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Climate Physics and Chemistry
Fall 2006

Atmospheric Chemistry I:
Ozone, Chlorofluorocarbons, Nitrogen Oxides, and Dimethyl Sulfide

A brief history of the atmospheric chemistry of O_3, nitrogen oxides, and CFC's

- 1970: Paul Crutzen shows that destruction by NO_x can account for discrepancy between factor of three excess of calculated ozone layer relative to observed.
- 1971: Crutzen shows that dominant source of NO_x in stratosphere is transport of N_2O released from biosphere.
- Harold Johnston suggests that nitrogen oxides released by supersonic transports might affect ozone layer (but US SST rejected on grounds of economics rather than environmental concerns).
- 1973: James Lovelock, inventor of "electron capture" detector, shows that CFC concentrations in the atmosphere were increasing.
- 1974: Molina and Rowland suggest that CFCs would deplete ozone layer [at about same time, Ralph Cicerone and Johnston also suggest that Cl might deplete ozone, but focus on volcanism and the space shuttle as a source of Cl rather than CFC's].
- 1976: US bans use of aerosol spray CFCs after 1978.
- 1980: "Ozone hole" opens up in Antarctic, unbeknownst to the human race.
- 1985: Josephan Farman found that mean Antarctic ozone (column) had decreased by nearly half of what it had been in the early 1970's.
- Ozone hole intensity continues to increase, with Antarctic ozone virtually disappearing at 15-21 km altitude every spring. This event was not predicted by Molina-Rowland model.
- Late 1980's: Antarctic ozone hole linked to heterogeneous catalysis by polar stratospheric clouds.
- 1987: Signing of multinational "Montreal Protocol" regulating CFC production.

Gas phase chemical kinetics I

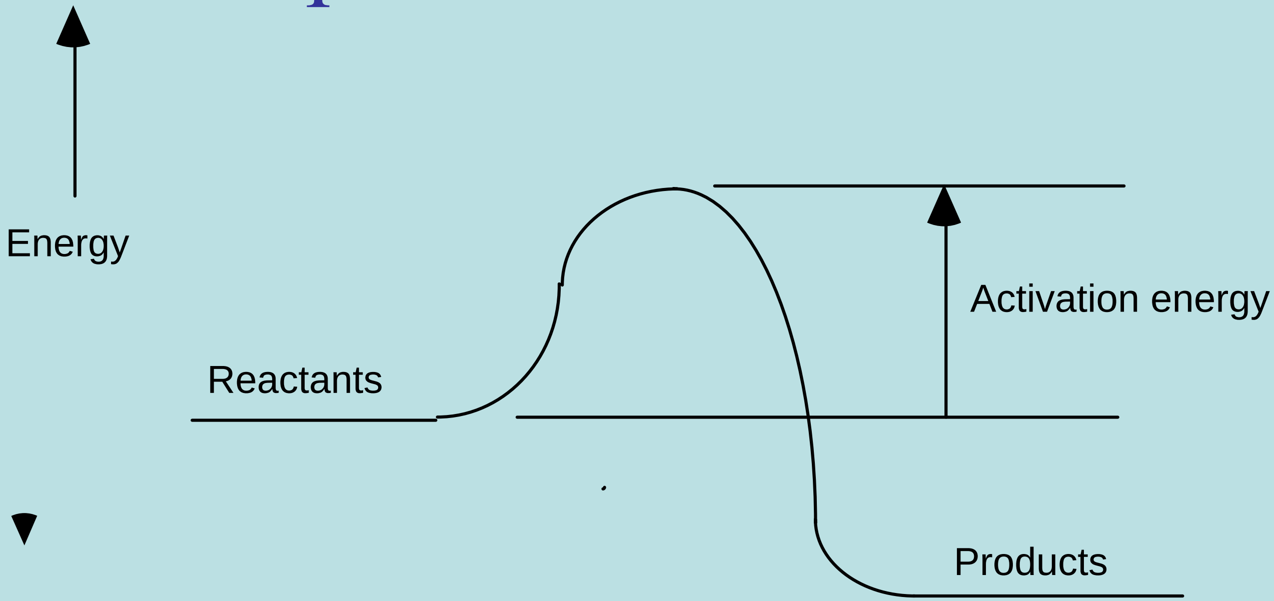
- Elementary bimolecular reaction

  A + B -> AB

- probability of reaction depends on frequency of collision, orientation (random probability), and ability to overcome activation energy threshold

$$\frac{d[AB]}{dt} = k[A][B]$$

Gas phase chemical kinetics II



$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

If E_a is constant:

