Biogeochemical Cycles of Methane and Nitrous Oxide
AOSC 433/633 & CHEM 433/633

Ross Salawitch

Class Web Site: **http://www.atmos.umd.edu/~rjs/class/spr2015**

Goals :
- **CH$_4$**
  - **sources and sinks**
  - **lifetime**
  - **human influence**
- **N$_2$O**
  - **sources and sinks**

- **Connection of CH$_4$ and N$_2$O to stratospheric O$_3$**

Lecture 06
12 February 2015

Group Quiz #2

If the mass of the atmosphere equals **5.27 × 10²¹** gm

if 1 ton = **10⁶** gm , if the mean atomic weight of air is **28.8** gm / mole,

and if the rise in $CO_{2\ MR}$ between years 1959 to 2012 was **82.5** ppm

then how much did the mass of carbon (C, atomic weight 12) in the atmosphere rise between these years, in units of **Gt C** (gigatons of C or 10^9 tons of C) ?

Δ mass of C = 82.5 ppm (10^{-6} / ppm) × 5.27 × 10^{21}gm × (12 gm C/mole / 28.8 gm/mole)
        = 1.81 × 10^{16} gm C
        = 1.81 × 10^{17}gm C × 10^{-6} ton/gm
        = 1.81 × 10^{11} tons C
        = 181 × 10^9 tons C = **181 Gt C**
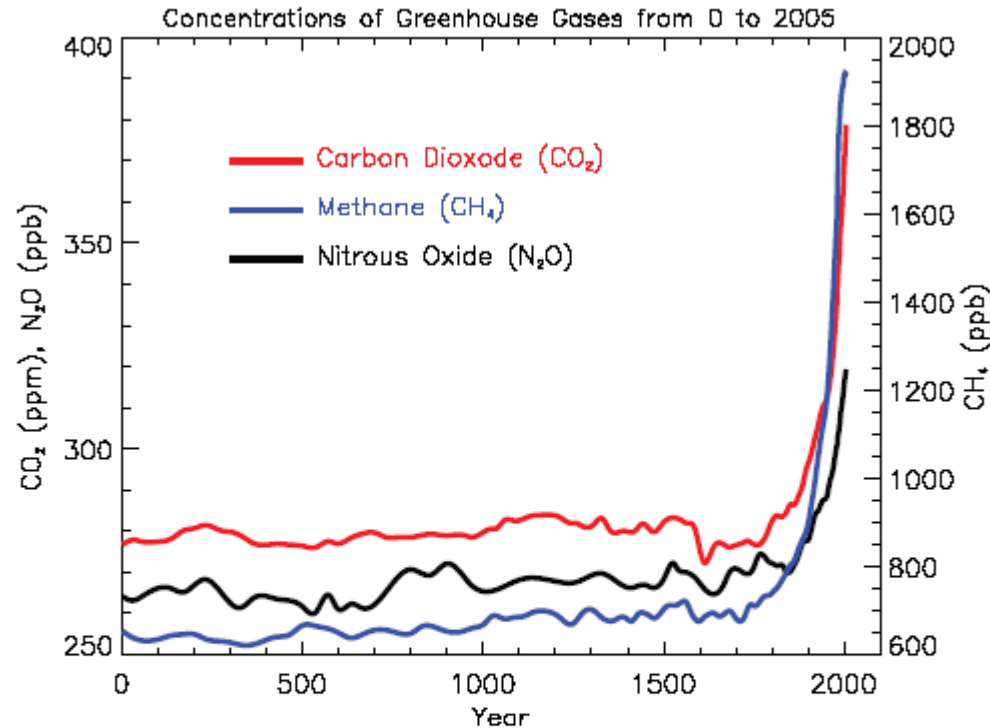
Radiative Forcing of Climate, 1750 to 2005

Radiative forcing of climate between 1750 and 2005
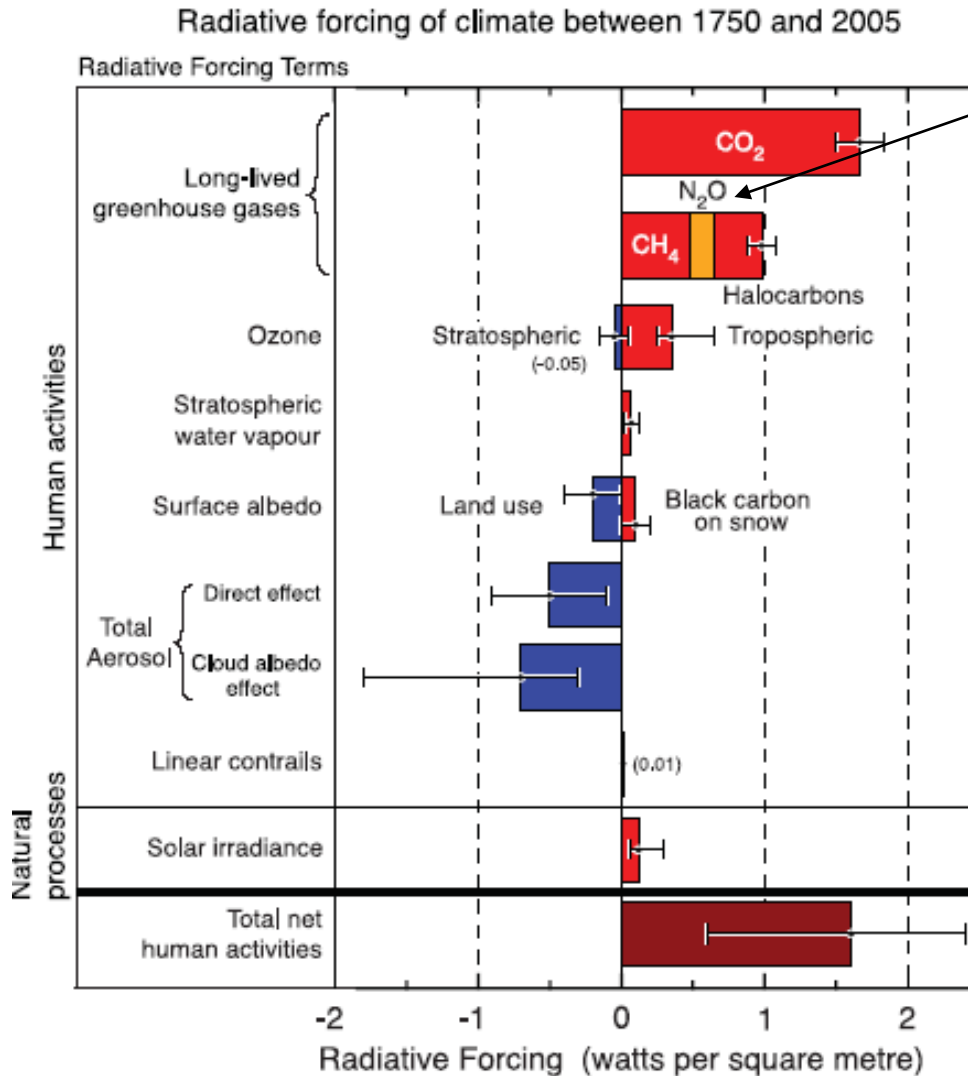
CH₄ & N₂O have contributed about 38% of the RF of CO₂

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

CO$_2$, CH$_4$ & N$_2$O time series

Concentrations of Greenhouse Gases from 0 to 2005

Carbon Dioxode (CO$_2$)
Methane (CH$_4$)
Nitrous Oxide (N$_2$O)

IPCC 2007 FAQ

FAQ 2.1, Figure 1. *Atmospheric concentrations of important long-lived green-house 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.)*

What do these time series resemble ?
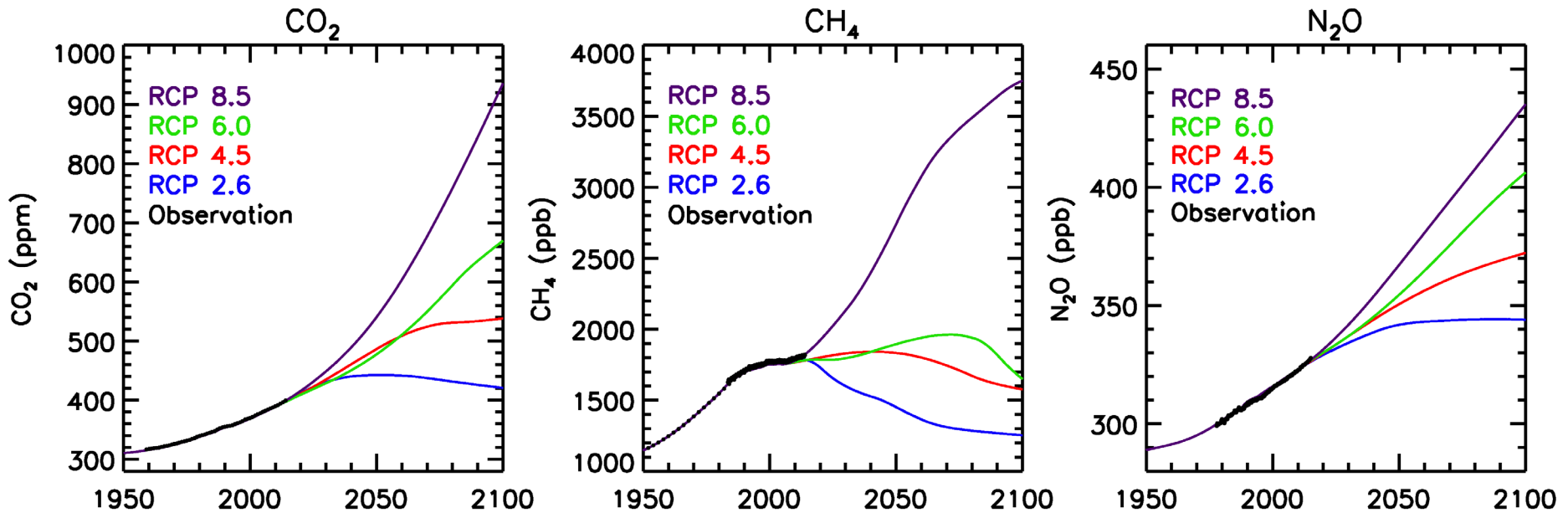
CO_2, CH_4 & N_2O time series

Figure courtesy Austin Hope

- **RCP**: Representative Concentration Pathway
    Integer represents W m^{-2} RF of climate that occurs at end of this century, for each scenario

- Mixing ratio time series for GHGs CO_2, CH_4, N_2O as well as CFCs, HCFCs, & HFCs
    provided to climate model groups

CO$_2$, CH$_4$, N$_2$O, & CFC-12

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 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*

