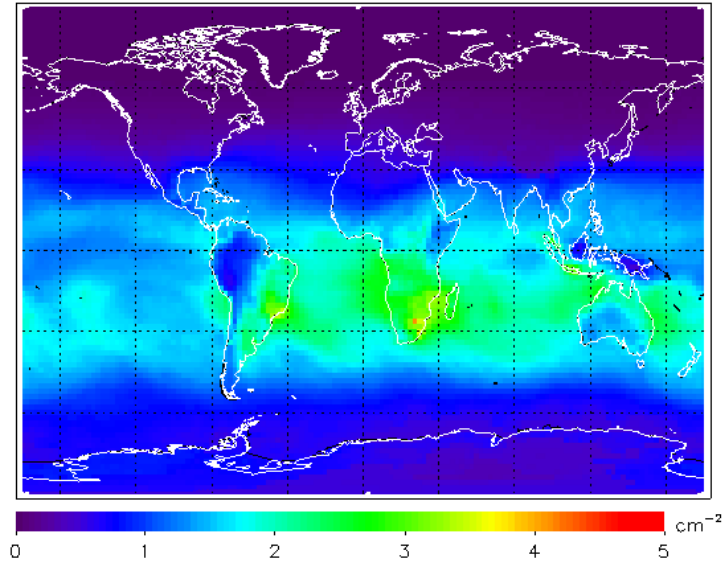
So Why Do Both Readings Give a Lifetime for CH₄ of 12 Years?

The feedback of CH₄ on tropospheric OH and its own lifetime is re-evaluated with contemporary CTMs as part of OxComp, and results are summarised in [Table 4.3](#). The calculated OH feedback, $\partial \ln(\text{OH}) / \partial \ln(\text{CH}_4)$, is consistent between the models, indicating that tropospheric OH abundances decline by 0.32% for every 1% increase in CH₄. The TAR value for the sensitivity coefficient $s = \partial \ln(\text{LT}) / \partial \ln(\text{CH}_4)$ is then 0.28 and the ratio PT/LT is 1.4. This 40% increase in the integrated effect of a CH₄ perturbation does not appear as a 40% larger amplitude in the perturbation but rather as a lengthening of the duration of the perturbation to 12 years. This feedback is difficult to observe, since it would require knowledge of the increase in CH₄ sources plus other factors affecting OH over the past two decades. Unlike for the global mean tropospheric OH abundance, there is also no synthetic compound that can calibrate this feedback; but it is possible that an analysis of the budgets of ¹³CH₄ and ¹²CH₄ separately may lead to an observational constraint (Manning, 1999).

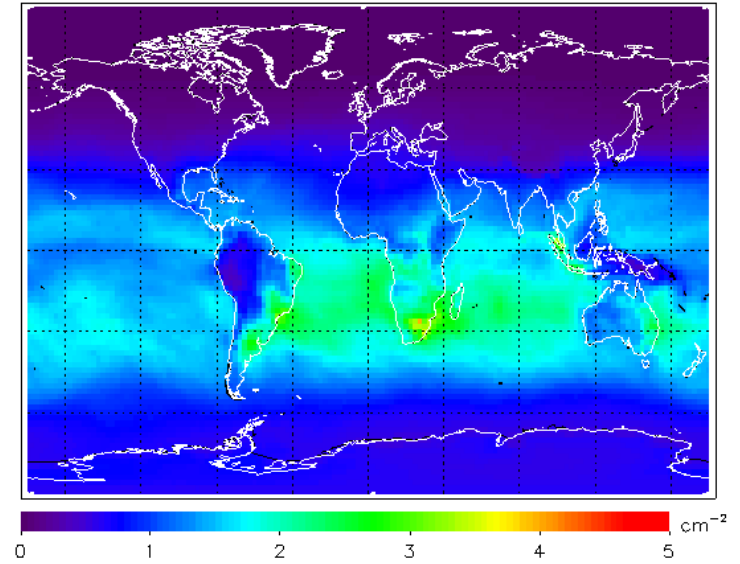
http://www.grida.no/publications/other/ipcc%5Ftar/?src=/climate/ipcc_tar/wg1/134.htm

Distribution of tropospheric OH in Global Models – Recent Paper

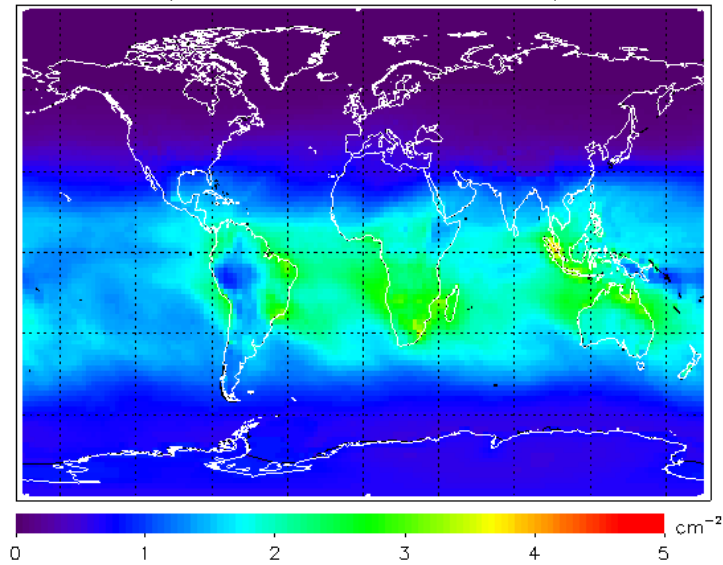
Monthly Trop OH Column, GEOSCHEM, 01/2008