$$k = Ae^{-E_a/RT} \qquad (Arrhenius\,equation)$$

Example: temperature dependence of rate constant for formation of hydrogen iodide

$$H_2 + I_2 \rightarrow 2\ HI$$

$$d\ HI / dt = [H_2][I_2]\ A\ e^{-E_a/RT}$$

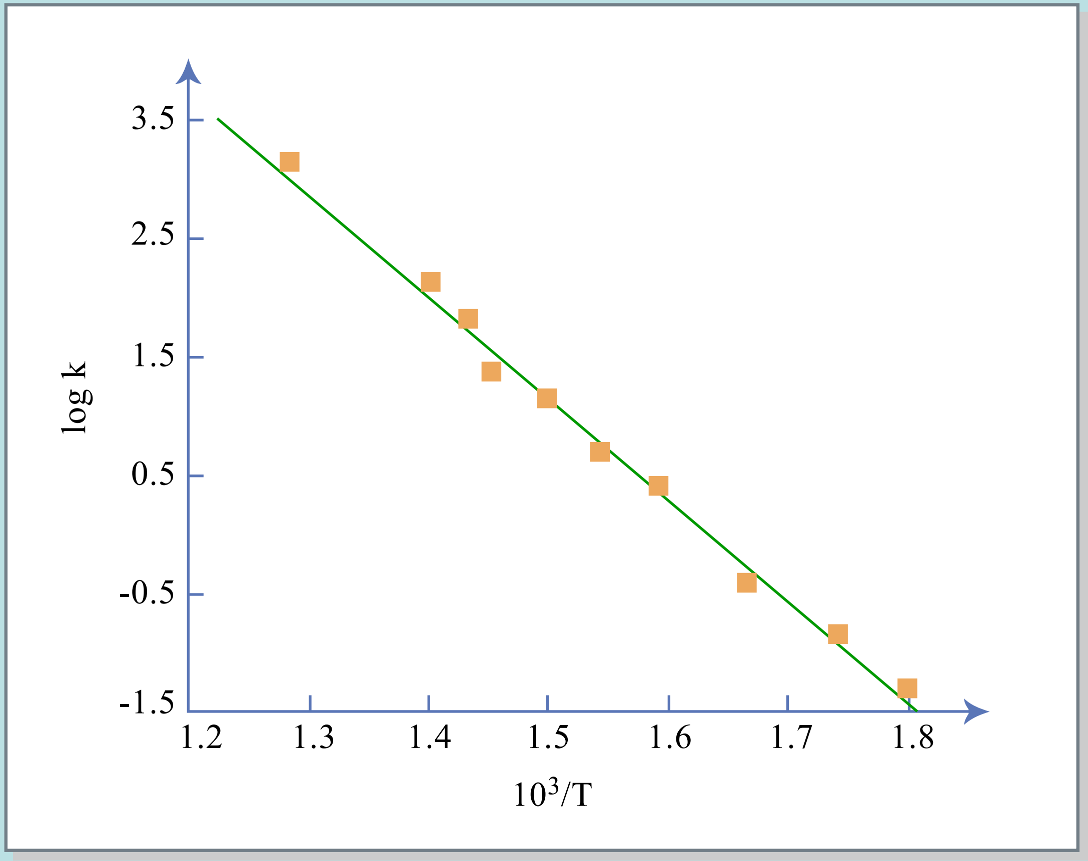


Figure by MIT OCW. Adapted from Moore. *Physical Chemistry*. 3rd ed. (1962): 274.

But things can get complicated: the example of hydrogen bromide

$$H_2 + Br_2 \text{ -> } 2\ HBr$$

Reaction kinetics, as determined by Bedenstein (~1900) :

$$\frac{d[HBr]}{dt} = \frac{k[H_2]\sqrt{[Br_2]}}{M + \frac{[HBr]}{[Br_2]}}$$

The reaction actually proceeds by 5 separate reactions:

Br_2 -> 2 Br

Br + H_2 -> HBr + H

H + Br_2 -> HBr +Br

H + HBr -> H_2 + Br

2 Br + M -> Br_2 + M

Statospheric Ozone - key equations I

A. Ozone production

- 1. $O_2 + h\nu \rightarrow O + O$
- 2. $O + O_2 + M \rightarrow O_3 + M$

(M is some other molecule that acts as a catalyst)