Chapter 3, *Chemistry in Context*

CH$_4$ & N$_2$O

IPCC (2013) raises GWP of CH$_4$, lowers GWP of N$_2$O, and adds complexity of another GWP found upon consideration of Carbon Cycle Feedback

Table 8.7

	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 CH$_4$) global warming potentials (GWP) relative to CO$_2$. {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)

CH_4 is the most reduced form of carbon

-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:
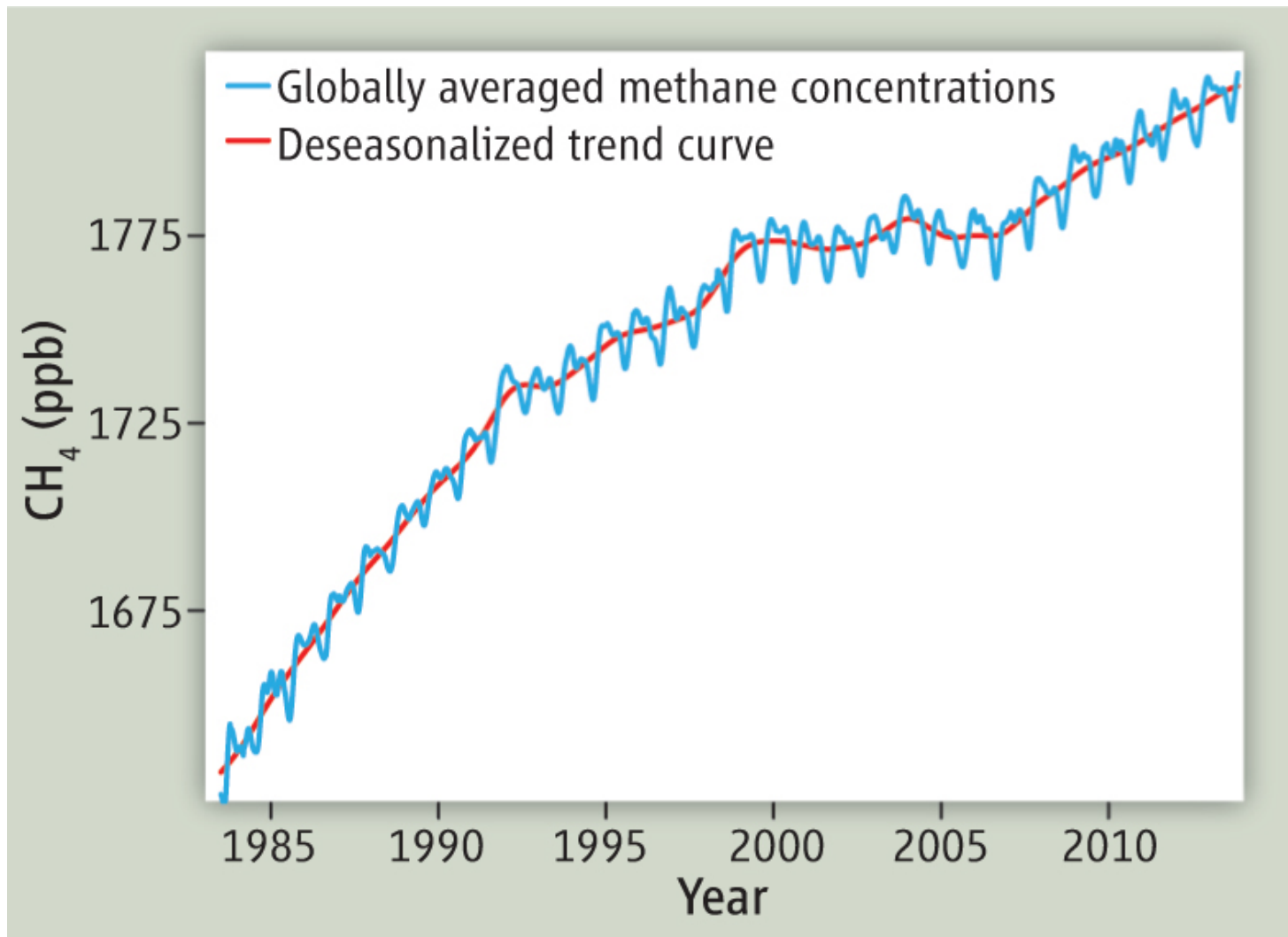added to an element (negative #) or removed from an element (positive #)
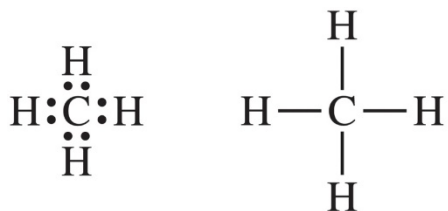
C in CH_4: has received an electron from each H atom.
All electrons are paired compound relatively stable

C in CO_2: has donated two electrons to each oxygen atom, completing L shell & resulting in electron configuration analogous to helium

Atmospheric Time Series of CH_4 – Recent Data

Globally averaged methane concentrations
Deseasonalized trend curve

CH$_4$ (ppb)

1985 1990 1995 2000 2005 2010
Year

Nisbet *et al., Science*, 2014.

Biological Production of CH$_4$

CH$_4$ produced by "methanogenic" bacteria:
- grow only in low O$_2$ environments
- fermentation of cellulose and other organic material
- swamps, marshes, rice paddy fields
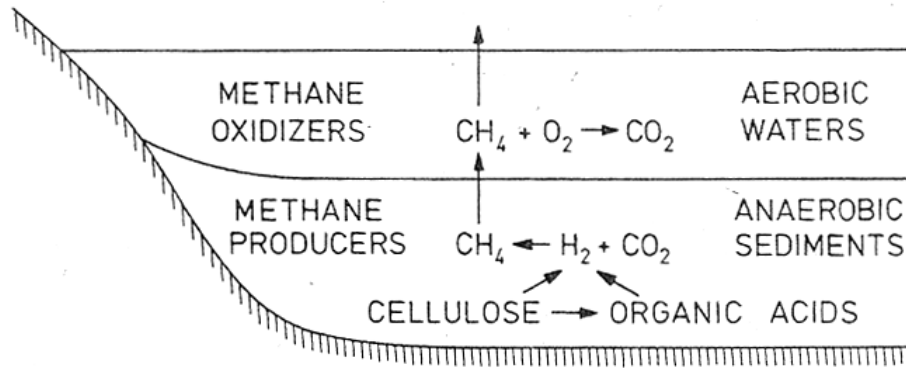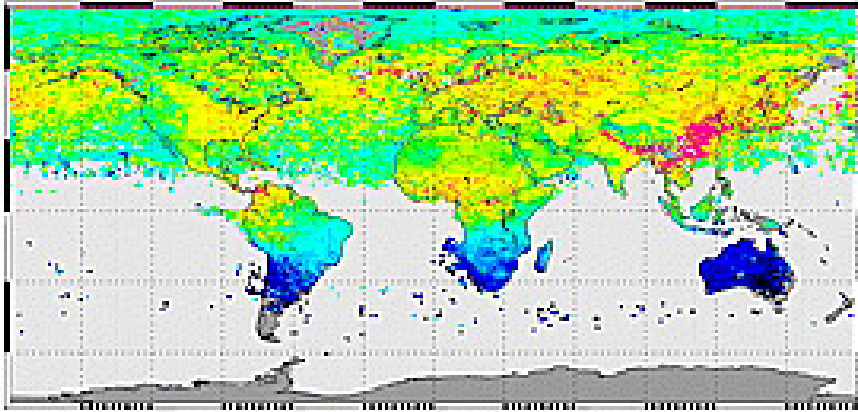- rumina of cows and sheep.

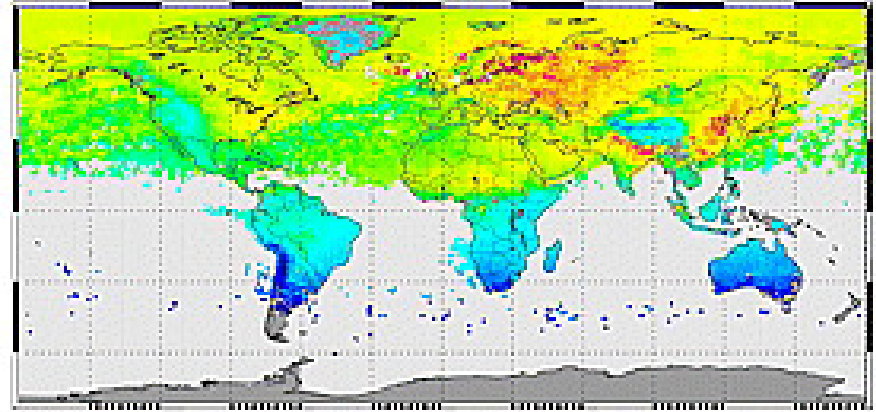FIGURE 4.6   Production and consumption of methane at the bottom of a lake. (Adapted from Schlegel (1974).)