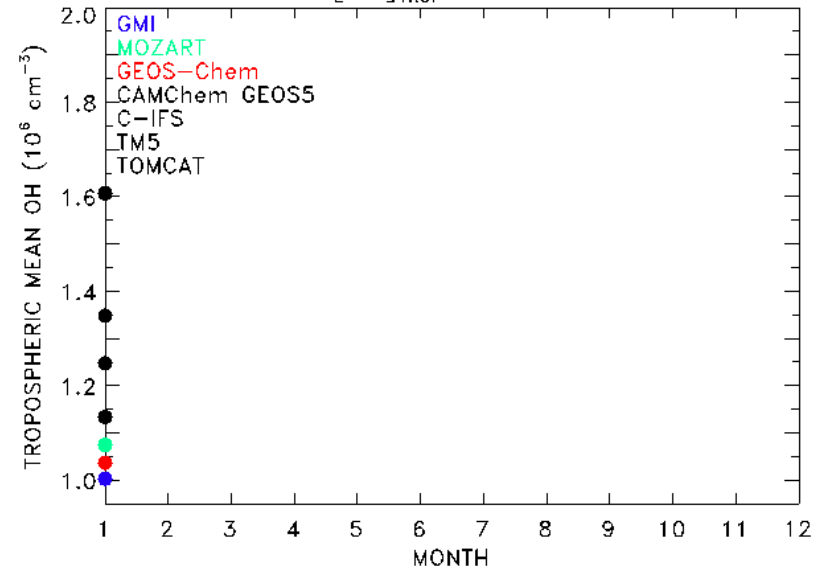
Monthly Trop OH Column, GMI, 01/2008



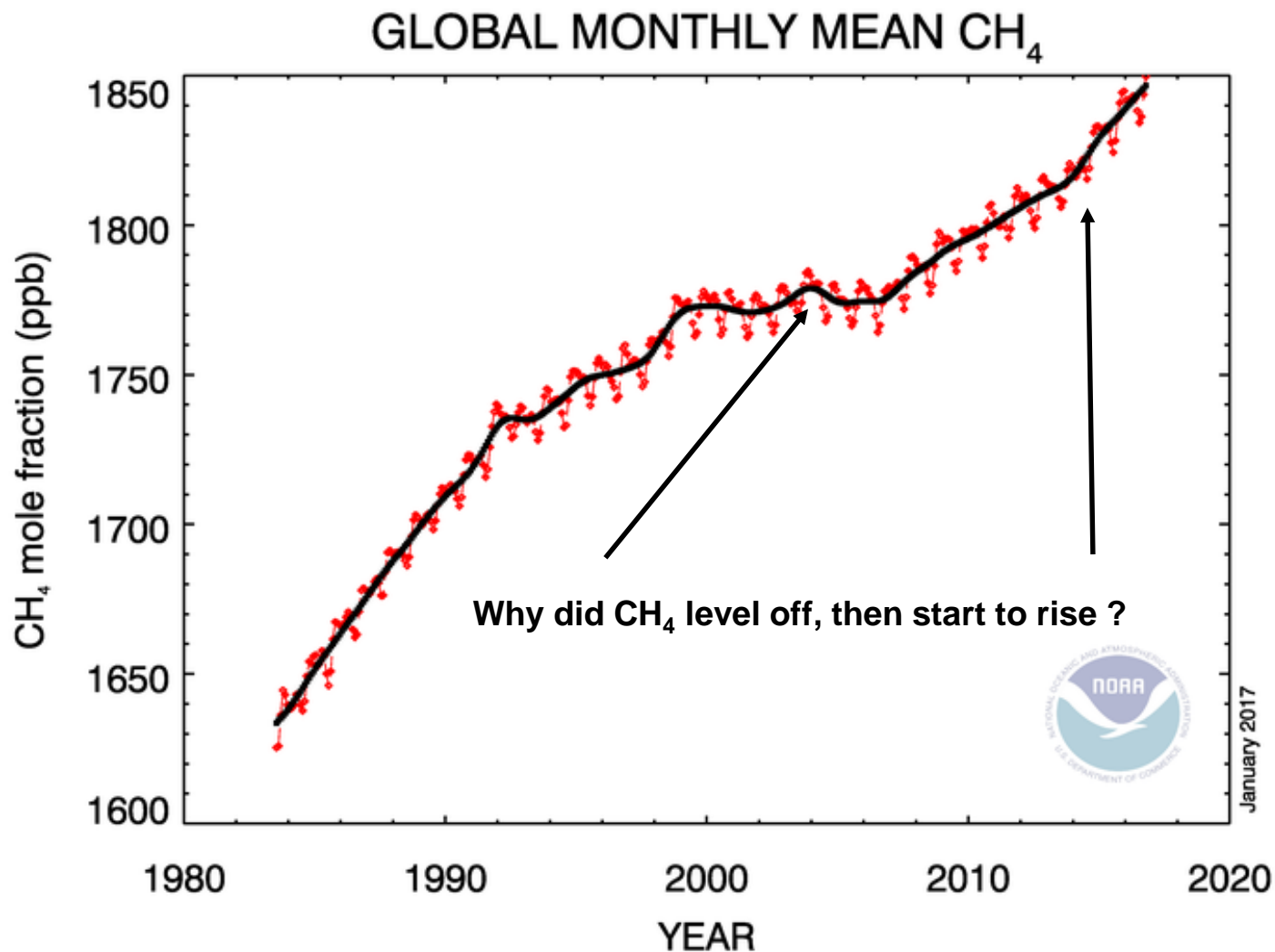
Monthly Trop OH Column, MOZART, 01/2008



$[\text{OH}]_{\text{TROP}}$, POLMIP



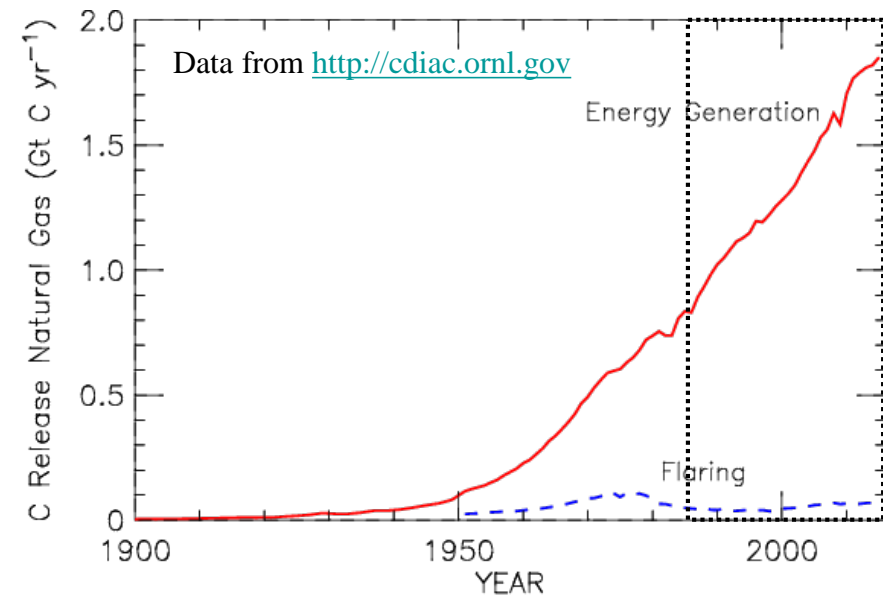
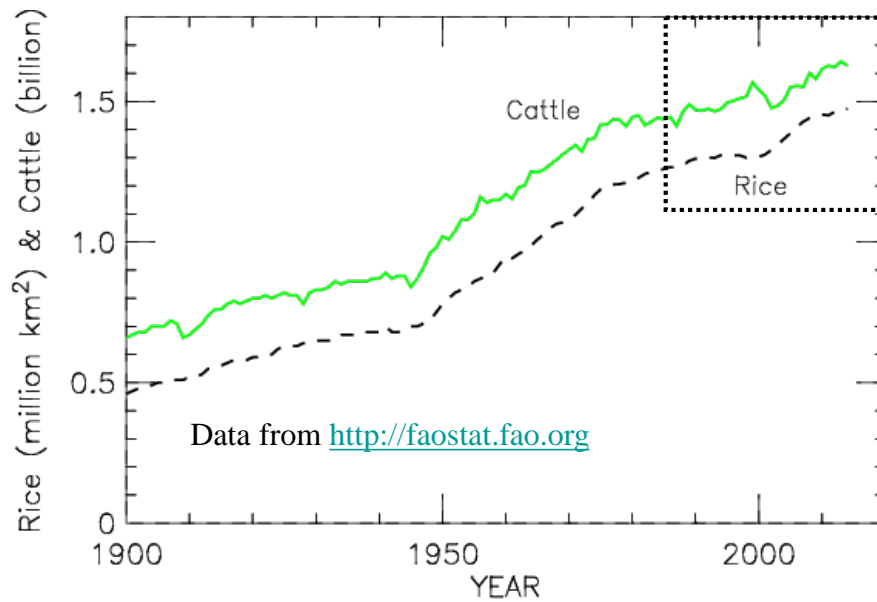
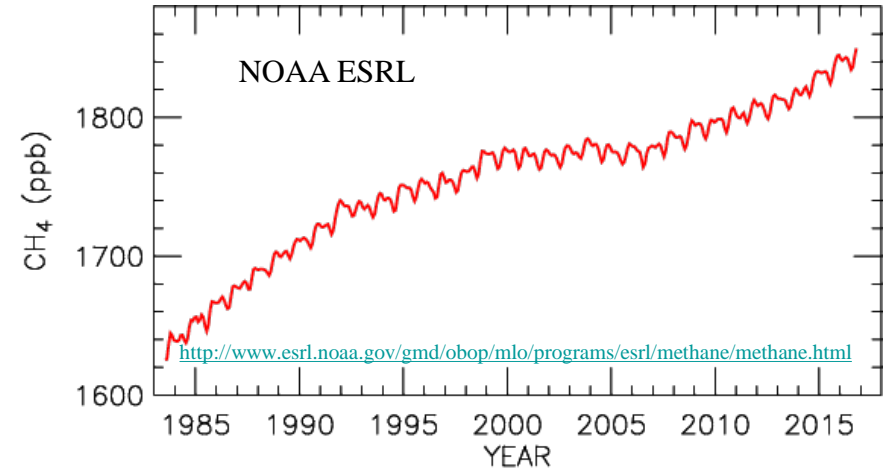
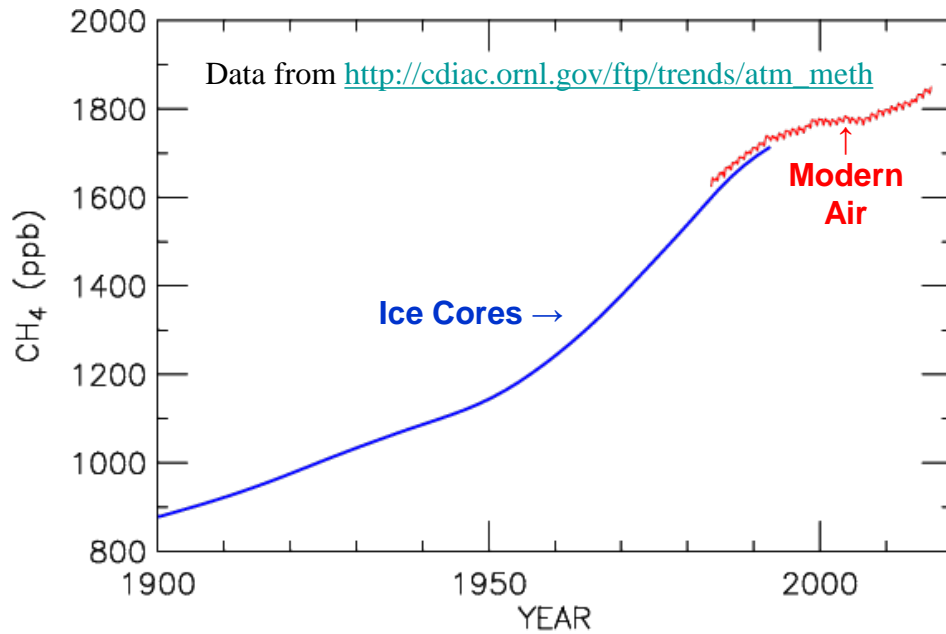
Atmospheric Time Series of CH₄ – Recent Data