Statospheric Ozone - key equations II

B. Ozone destruction

- 1. O_3 + hv -> O2 + O
- 2. O + O_3 -> 2 O_2 (A1+A2+B1+B2 are sometimes referred to as the Chapman Cycle)
- 3a. O_3 + OH -> HO_2 + O_2
- 3b. HO_2 + O_3 -> OH + 2O_2 (3a and 3b involving OH are part of a more general class of reactions involving "O_X" where "O_X" = HO_x, NO_x, ClO_x)
- 4a. N_2O + hv -> N_2 + O (1D) (most N_2O destruction occurs this way; note that this reaction converts N_2O into forms which do not deplete ozone; O (1D) is an energetically excited oxygen atom)
- 4b. N_2O + O (1D) -> 2 NO (only 5% of N_2O is destroyed this way - but it leads to products that deplete ozone)
- 4c. NO + O_3 -> NO_2 + O_2 (note: NO, NO_2 and NO_3 are collectively referred to as "NO_x": these plus all oxidized nitrogen species of NO_x on relatively short time scales (e.g. N_2O_5, HNO_3) are referred to as "NO_y"

- 4d. O_3 -> O + O_2
- 4e. NO_2 + O -> NO + O_2
- 5a. Cl + O_3 -> ClO + O_2
- 5b. O_3 + hv -> O + O_2
- 5c. ClO + O -> Cl + O_2

Statospheric Ozone - key equations III

B. Ozone destruction (cont'd)

In the presence of ice clouds:

- 6a. $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$
- 6b. $Cl_2 + h\nu \rightarrow 2\ Cl$

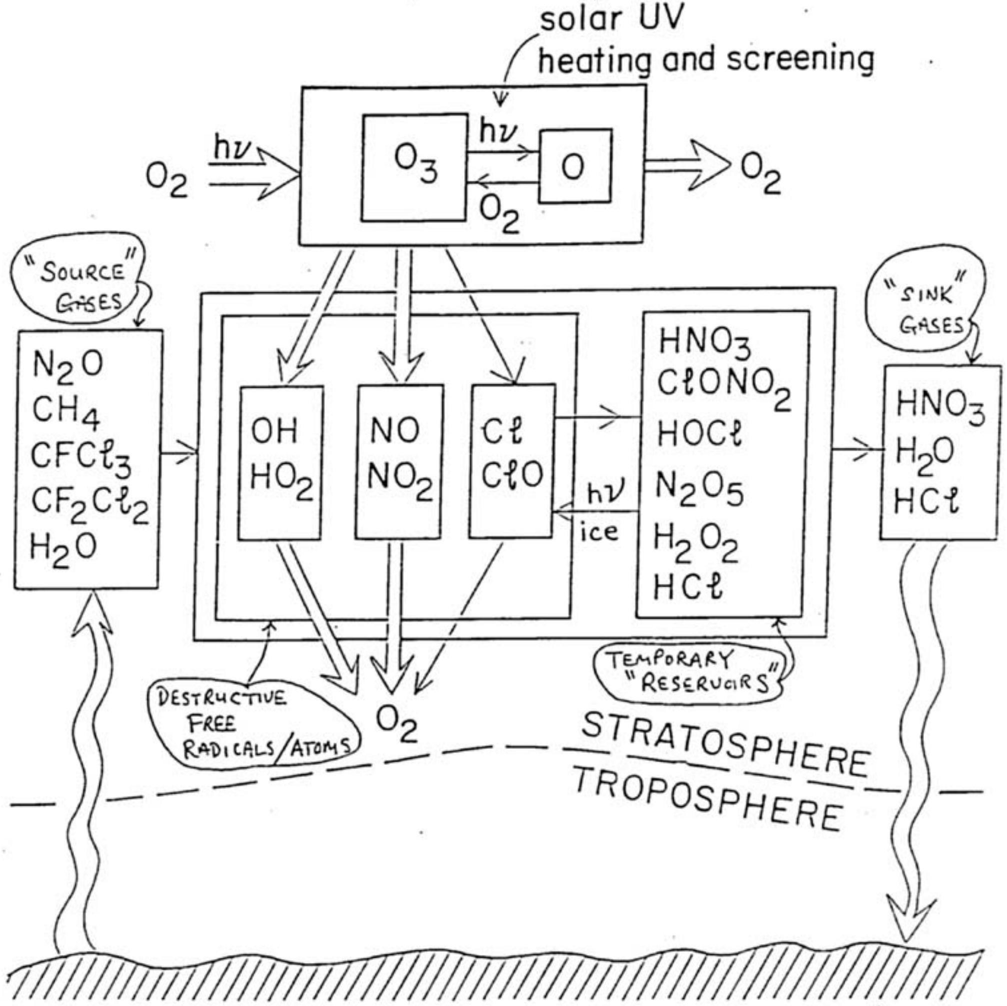
(these are the reactions responsible for the ozone hole)

Source of stratospheric HCl:

- 7. $Cl + CH_4 \rightarrow HCl + CH_3$

OZONE LAYER CHEMISTRY

(simplified!)