Warneck, Chemistry of the Natural Atmosphere, 2000

Biological Production of CH$_4$


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

Sources and Sinks of CH$_4$
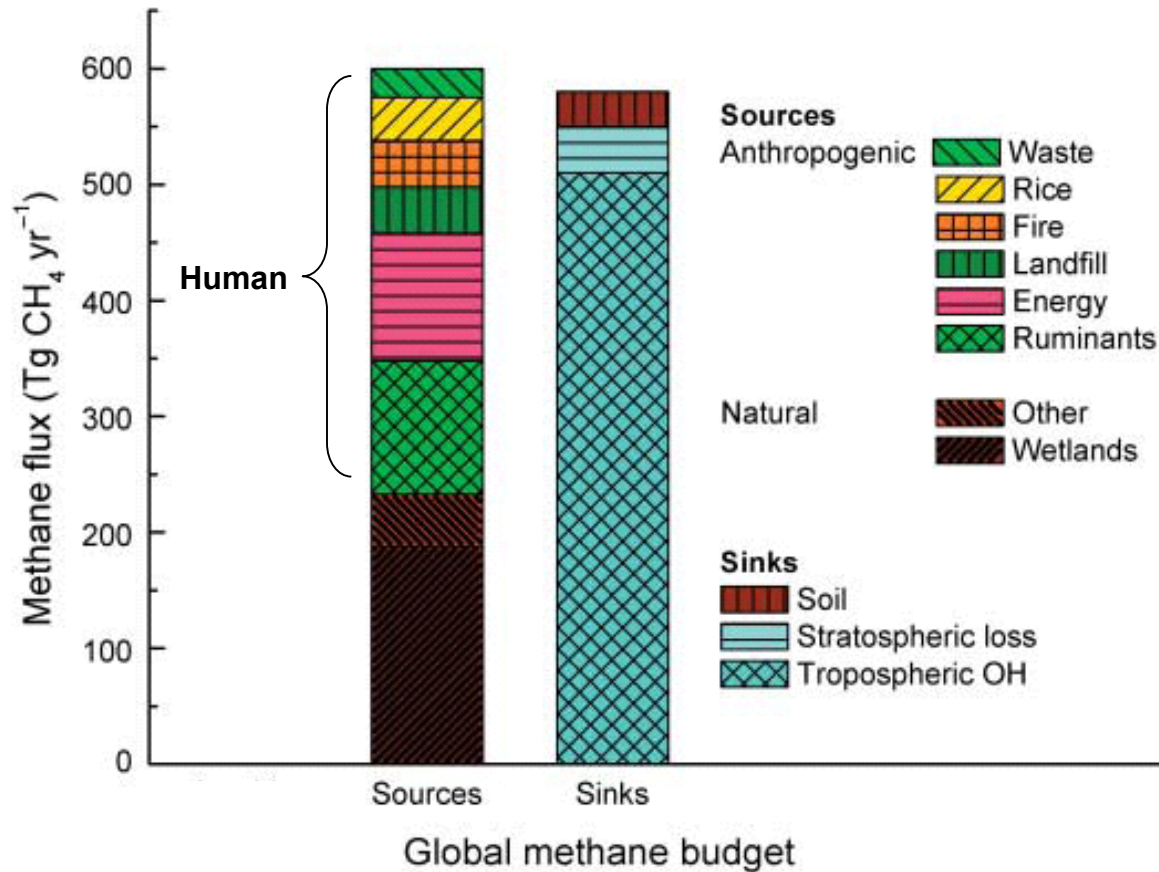
Evans, *New Phytologist*, 2007.
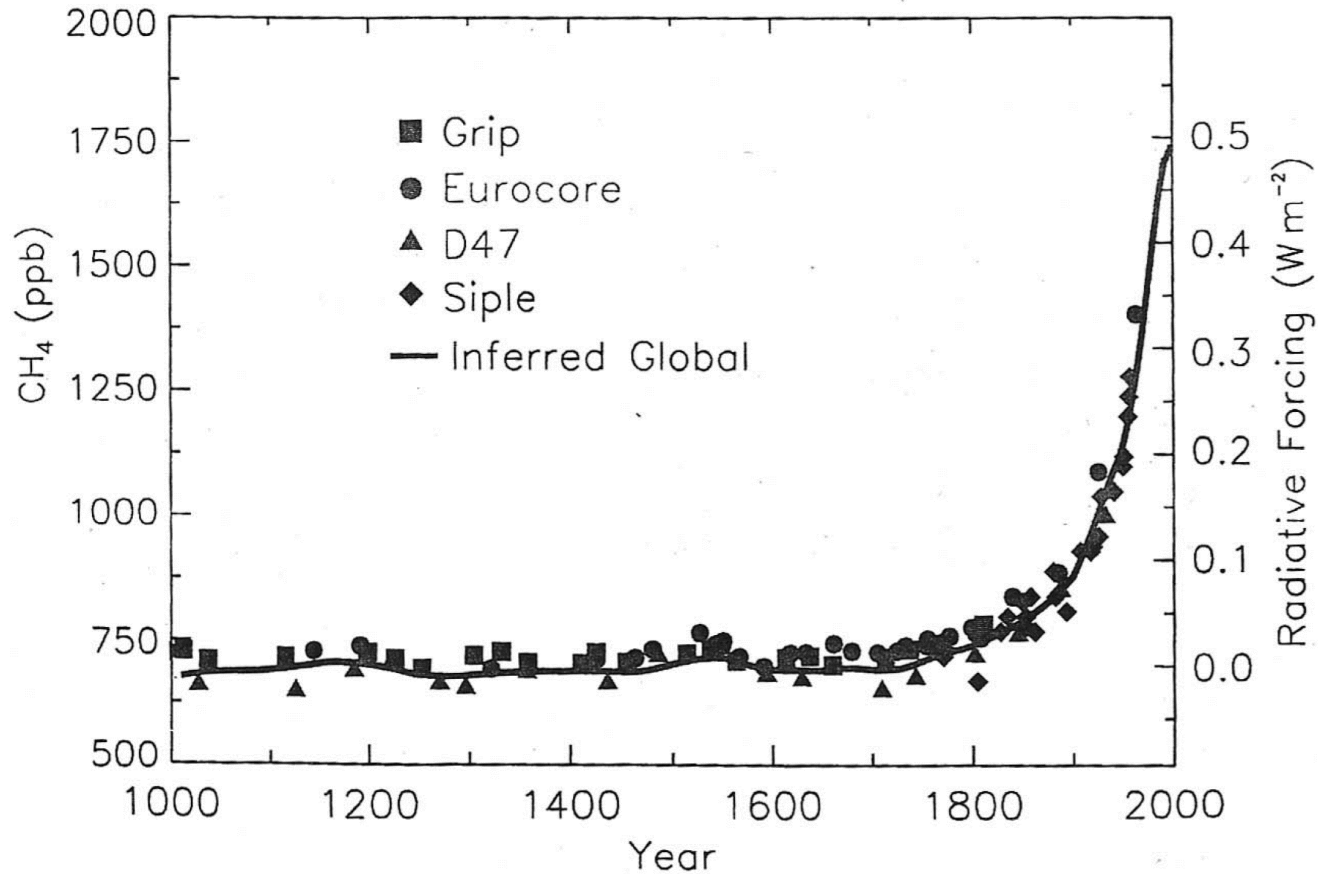
CH$_4$ versus time, past millennia

Fig 3.6, Houghton

**What was the mixing ratio of CH$_4$ about 1000 years ago?**

Sources and Sinks of CH$_4$

Table 3.2 *Estimated sources and sinks of methane in millions of tonnes per year.[a] The first column of data shows the best estimate from each source; the second column illustrates the uncertainty in the estimates by giving a range of values*

Source	Best estimate	Uncertainty
Natural		
Wetlands	150	(90–240)
Termites	20	(10–50)
Ocean	15	(5–50)
Other (including hydrates)	15	(10–40)
Human-generated		
Coal mining, natural gas, petroleum industry	100	(75–110)
Rice paddies	60	(30–90)
Enteric fermentation	90	(70–115)
Waste treatment	25	(15–70)
Landfills	40	(30–70)
Biomass burning	40	(20–60)
Sinks		
Atmospheric removal	545	(450–550)
Removal by soils	30	(15–45)
Atmospheric increase	22	(35–40)

[a] From Prather, M., Ehhalt, D. *et al.* 2001. Atmospheric chemistry and greenhouse gases. Chapter 4 in Houghton *et al.*, *Climate Change 2001*. See also Prather, M. *et al.* 1995. Other trace gases and atmospheric chemistry. In *Climate Change 1994*. Cambridge: Cambridge University Press. The figure for atmospheric increase is an average for the 1990s.

Chapter 3, Global Warming, Houghton
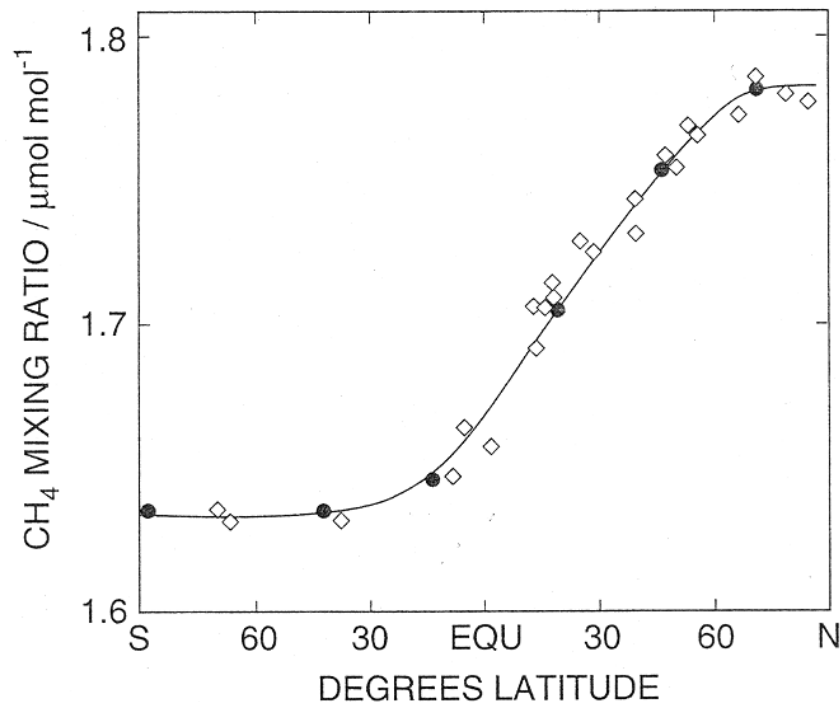
Latitudinal Distribution of CH$_4$

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 CH$_4$ vs latitude, as time evolves, is at
http://www.esrl.noaa.gov/gmd/ccgg/globalview/ch4/ch4_intro.html

CH$_4$ is lost by reaction with OH

CH$_4$ + OH → H$_2$O + CH$_3$
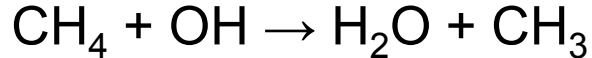
$$\frac{d\text{CH}_4}{dt} = \text{Production} - \text{Loss} = \text{Production} - k\,[\text{OH}][\text{CH}_4]$$

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 × 10^6 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		
Chlorine gases		
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_3CCl_3)	5	0.16
Methyl chloride (CH_3Cl)	1	0.02
Bromine gases		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH_3Br)	0.8	0.66
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