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



Recent trends in CH₄

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

- Turner et al., GRL, 2016:

The global burden of atmospheric methane has been increasing over the past decade, but the causes are not well understood. National inventory estimates from the U.S. Environmental Protection Agency indicate no significant trend in U.S. anthropogenic methane emissions from 2002 to present. Here we use satellite retrievals and surface observations of atmospheric methane to suggest that U.S. methane emissions have increased by more than 30% over the 2002–2014 period. The trend is largest in the central part of the country, but we cannot readily attribute it to any specific source type. **This large increase in U.S. methane emissions could account for 30–60% of the global growth of atmospheric methane seen in the past decade.**

- 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.

Thermogenic:

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

Recent trends in CH₄

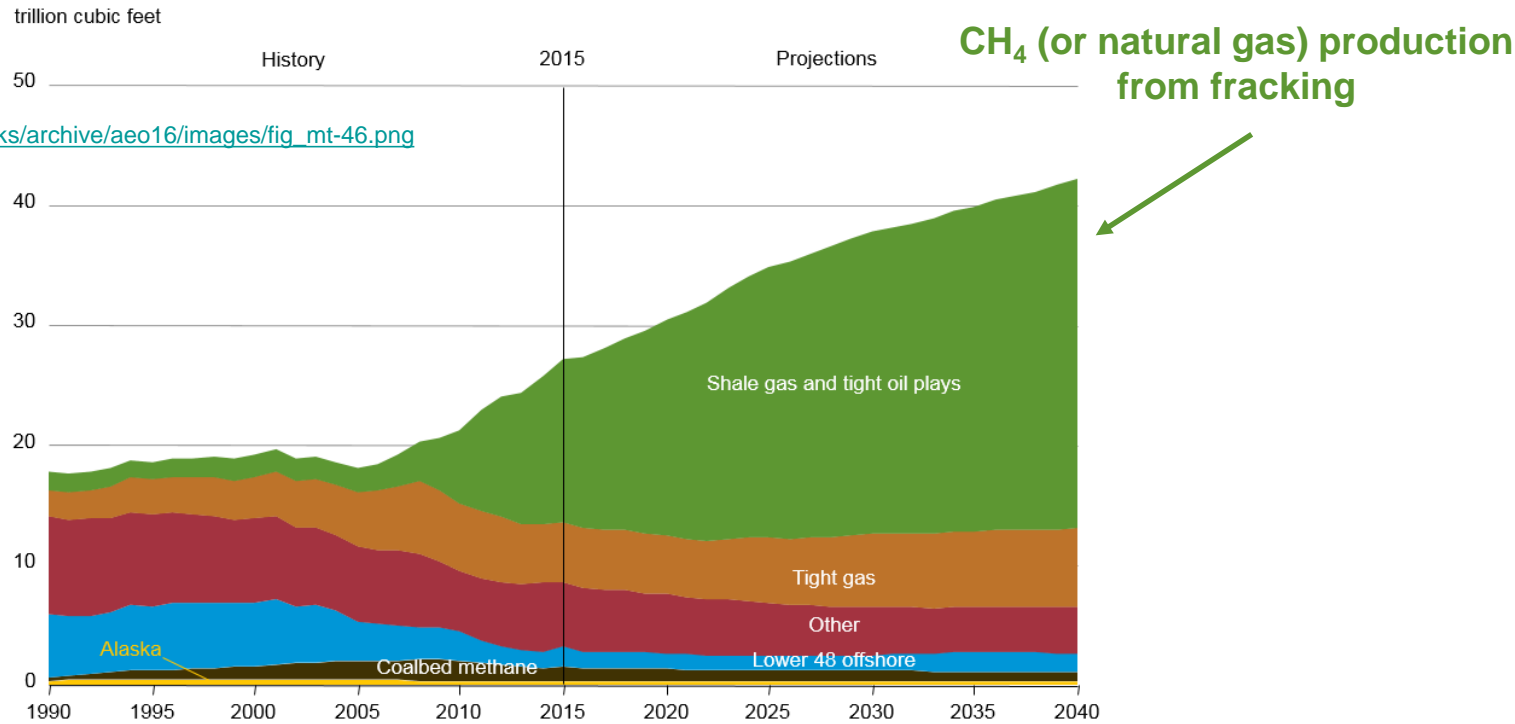
These papers offer conflicting views on the cause of the recent rise in CH₄

- 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.**

Fracking

Figure MT-46. U.S. dry natural gas production by source in the Reference case, 1990–2040