CATALYSTS FOR OZONE DESTRUCTION!

	NO_x CYCLE	ClO_x CYCLE	HO_x CYCLE(S)
	$NO + O_3 \rightarrow NO_2 + O_2$	$Cl + O_3 \rightarrow ClO + O_2$	$OH + O_3 \rightarrow HO_2 + O_2$
	$NO_2 + O \rightarrow NO + O_2$	$ClO + O \rightarrow Cl + O_2$	$HO_2 + O \rightarrow OH + O_2$
NET	$O_3 + O \rightarrow O_2 + O_2$	$O_3 + O \rightarrow O_2 + O_2$	$O_3 + O \rightarrow O_2 + O_2$

N_2O (nitrous oxide): Greenhouse gas (and ozone sink)

(no laughing matter)

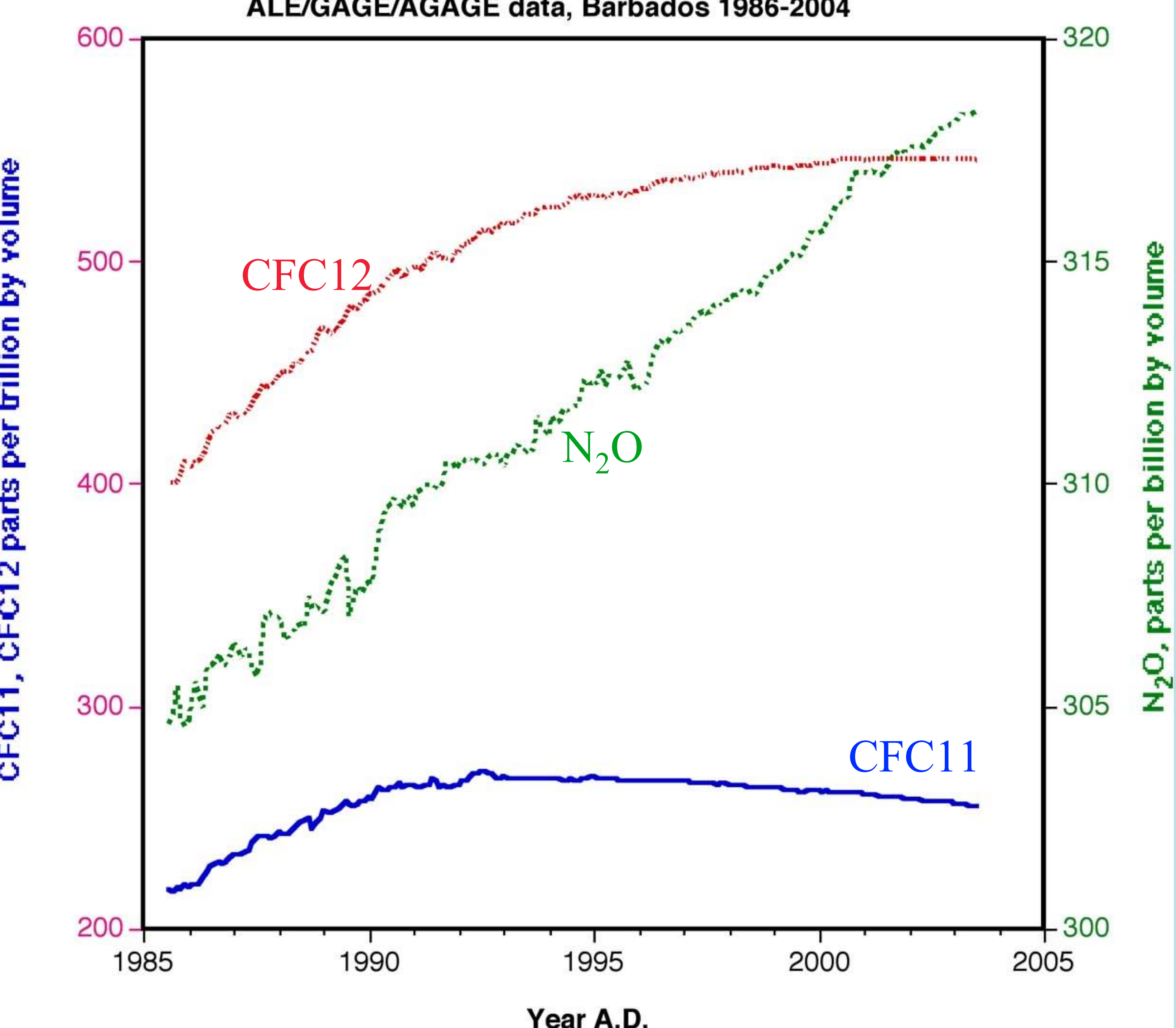
- N_2O is produced from dissolved nitrate by microbes in the earth surface environment:

$$2\ \text{"}CH_2O\text{"} + 2\ NO_3^- + 2\ H^+ \rightarrow N_2O + 2\ CO_2 + 3\ H_2O$$