CH$_3$CCl$_3$ (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

CH$_3$CCl$_3$ + OH → CH$_2$CCl$_3$+H$_2$O
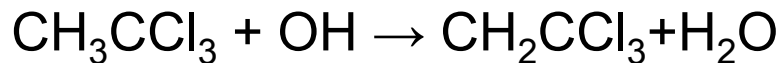
$$\frac{d\text{CH}_3\text{CCl}_3}{dt} = \text{Production} - \text{Loss} = \text{Production} - k\,[\text{OH}][\text{CH}_3\text{CCl}_3]$$
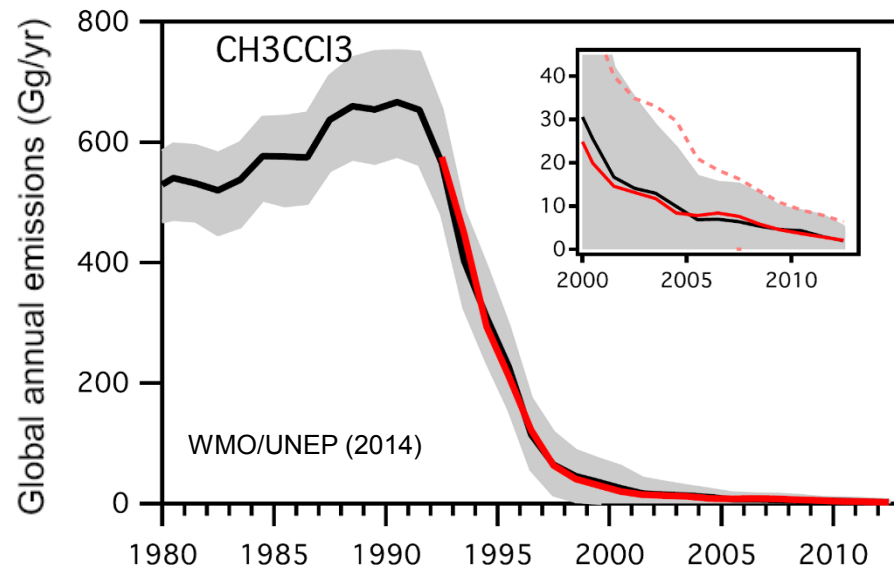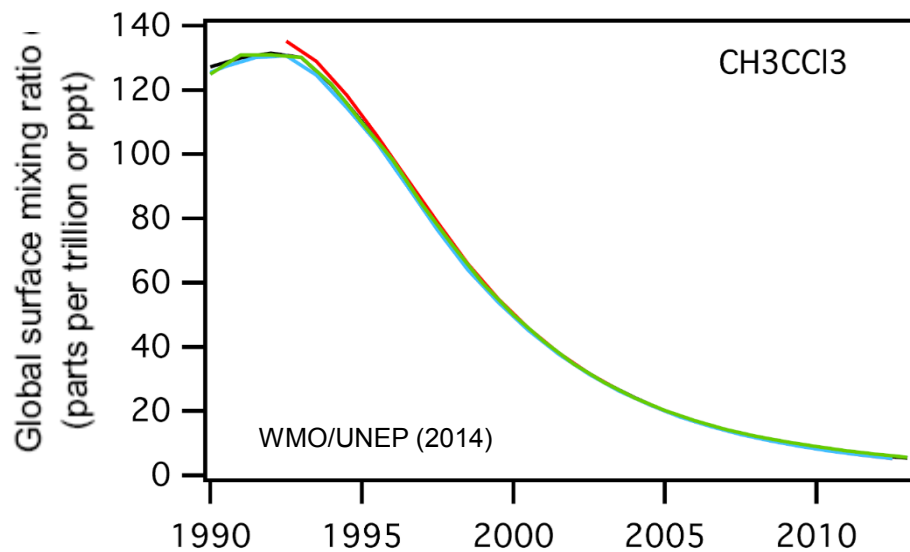
The global average OH concentration, $9.4 \pm 1.3 \times 10^5$ molec cm^{-3}, for observations obtained from 1978 to 2000, does not vary statistically from that derived by us earlier for the 1978 to 1994 period **$9.7 \pm 1.3 \times 10^5$ molec cm^{-3}**

Prinn et al., *Science*, 2001

So Why Do Both Readings Give a Lifetime for CH_4 of 12 Years?

The feedback of CH_4 on tropospheric OH and its own lifetime is re-evaluated with contemporary CTMs as part of OxComp, and results are summarised in <u>Table 4.3</u>. The calculated OH feedback, $\partial\ln(OH) / \partial\ln(CH_4)$, is consistent between the models, indicating that tropospheric OH abundances decline by 0.32% for every 1% increase in CH_4. The TAR value for the sensitivity coefficient $s = \partial\ln(LT) / \partial\ln(CH_4)$ is then 0.28 and the ratio PT/LT is 1.4. This 40% increase in the integrated effect of a CH_4 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 CH_4 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 $^{13}CH_4$ and $^{12}CH_4$ separately may lead to an observational constraint (Manning, 1999).

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

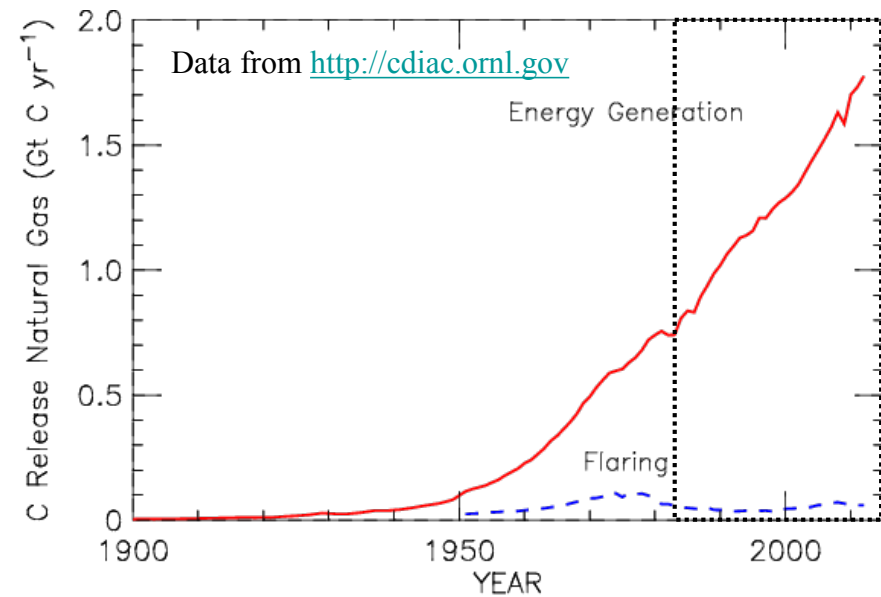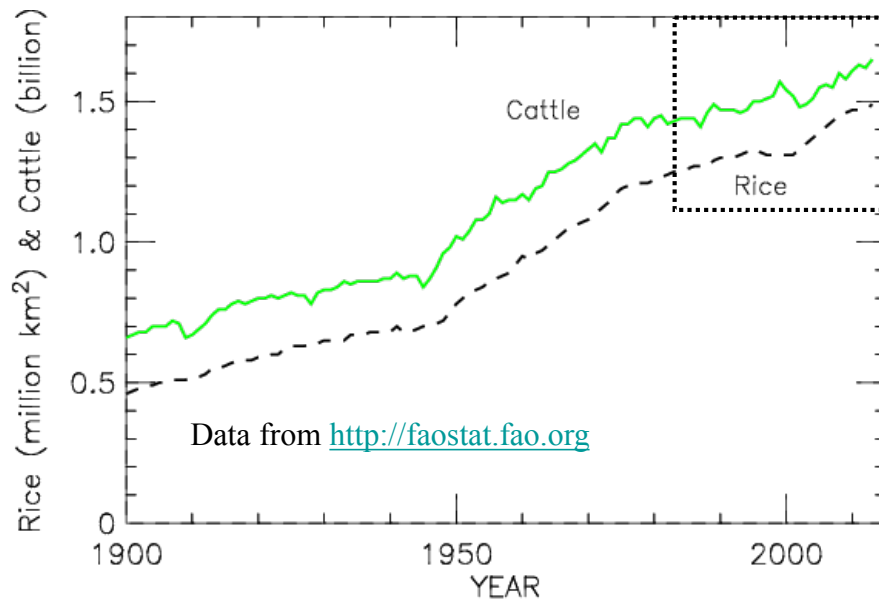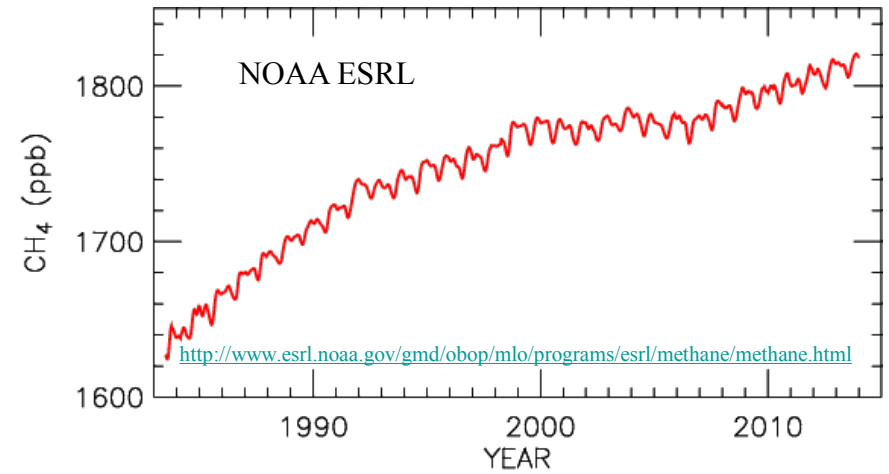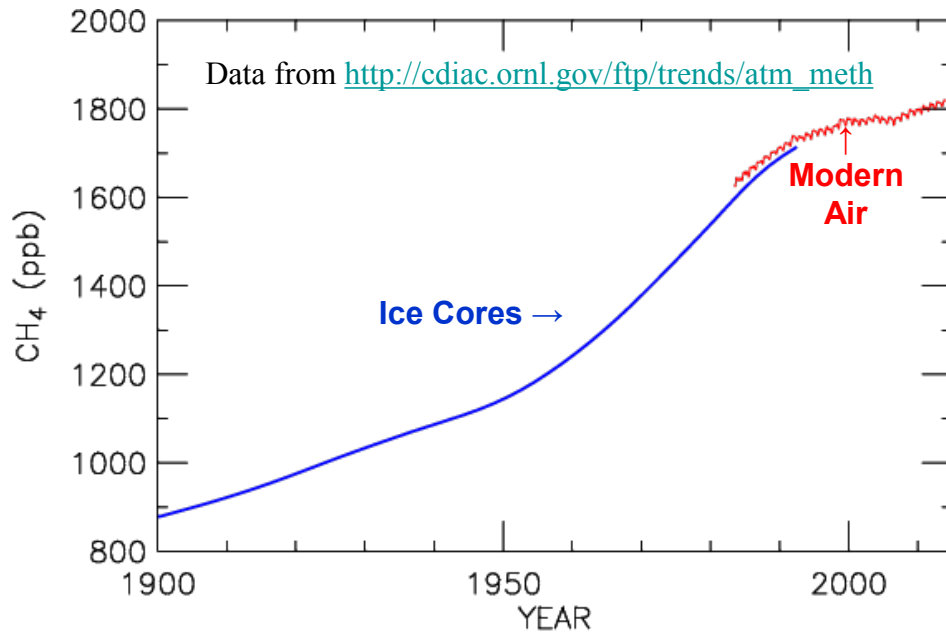# CH$_4$ and Stratospheric Ozone
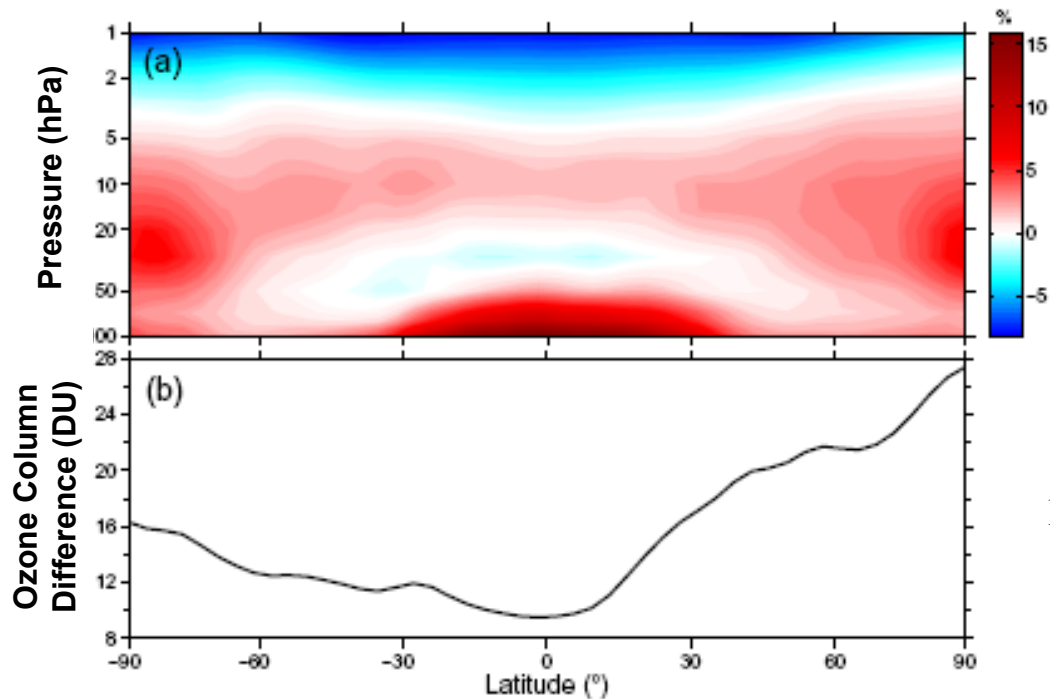
Revell *et al.*, *ACP*, 2012