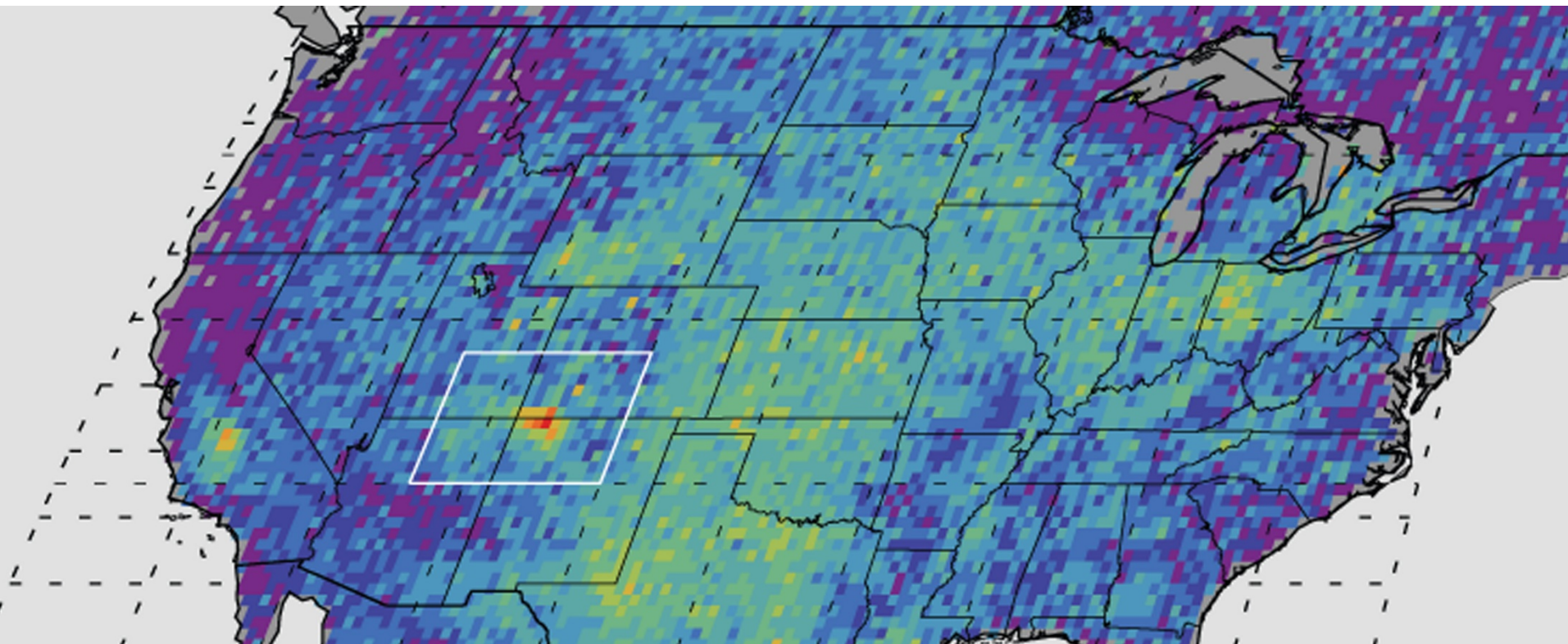


Airborne measurements by Karion *et al.* *GRL* 2013 over Utah indicate fugitive CH₄ emission is ~9 % of average hourly CH₄ production

Surface measurements at 190 onshore natural gas sites by Allen *et al.* *PNAS* 2013 show fugitive CH₄ emission is ~0.42 % of gross CH₄ production

Break even point for “climate” is leakage of 2.3% for 20-yr time horizon
and 6.9% for 100-yr time horizon
(footnote #35, Chapter 4, *Paris Beacon of Hope*)

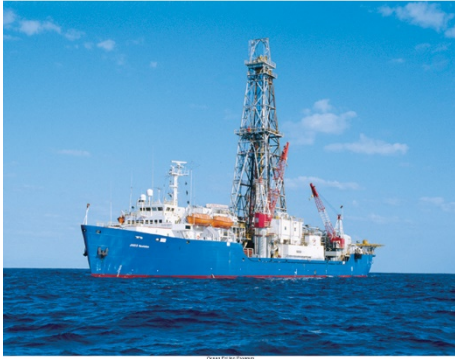
Four Corners



- **Box shows major hot spot for CH₄ emissions, 2003 to 2009 from SCIAMACHY**
- **Likely source is leakage from CH₄ extracted from coal**
- **About 10% of the total US CH₄ emissions estimated by EPA inventory, that does not consider this source**

Kort et al., GRL, 2014.

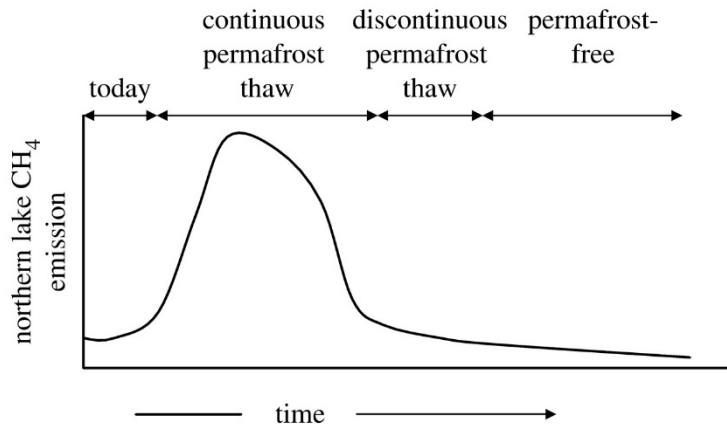
CH₄ Hydrates and Permafrost



Methane is also released from the oceans, where a substantial amount of it appears to be trapped in cages made of water molecules. Such deposits are known as methane hydrates. Australia's CSIRO has been taking a series of ocean core measurements to gather evidence about methane hydrates and their role in global warming.

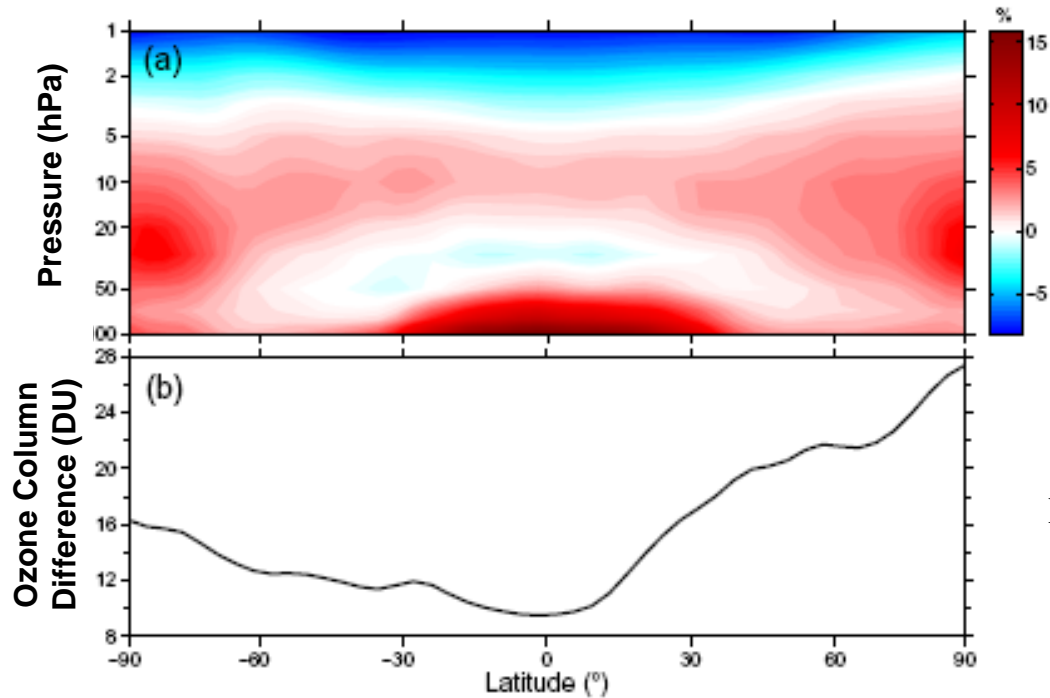
Chapter 3, *Chemistry in Context*

There is concern that melting of the surface in the Northern latitudes might trigger a massive release of methane into the atmosphere ... there is geological evidence that such a release has occurred in the past, and led to higher global temperatures.



Schematic depicting future of CH₄ emissions from northern lakes, as the north changes from a permafrost-rich landscape to a landscape free of surface permafrost.