- Some microbes in the same environment will further reduce N_2O to N_2. However, gaseous N_2O can diffuse out of the environments where this sink reaction can occur, and once it enters the troposphere, it is relatively unreactive.
- The primary sink for tropospheric N_2O is the stratospheric photochemistry. It takes about a century for the troposphere to cycle through the stratosphere, so the residence time of N_2O in the atmosphere is about a century.

$N_2O + h\nu \rightarrow N_2 + O\ (^1D)$ (most N_2O destruction occurs this way; note that this reaction converts N_2O into forms which do not deplete ozone; $O\ (^1D)$ is an energetically excited oxygen atom)

$N_2O + O\ (^1D) \rightarrow 2\ NO$ (only 5% of N_2O is destroyed this way but it leads to products which deplete ozone)



N_2O is increasing with time

N_2O is increasing with time…

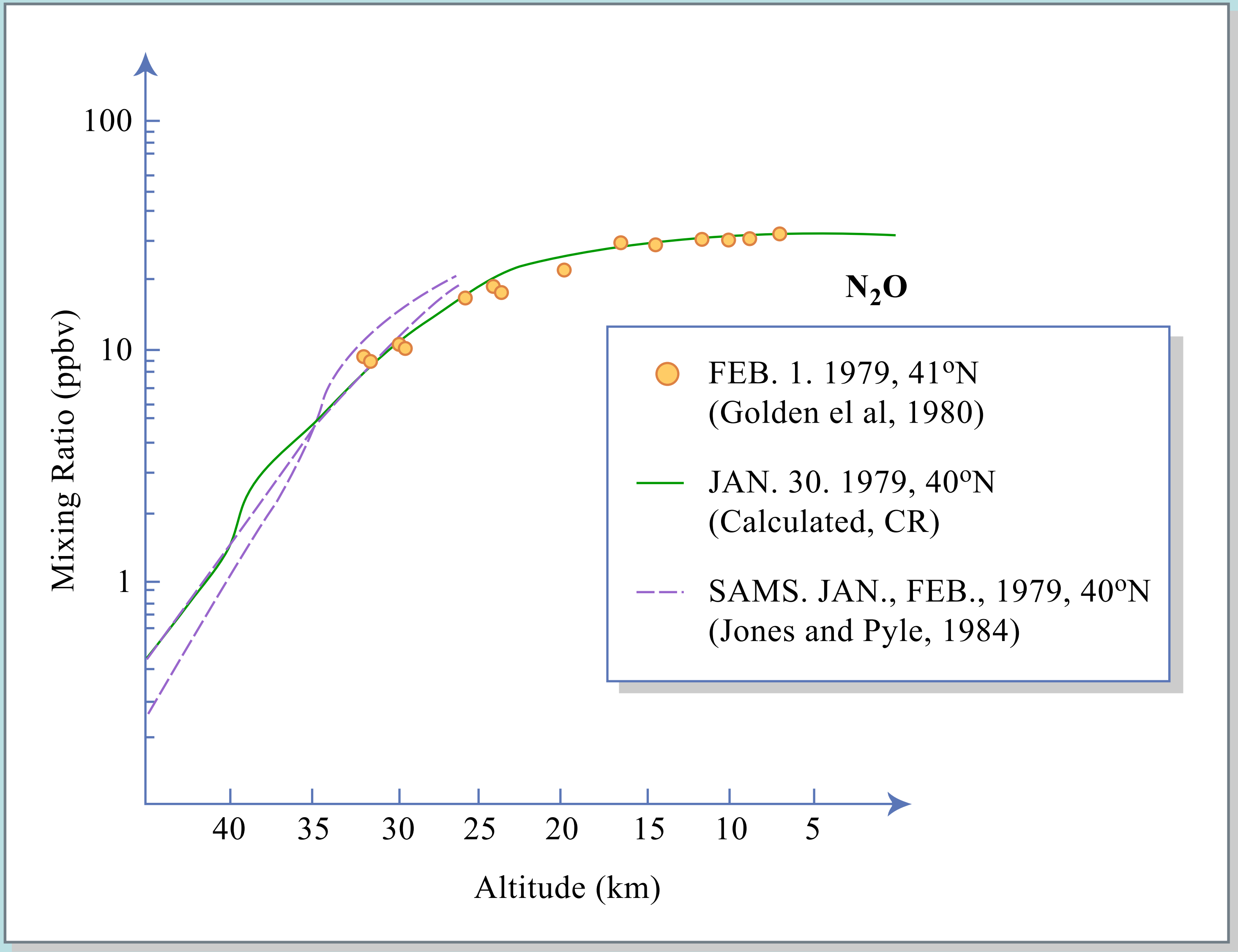
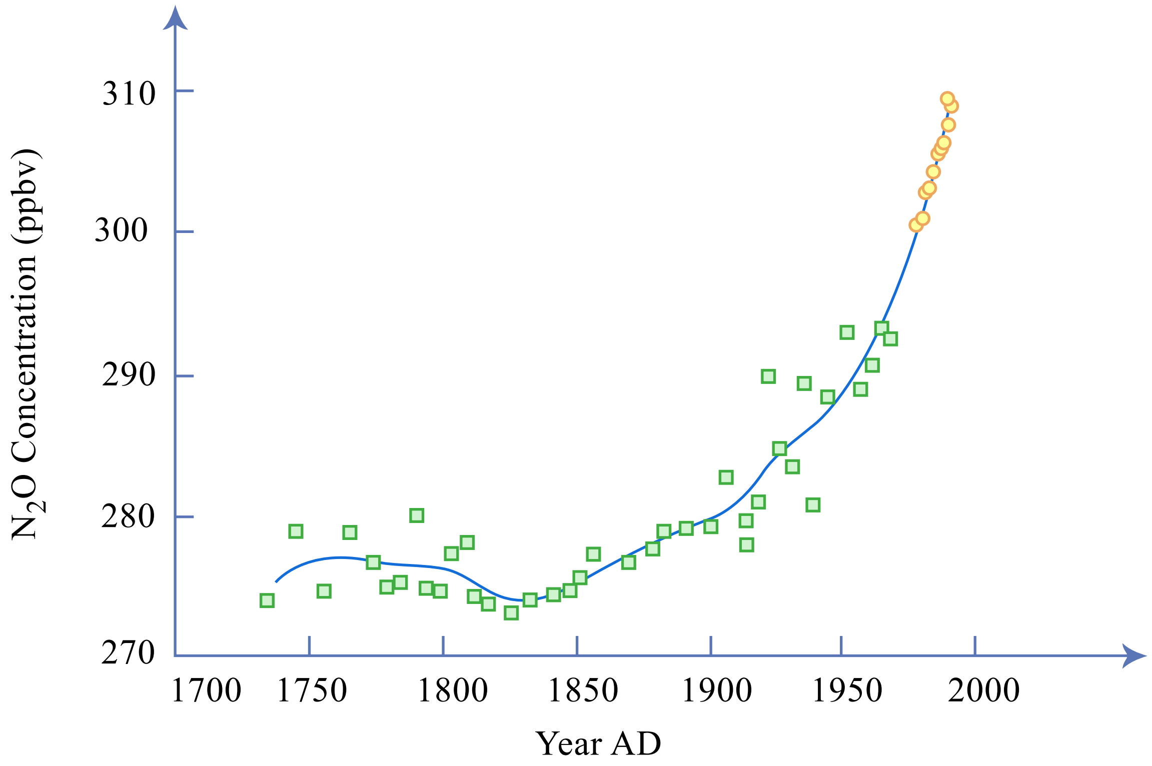


Figure by MIT OCW.

N_2O is a greenhouse gas and contributes to global warming



Atmospheric N_2O concentrations during the last 250 years obtained by analyzing the H15 ice core collected in Antarctica. Measured values are shown by filled squares. Annual mean values of the N_2O concentration at the South Pole for the period 1977-1991 AD are also plotted by circles for reference. Solid curve represents the result obtained by fitting the Reinsch-type cubic spline with a cutoff period of 50 years to the data.

Figure by MIT OCW based on Machida et al., 1995.

But it has also changed before large-scale human activities:

N_2O in a Greenland ice core

Image removed due to copyright restrictions.
Citation: Figure 1. Sower, et al. *Science* 301 (August 15, 2003): 946.

The nitrogen cycle

See image about “The Nitrogen Cycle.” In *Galloway*, 2004.

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Citation: Figure 12.1. Schlesinger, W. T. *Biogeochemistry: An Analysis of Global Change*. San Diego: Academic Press, 1991, p. 443. ISBN: 0126251568.