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

Atmospheric CH$_4$ and Energy from Gas, Rice, Cattle Trends

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

Modern Air

Ice Cores →

NOAA ESRL

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

Cattle

Rice

Data from http://faostat.fao.org

Data from http://cdiac.ornl.gov
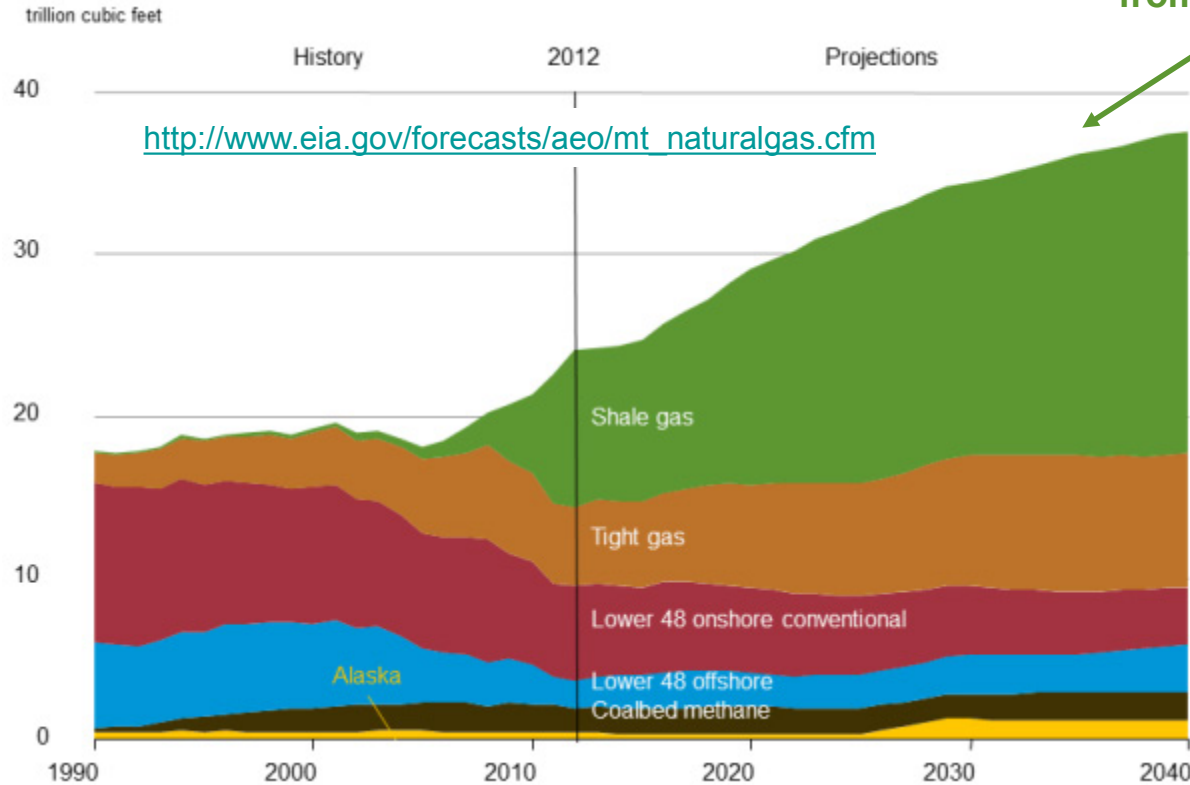
Energy Generation

Flaring

Recent trends in CH$_4$

These papers offer conflicting views on the cause of the leveling off of methane:

- **Aydin et al. (Nature, 2011) suggest "rising economic value of natural gas" and "development of cleaner technologies" have led to a sharp decline in unintentional release of CH$_4$ by the petroleum industry, based on the temporal evolution of CH$_4$ and ethane (C$_2$H$_6$)**

- **Kai et al. (Nature, 2011) suggest changes in agricultural practices, particularly in China, including new high yield rice species, use of more fertilizer, and most importantly shorter water inundation periods have led to a sharp decline in microbial release of CH$_4$, based on the temporal evolution of the isotopic composition of CH$_4$**

Fracking

CH_4 (or natural gas) production from fracking

trillion cubic feet

History   2012   Projections

http://www.eia.gov/forecasts/aeo/mt_naturalgas.cfm

Shale gas

Tight gas

Lower 48 onshore conventional

Alaska
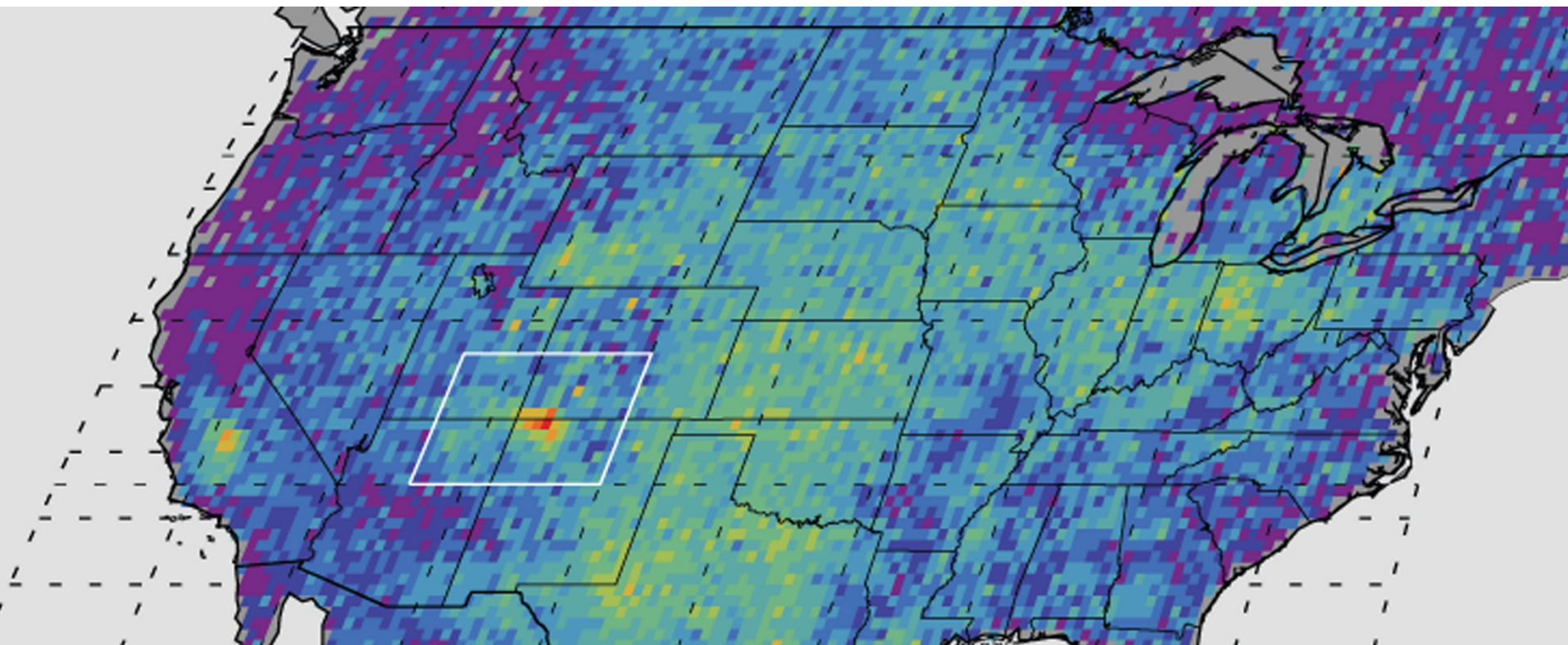
Lower 48 offshore
Coalbed methane

Airborne measurements by Karion *et al*. *GRL* 2013 over Utah indicate fugitive CH_4 emission is ~9 % of average hourly CH_4 production

Surface measurements at 190 onshore natural gas sites by Allen *et al*. *PNAS* 2013 show fugitive CH_4 emission is ~0.42 % of gross CH_4 production

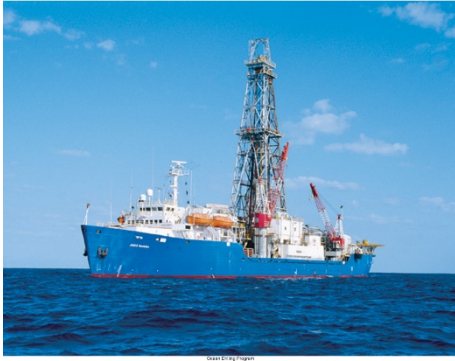**Break even point for "climate" is _____ ? (Problem Set #1)**

Four Corners

- **Box shows major hot spot for CH$_4$ emissions, 2003 to 2009 from SCIAMACHY**

- **Likely source is leakage from CH$_4$ extracted from coal**

- **About 10% of the total US CH$_4$ emissions estimated by EPA inventory, that does not consider this source**

Kort *et al.*, *GRL*, 2014.