CH₄ and Stratospheric Ozone



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

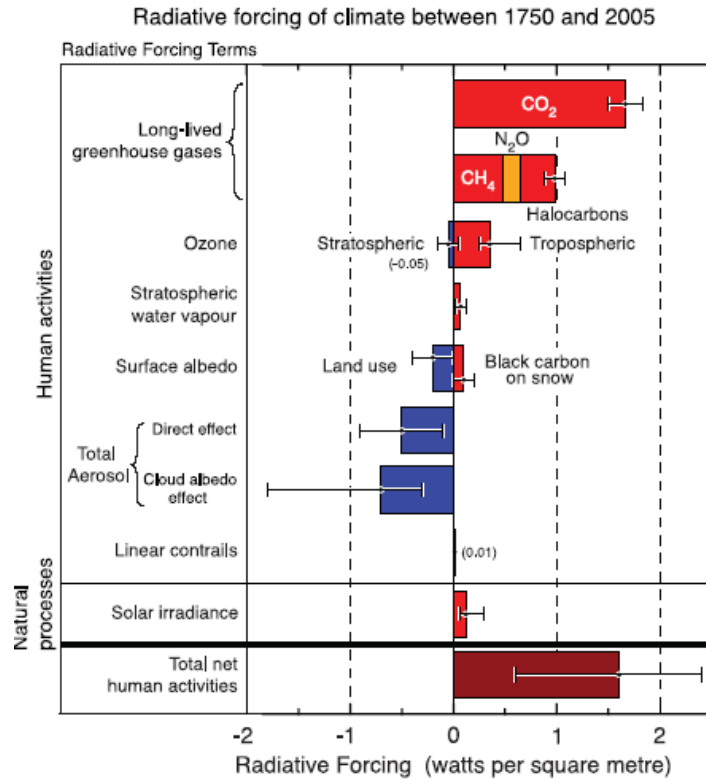
Stratospheric O₃ difference in the 2090s found for a computer simulation run using CH₄ from RCP 8.5 minus that of a simulation using CH₄ from RCP 2.6

Rising CH₄ leads to:

- a) ozone loss in the upper stratosphere by increasing the speed of OH and HO₂ (HO_x) mediated loss cycles.
- b) a cooler stratosphere, slowing the rate of all ozone loss cycles.
- c) speeds up the rate of Cl+CH₄, shifting chlorine from ClO into HCl
- d) more HO₂ in the lowermost stratosphere where there is sufficient CO to result in O₃ production by smog chemistry

Computer models project stratospheric column O₃ will increase as CH₄ rises

Nitrous Oxide: N₂O



FAQ 2.1, Figure 2. Summary of the principal components of the radiative forcing of climate change. All these

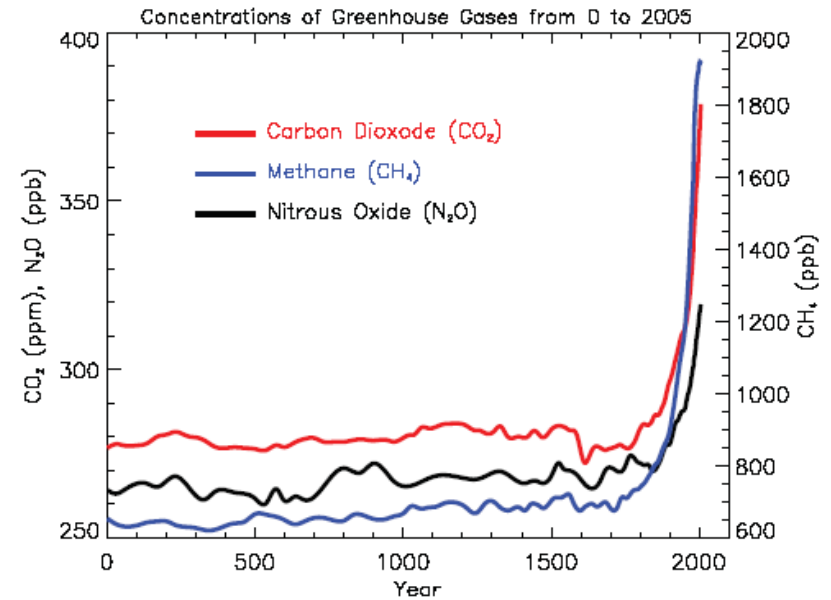
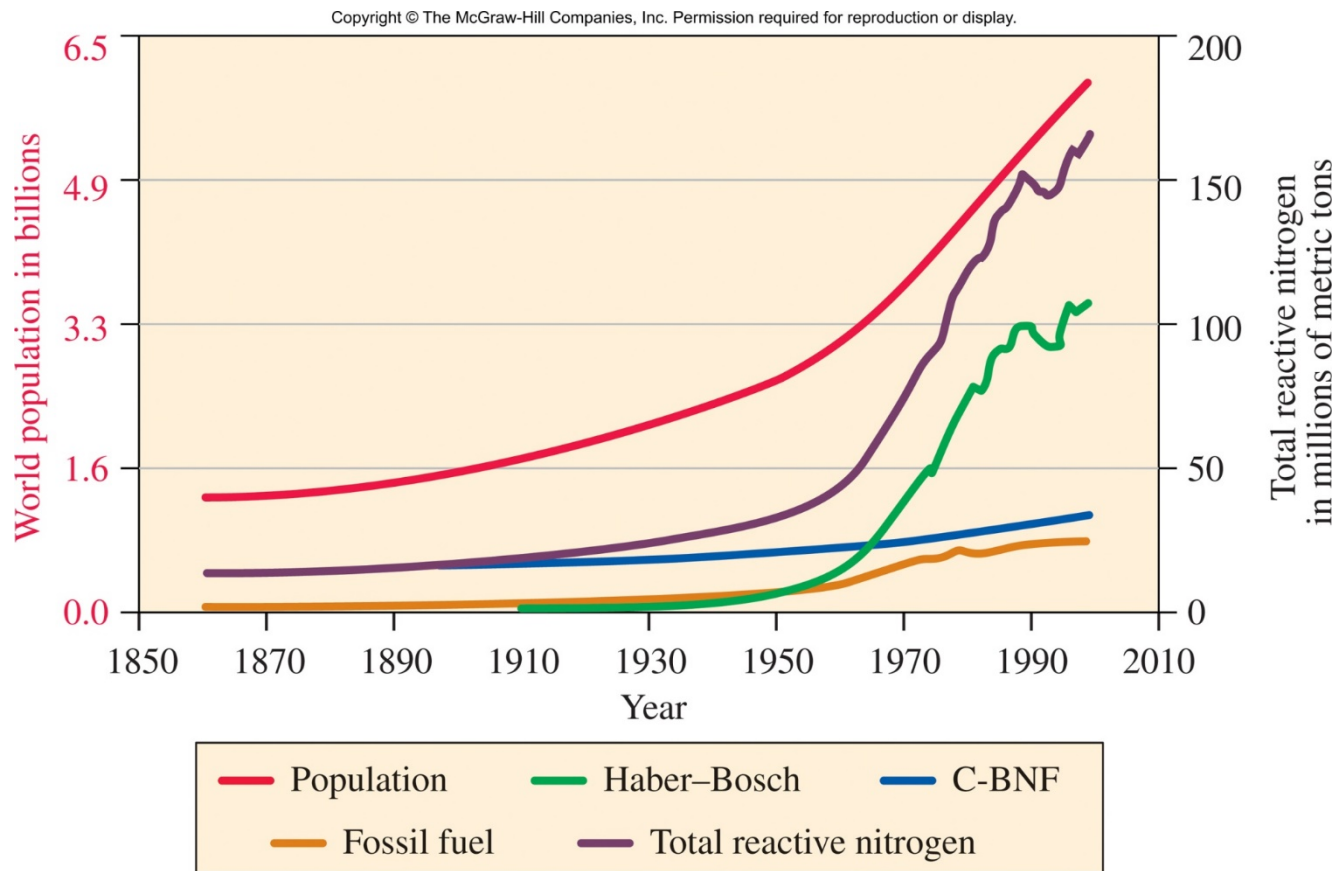