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Citation: Figure 12.2. Schlesinger, W. T. *Biogeochemistry: An Analysis of Global Change*. San Diego: Academic Press, 1991, p. 443. ISBN: 0126251568.

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Citation: Figure 4. Ambio, J. *Galloway* 31 (March 2002): 2.

Fertilizer production

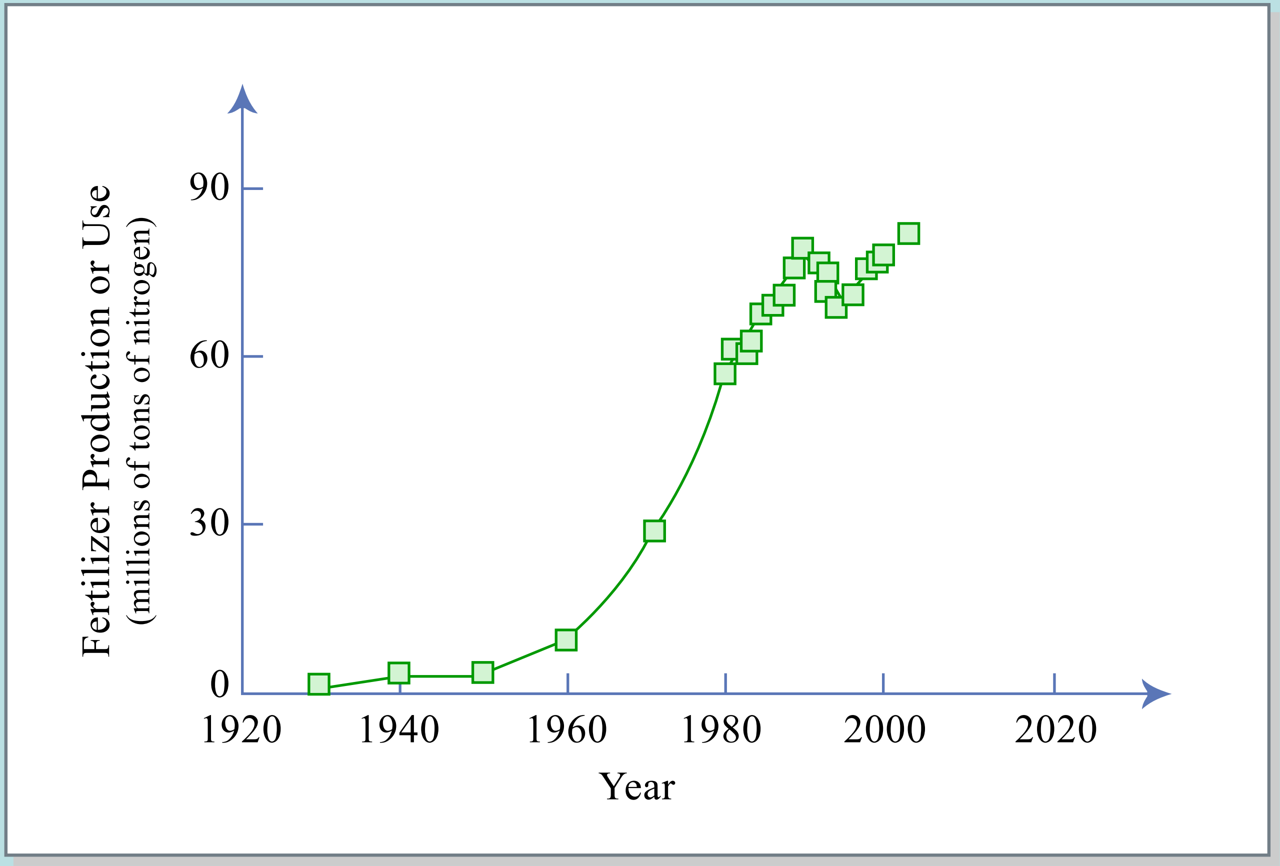

Figure by MIT OCW based on Physics Today.