CH$_4$ 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.
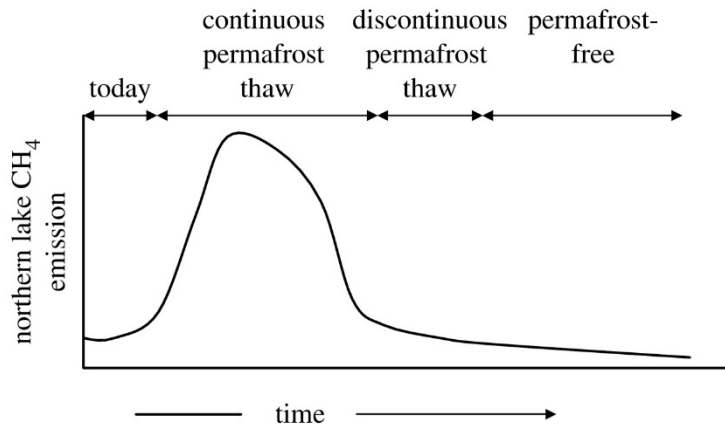
Schematic depicting future of CH$_4$ emissions from northern lakes, as the north changes from a permafrost-rich landscape to a landscape free of surface permafrost.

Nitrous Oxide: N$_2$O
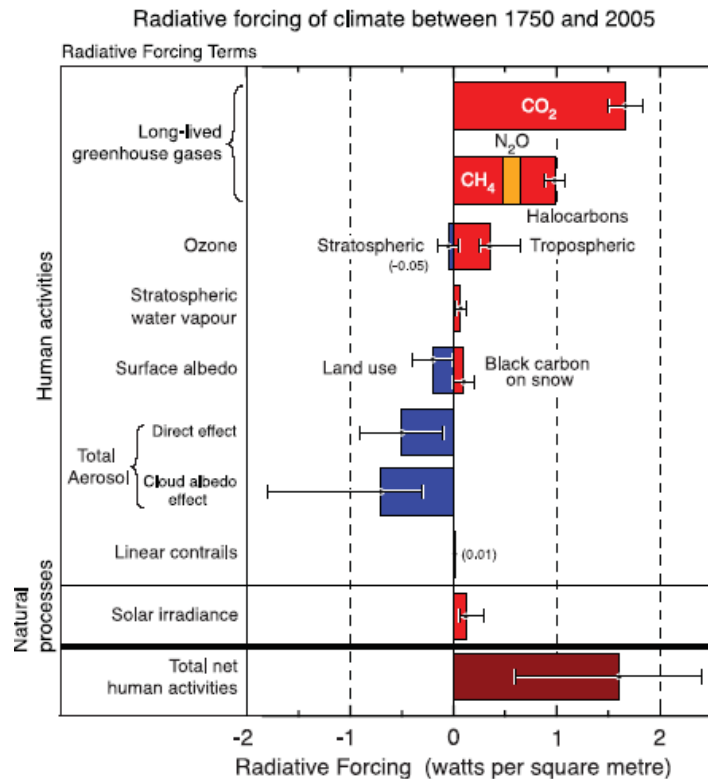
Radiative forcing of climate between 1750 and 2005

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

Concentrations of Greenhouse Gases from 0 to 2005
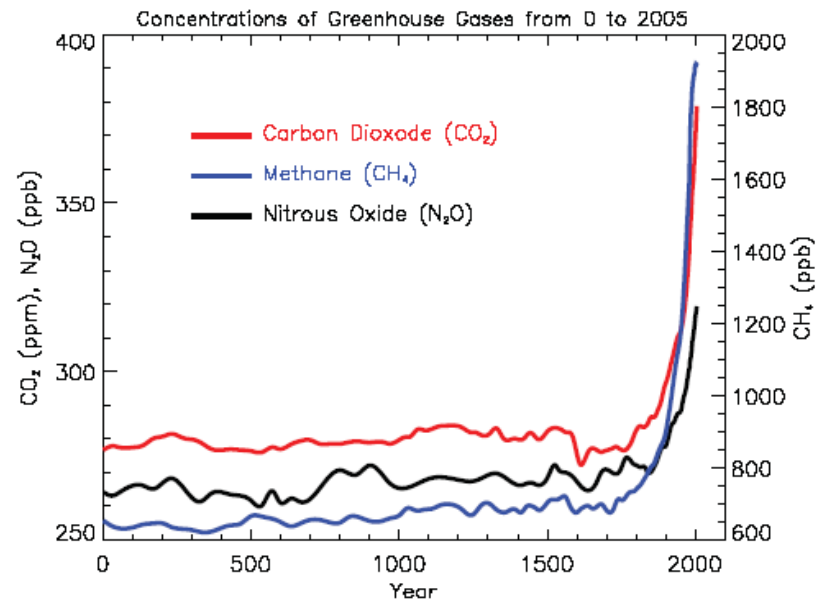
Table 3.2	Examples of Greenhouse Gases				
Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
nitrous oxide N$_2$O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

N$_2$O Lifetime ≈ 120 yrs

←

-3	0	+1	+2	+3	+4	+5
NH_3 Ammonia	N_2	N_2O Nitrous oxide	NO Nitric oxide	HONO Nitrous acid NO_2^- Nitrite	NO_2 Nitrogen dioxide	HNO_3 Nitric acid NO_3^- Nitrate

→

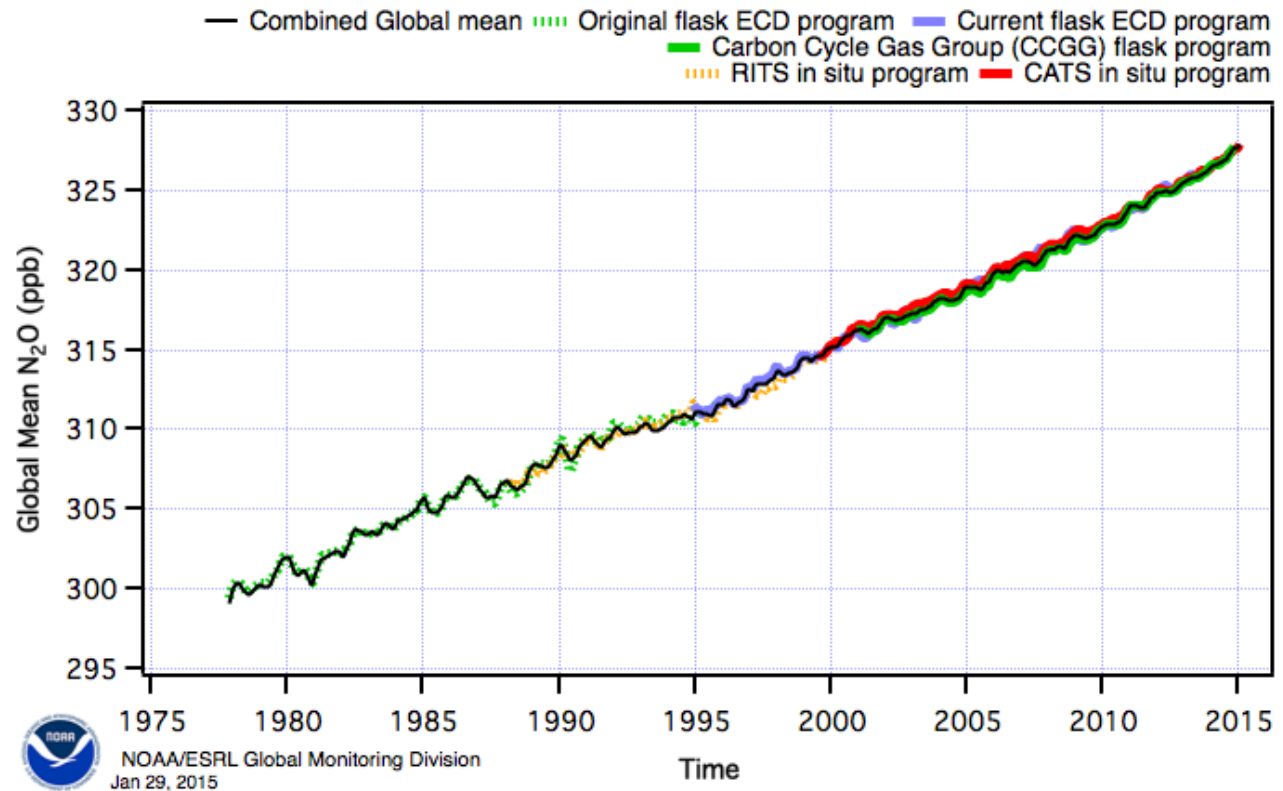**Increasing oxidation number (oxidation reactions)**

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

$$:\ddot{N}—N≡O:$$

See http://guweb2.gonzaga.edu/faculty/cronk/chemistry/L00-index.cfm?L00resource=Lewis_structures
for Lewis Dot Structure of N_2O … please note we will not ask questions
about Lewis Dot Structures on exams !