Table 3.2 Examples of Greenhouse Gases					
Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

N₂O Lifetime ≈ 120 yrs

The Nitrogen Cycle

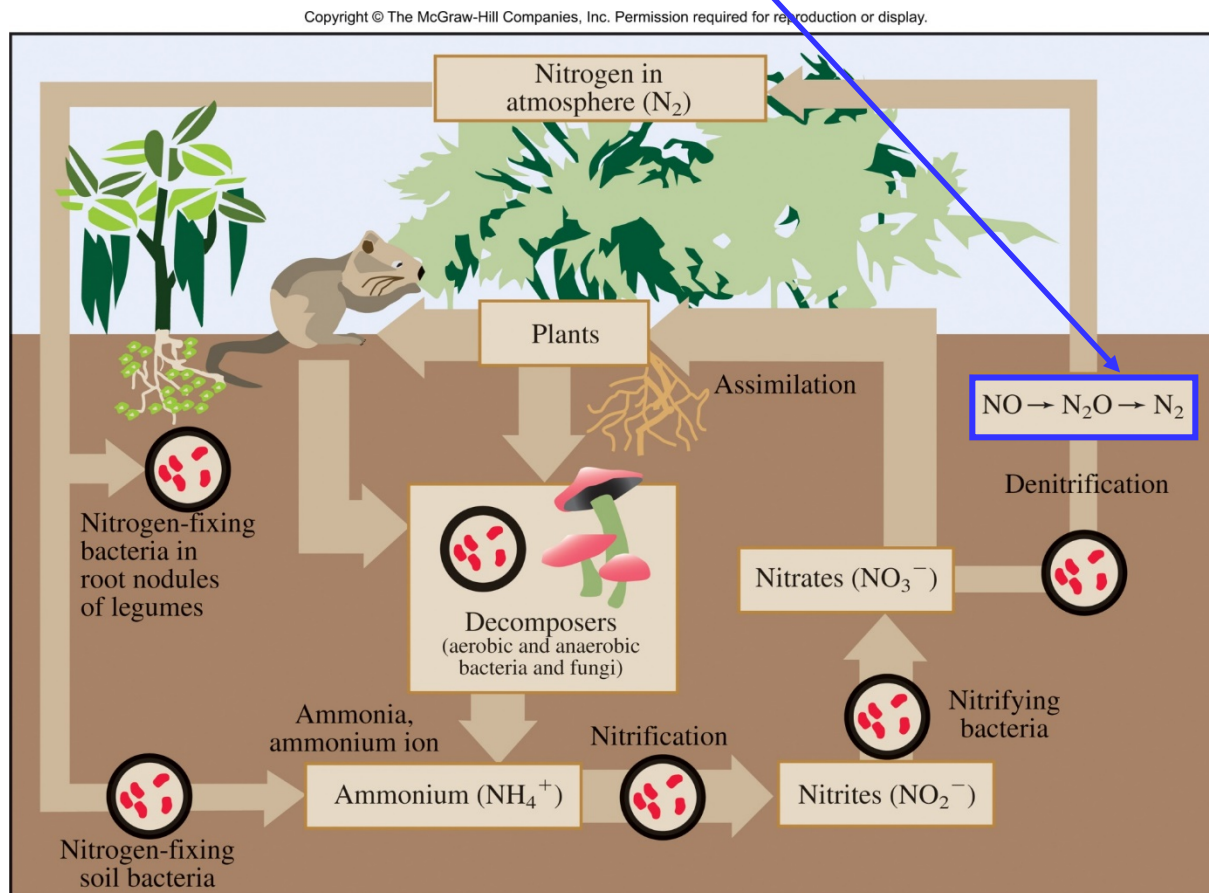
Haber-Bosch: $\text{N}_2(\text{gas}) + 3 \text{H}_2(\text{gas}) \rightarrow 2 \text{NH}_3(\text{gas})$
Led to large scale, economical production of ammonia based fertilizer



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*

Decreasing oxidation number (reduction reactions)

-3	0	+1	+2	+3	+4	+5
NH₃ Ammonia	N₂	N₂O Nitrous oxide	NO Nitric oxide	HONO Nitrous acid NO₂⁻ Nitrite	NO₂ Nitrogen dioxide	HNO₃ Nitric acid NO₃⁻ Nitrate

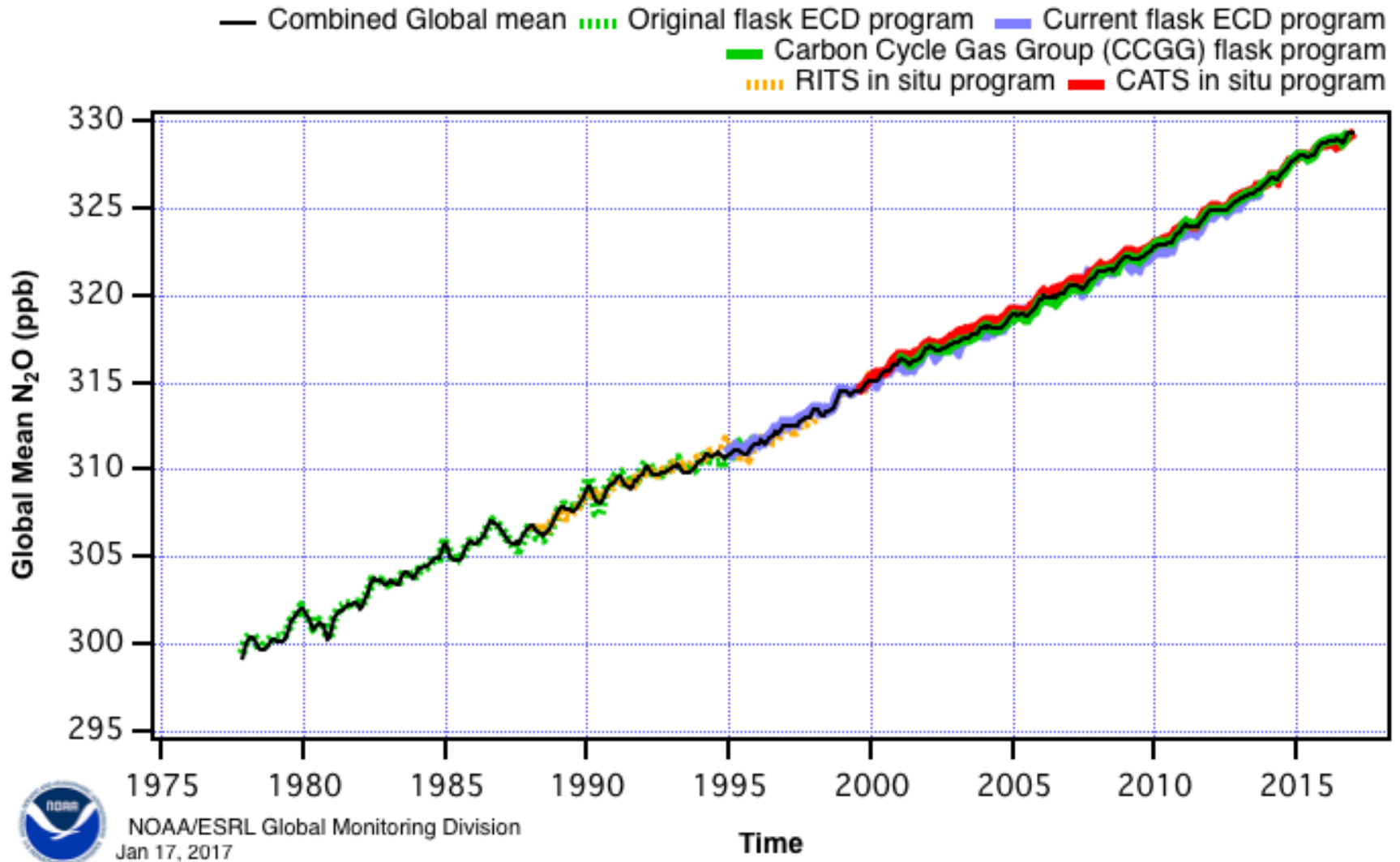
Increasing oxidation number (oxidation reactions)

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



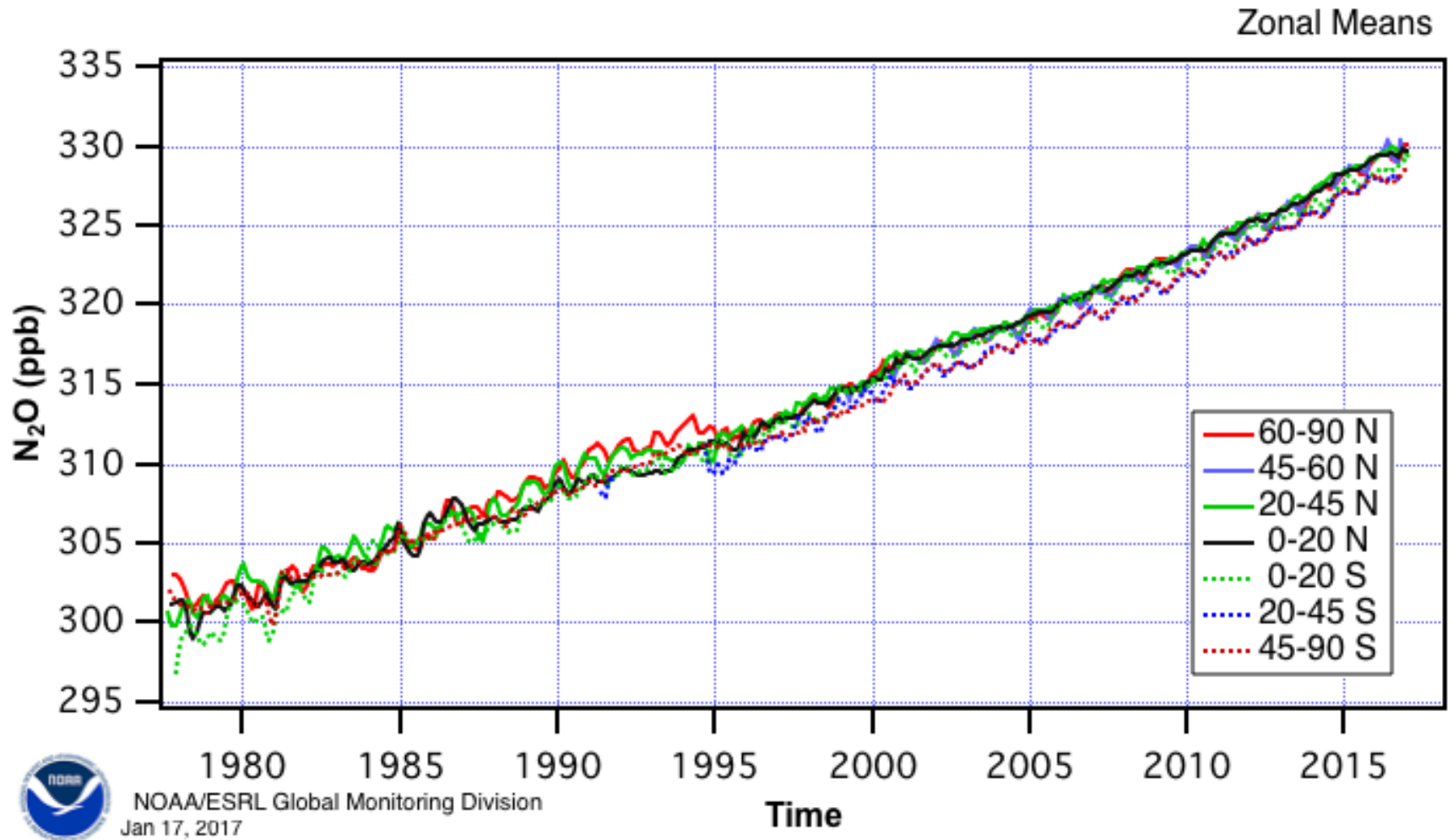
See http://guweb2.gonzaga.edu/faculty/cronk/chemistry/L00-index.cfm?L00resource=Lewis_structures
for Lewis Dot Structure of N₂O ... please note we will not ask questions
about Lewis Dot Structures on exams !

N₂O Time Series



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

N₂O Time Series



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

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

Sources and Sinks of N₂O

Table 6.9 Notes:

a All units for N₂O 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(¹D) 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, N₂O budget reduced based on recently published longer lifetimes of 131±10 yrs, see Annex II.2.3 and II.4.3.

CO₂ – equivalent emissions of N₂O

CO₂ – equivalent emissions:

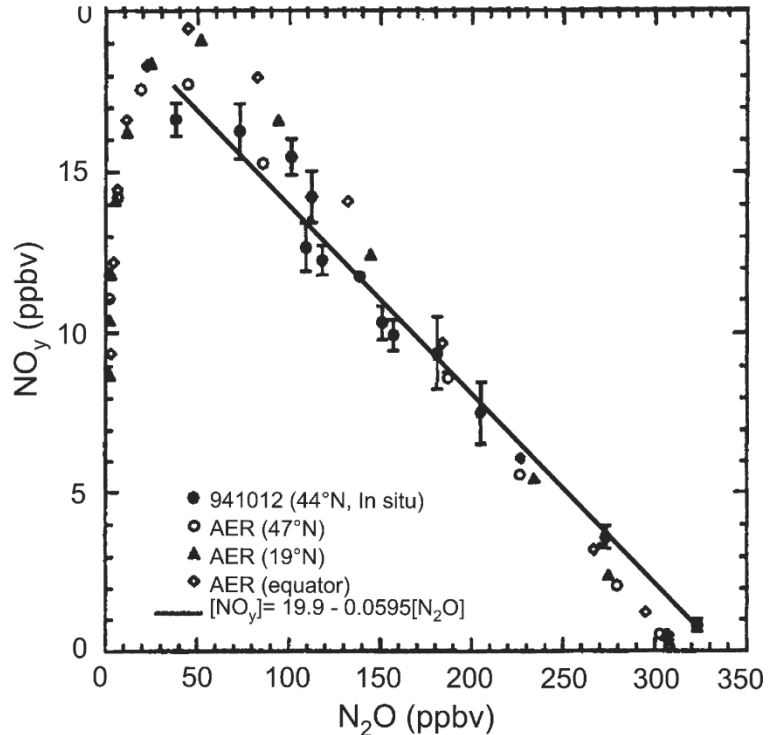
CO₂^{FF+LUC}: 10.6 Gt C /year or $(44/12) \times 10.6 \text{ Gt CO}_2 / \text{year} = 39 \text{ Gt CO}_2 / \text{yr}$

N₂O: **6.9 Tg** N x 1 Gt / 1000 Tg = 0.0069 Gt N

100 year horizon, new GWP : 0.0069 Gt N x 265 = 1.8 Gt CO₂-eq /yr

100 year horizon, old GWP : 0.0069 Gt N x 298 = 2.1 Gt CO₂-eq /yr

N₂O and NO_y



Chapter 6, WMO 1998 Ozone Assessment Report.