Sources and Sinks of N$_2$O

Source	N$_2$O
Anthropogenic sources	
Fossil fuel combustion & industrial processes	0.7 (0.2–1.8)[d]
Aircraft	-
Agriculture	2.8 (1.7–4.8)[g]
Biomass and biofuel burning	0.7 (0.2–1.0)[g]
Human excreta	0.2[g] (0.1–0.3)[h]
Rivers, estuaries, coastal zones	1.7 (0.5–2.9)[i]
Atmospheric deposition	0.6[j] (0.3–0.9)[h]
Anthropogenic total	**6.7**
Natural sources	
Soils under natural vegetation	6.6 (3.3–9.0)[g]
Oceans	3.8 (1.8–5.8)[k]
Lightning	–
Atmospheric chemistry	0.6 (0.3–1.2)[c]
Natural total	**11.0**
Total sources	**17.7** (8.5–27.7)

— Combined Global mean ⋯⋯ Original flask ECD program ▬ Current flask ECD program
▬ Carbon Cycle Gas Group (CCGG) flask program
⋯⋯ RITS in situ program ▬ CATS in situ program

NOAA/ESRL Global Monitoring Division
Jan 29, 2015

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

Chapter 7, IPCC 2007

[c] Values are from the TAR, Table 4.4; Mosier et al. (1998); Kroeze et al. (1999)/Olivier et al. (1998): a single value indicates agreement between the sources and methodologies of the different studies.
[d] Van Aardenne et al. (2001), range from the TAR.
[g] Bouwman et al. (2001, Table 1); Bouwman et al. (2002) for the 1990s; range from the TAR or calculated as ±50%.
[h] Estimated as ±50%.
[i] Kroeze et al. (2005); Nevison et al. (2004); estimated uncertainty is ±70% from Nevison et al. (2004).
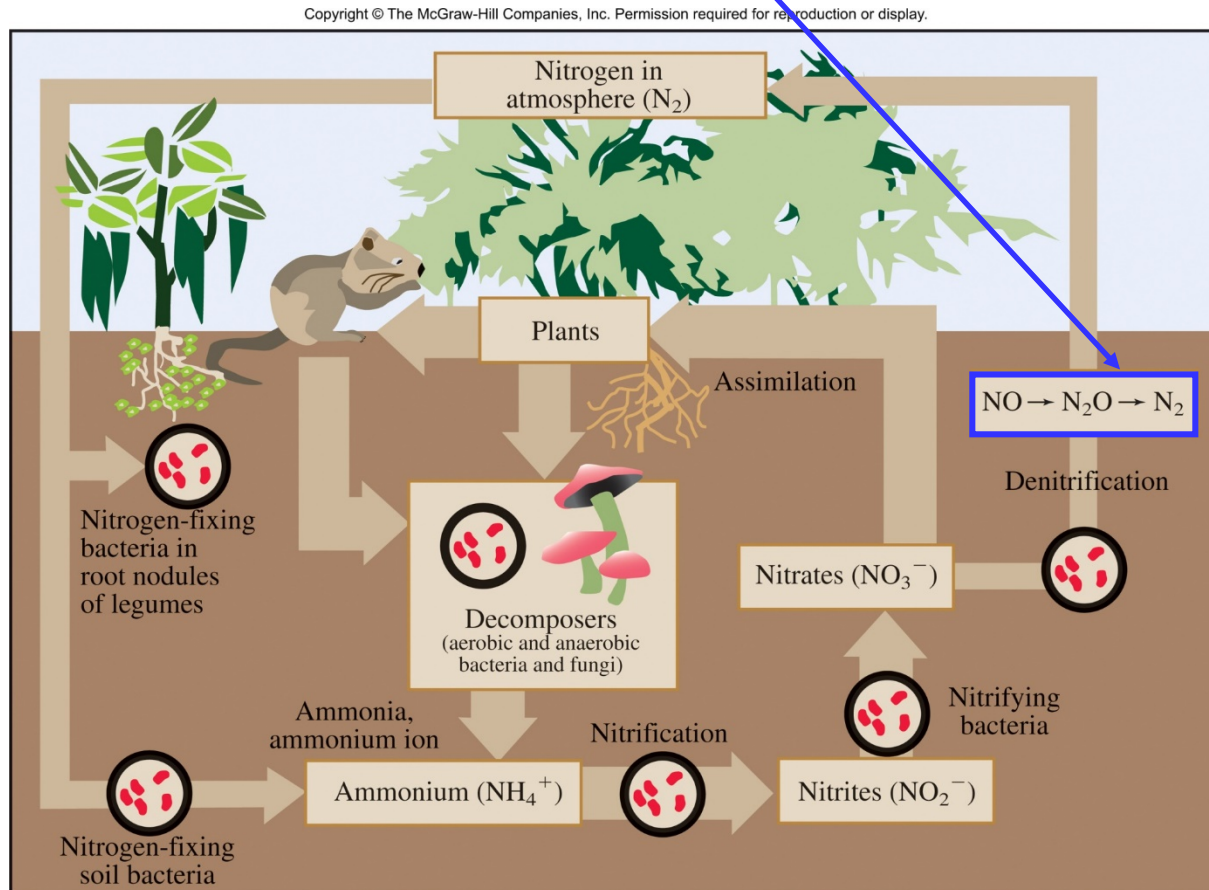[j] All soils, minus the fertilized agricultural soils indicated above.

The Nitrogen Cycle

Haber-Bosch: N_2(gas) + 3 H_2 (gas) $\rightarrow$ 2 NH_3 (gas)
Led to large scale, economical production of ammonia based fertilizer
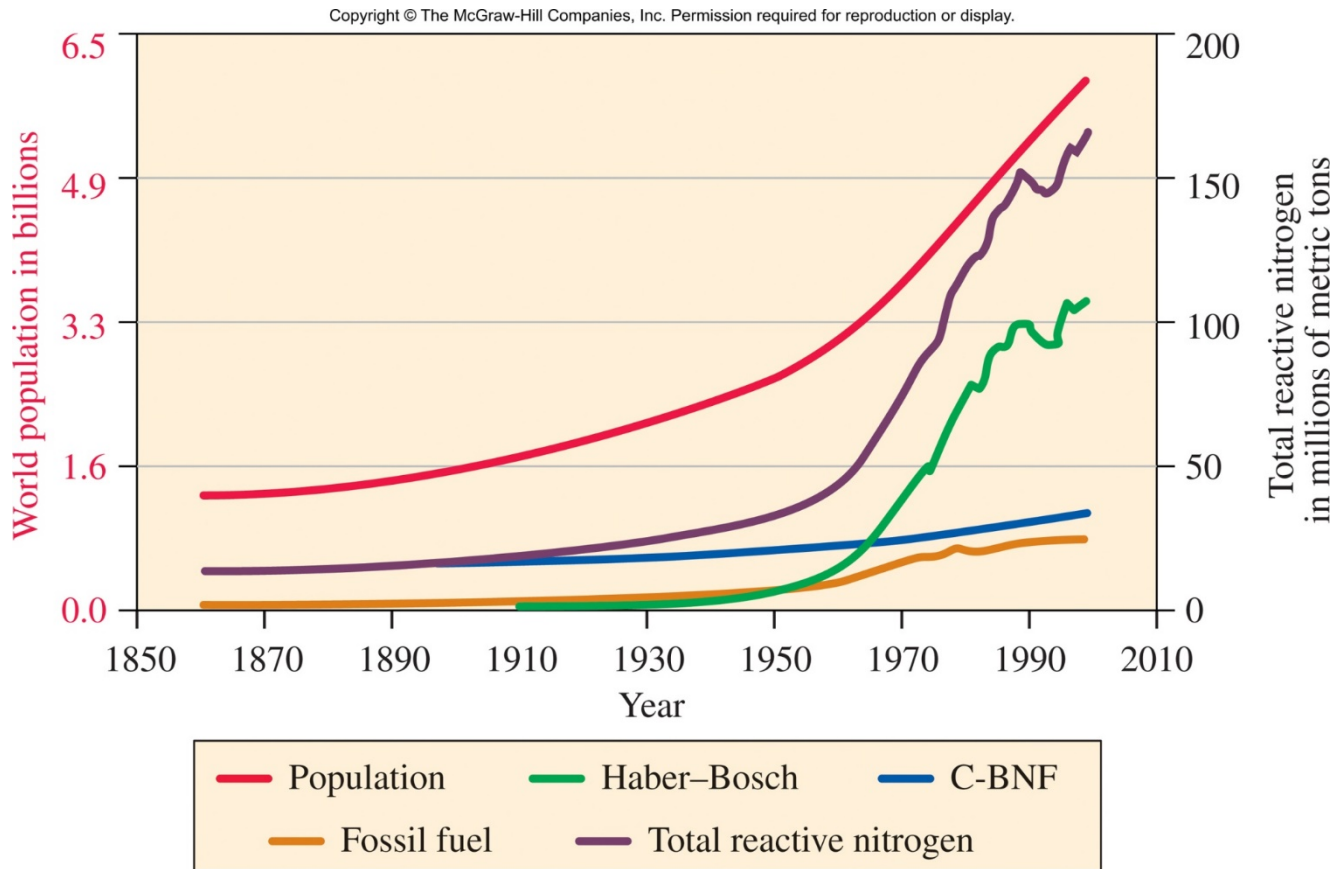
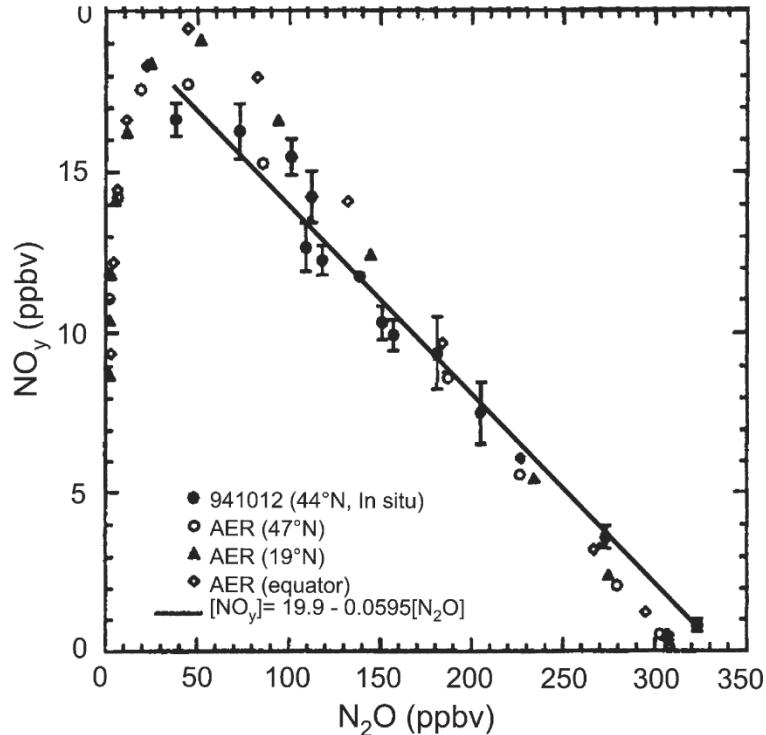**Chapter 6, *Chemistry in Context***

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$_2$O, a GHG that is currently rising.

Nitrogen in atmosphere (N$_2$)

Plants

Assimilation

NO → N$_2$O → N$_2$

Denitrification

Nitrogen-fixing bacteria in root nodules of legumes

Decomposers (aerobic and anaerobic bacteria and fungi)

Nitrates (NO$_3^-$)

Ammonia, ammonium ion

Nitrification

Nitrifying bacteria

Ammonium (NH$_4^+$)

Nitrites (NO$_2^-$)

Nitrogen-fixing soil bacteria

Chapter 6, *Chemistry in Context*

N$_2$O and NO$_y$

Chapter 6, WMO 1998 Ozone
Assessment Report.