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

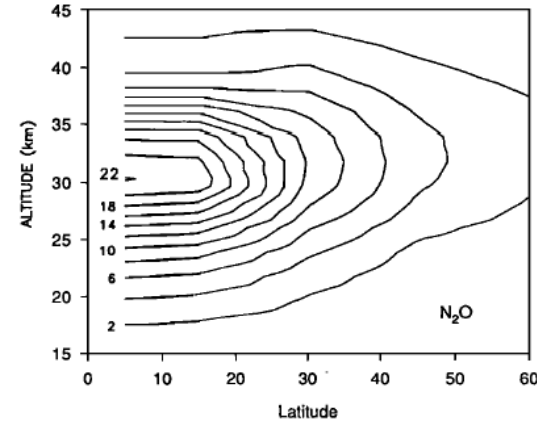
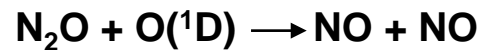


Fig. 11. Diurnally averaged loss rate for N₂O (10² molecules cm⁻³ s⁻¹) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N₂O by reaction with O(¹D) as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

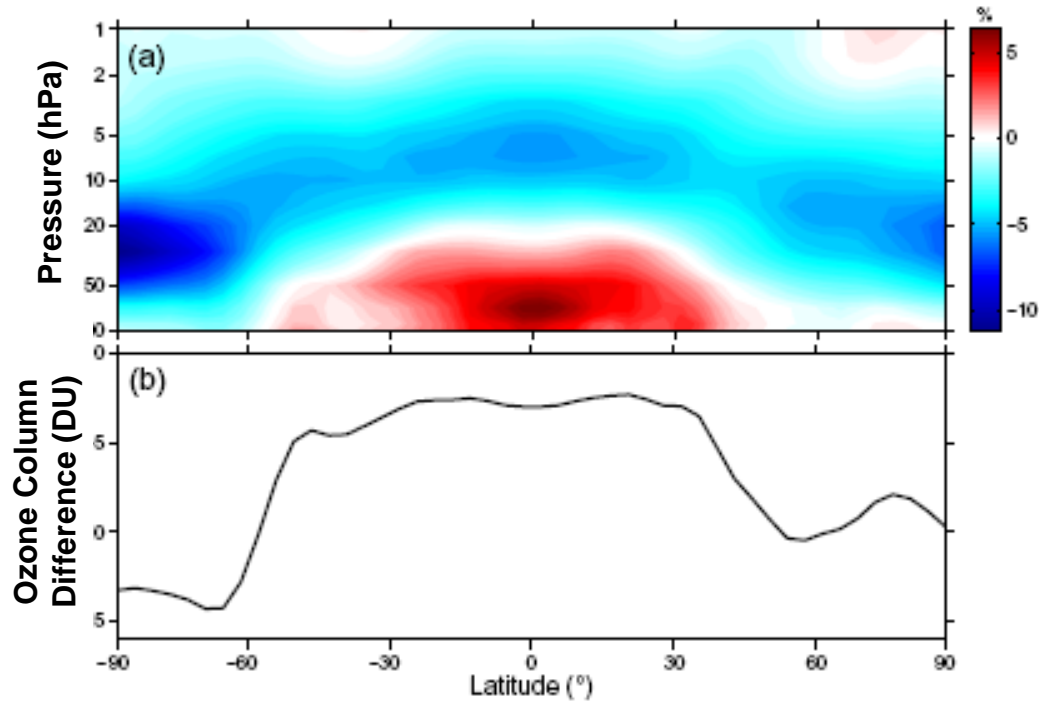
Minor sink for N₂O loss has a path that results in “fixed nitrogen”:



This is critical: source of stratospheric total fixed nitrogen (NO_y) is crucial to stratospheric chemistry

We'll later see that nitrogen oxides catalyze loss of O₃ & participate in a series of chemical reactions that affect partitioning of chlorine radicals, etc.

N₂O and Stratospheric Ozone



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

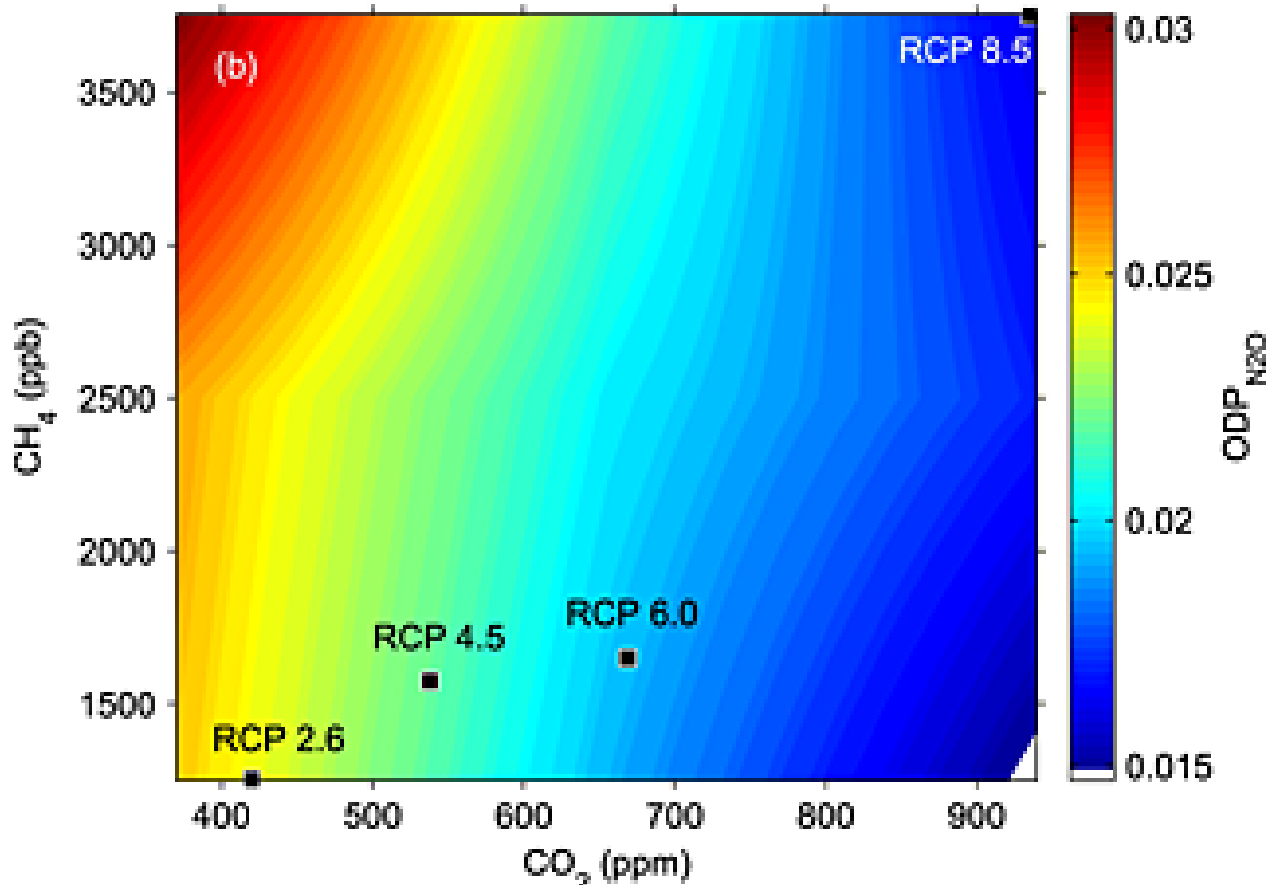
Stratospheric O₃ difference in the 2090s found for a computer simulation run using N₂O from RCP 8.5 minus that of a simulation using N₂O from RCP 2.6

Rising N₂O leads to:

- a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO₂ (NO_x) 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

Future ODP of N₂O depends on CH₄ & CO₂



ODP of N₂O in year 2100 found by a Swiss three dimensional, chemistry climate model called SOCOL (Solar Climate Ozone Links)

From Revell et al., *The changing Ozone Depletion Potential of N₂O in a future climate*, GRL, 2015.