Loss of N$_2$O occurs mainly in the stratosphere, due to:
photolysis – main sink
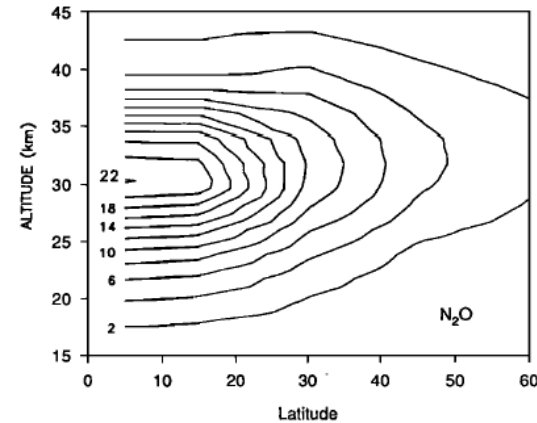**reaction with electronically excited O(^{1}D) – minor sink**

Fig. 11. Diurnally averaged loss rate for N$_2$O (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$_2$O by reaction with O(^{1}D) as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

Minor sink for N$_2$O loss has a path that results in "fixed nitrogen":

$$N_2O + O(^1D) \longrightarrow NO + NO$$
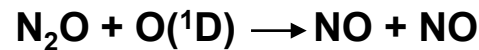
This is critical: source of stratospheric total fixed nitrogen (NO$_y$) is crucial to stratospheric chemistry

  We'll later see that nitrogen oxides catalyze loss of O$_3$ & participate in a series of chemical reactions that affect partitioning of chlorine radicals, etc.

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N$_2$O and Stratospheric Ozone
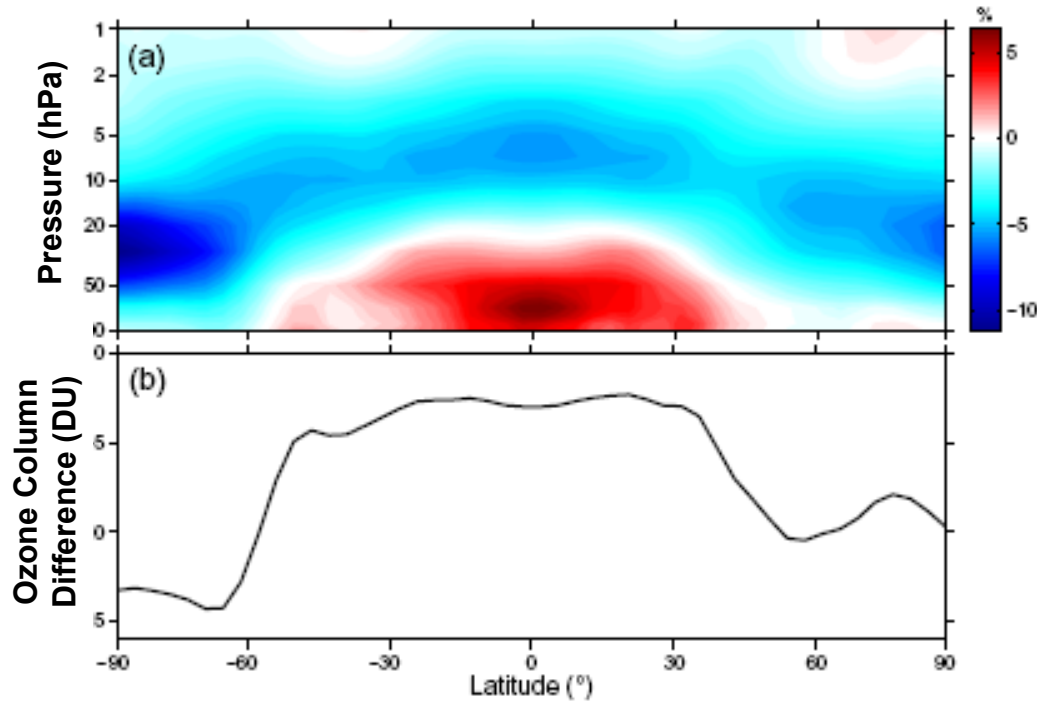
Revell *et al.*, *ACP*, 2012

Stratospheric O$_3$ difference in the 2090s found for a computer simulation run
using N$_2$O from RCP 8.5 minus that of a simulation using N$_2$O from RCP 2.6

Rising N$_2$O leads to:
  a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO$_2$ (NO$_x$) mediated loss cycles.

  b) speeds up the rate of OH+NO$_2$+M→HNO$_3$ & ClO+NO$_2$+M→ 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$_2$O rises

Nitrous Oxide (N$_2$O): The Dominant Ozone-Depleting Substance [to be] Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA.

By comparing the ozone depletion potential–weighted anthropogenic emissions of N$_2$O with those of other ozone-depleting substances, we show that N$_2$O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N$_2$O is unregulated by the Montreal Protocol. Limiting future N$_2$O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.
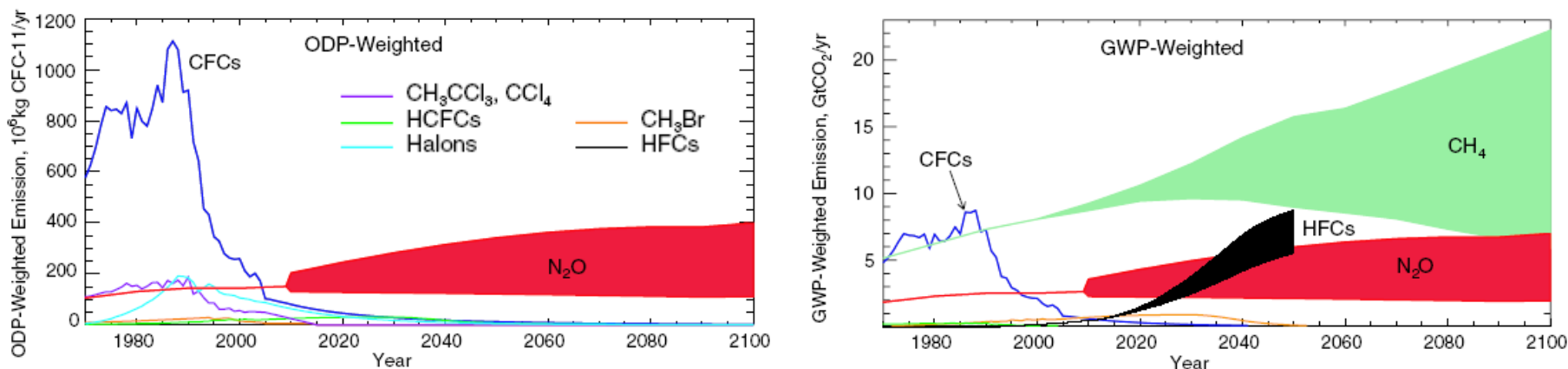
Fig. 2. Historical and projected ODP- and GWP-weighted emissions of the most important ODSs and non-CO$_2$ greenhouse gases. Non-N$_2$O ODS emissions are taken from WMO (*3*). Hydrofluorocarbon (HFC) projections are taken from Velders *et al.* (*24*), do not include HFC-23, and are estimated assuming unmitigated growth. The HFC band thus represents a likely upper limit for the contribution of HFCs to GWP-weighted emissions. CH$_4$ emissions represent the range of the Special Report on Emissions Scenarios (SRES) A1B, A1T, A1FI, A2, and B1 scenarios (*23*). The range of anthropogenic N$_2$O emissions is inferred from the mixing ratios of these same SRES scenarios [see (*13*) for details of calculation].

http://www.sciencemag.org/content/326/5949/123.full

Future ODP of N_2O depends on CH_4 & CO_2
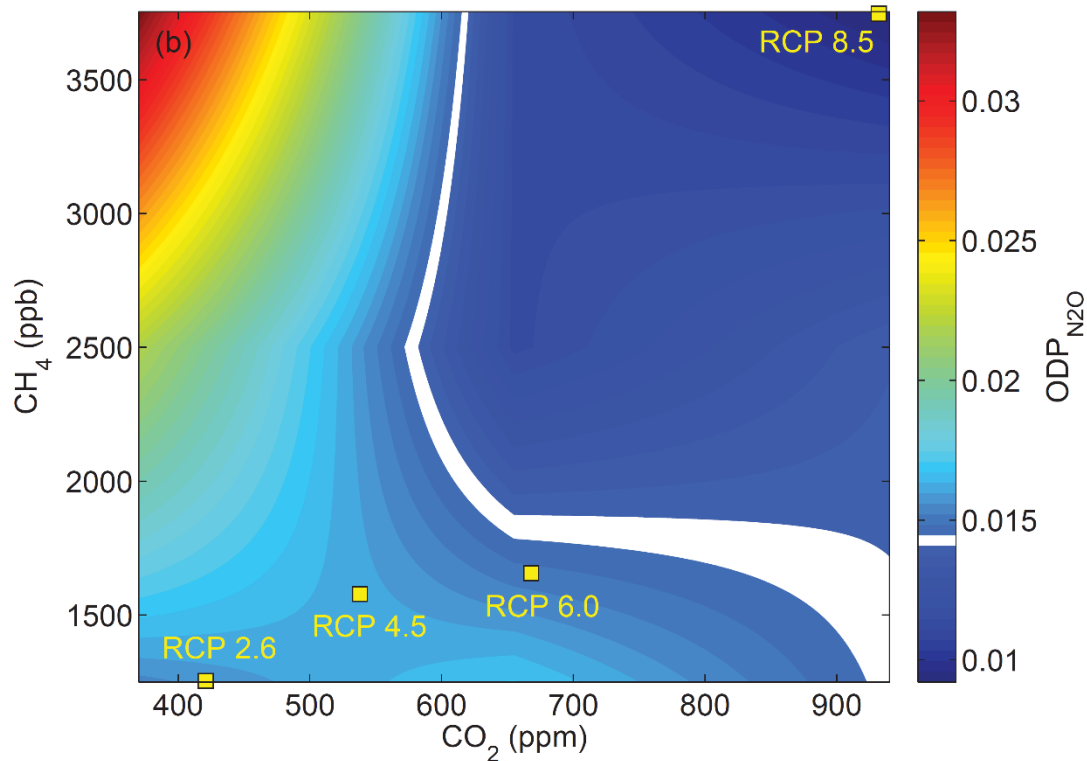
ODP of N_2O in year 2100 found by a Swiss three dimensional, chemistry climate model called SOCOL (Solar Climate Ozone Links)

From "The Changing Ozone Depletion Potential of N_2O in a Future Climate", Revell et al., *Nature Climate Change*, submitted 9 Feb 2015.