Nitrate in a Greenland ice core

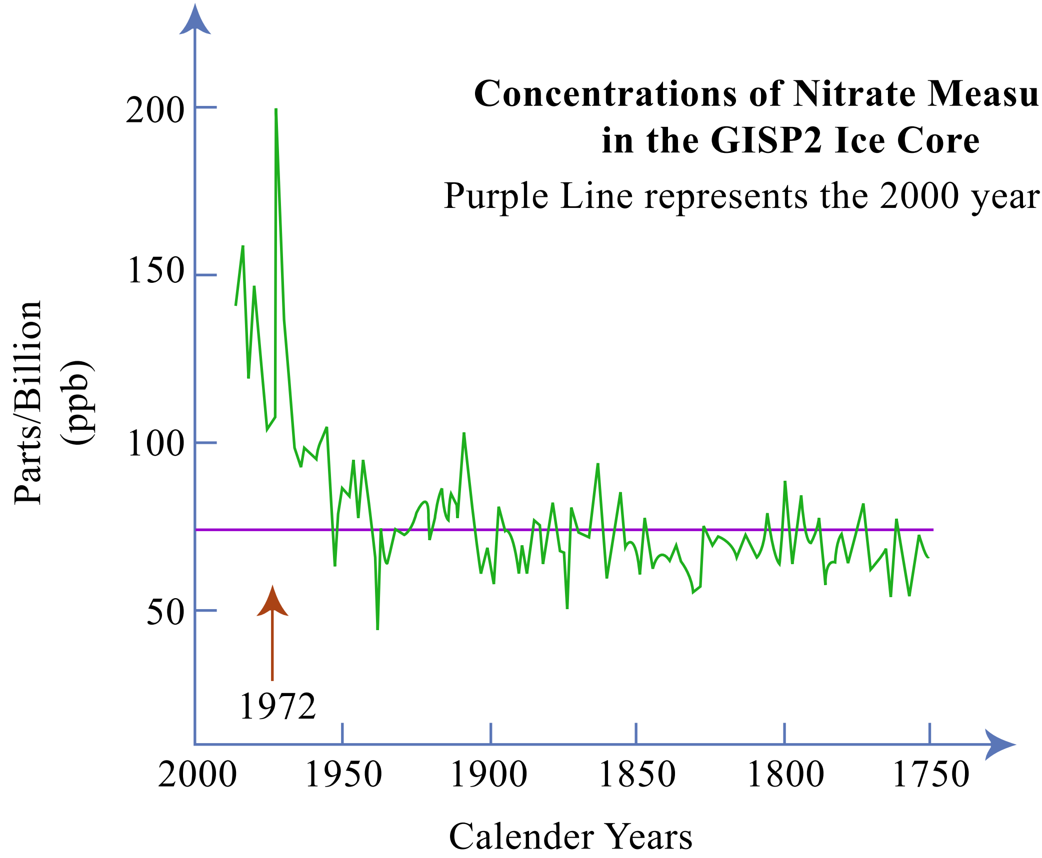

Figure by MIT OCW based on Mauewski et al., 1990 and Zielinski et al., 1994.

NH_4^+ (ammonium) in an Alpine ice core

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Citation: Figure 1a. Alpine NH3 1800-present. Doscher, A., et al. “A Historical Record of Ammonium Concentrations from a Glacier in the Alps.” *Geophys Res Lett* 23 (1996): 2741-2744.

ESTIMATED SOURCES AND SINKS OF N_2O TYPICAL OF THE LAST DECADE (Tg(N)/yr)

	Range of Estimates	Most Likely Value
Increase in Atmosphere	3.1 - 4.7	3.9#
Sinks		
Stratosphere ($N_2O + h \rightarrow N_2 + O$)	9 - 16	12.3
Soils	?	
Total Sinks	9 - 16	12.3
Implied Total Sources (atmospheric increase + total sinks)	13 - 20	16.2

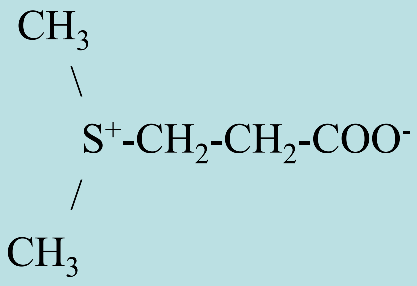
Known Sources	Range of estimates	Most Likely Value
Natural		
Oceans	1 - 5	3
Tropical Soils		
Wet Forests	2.2 - 3.7	3
Dry Savannas	0.5 - 2.0	1
Temperate Soils		
Forests	0.1 - 2.0	1
Grasslands	0.5 - 2.0	1
Total Known Natural Sources	6 - 12	9
Anthropogenic		
Cultivated Soils	1.8 - 5.3	3.5
Biomass Burning	0.2 - 1.0	0.5
Industrial Sources	0.7 - 1.8	1.3
Cattle and Feed Lots	0.2 - 0.5	0.4
Total Known Anthropogenic	3.7 - 7.7	5.7
KNOWN SOURCE TOTALS	10 - 17	14.7

The observed atmospheric increase implies that sources exceed sinks by 3.9 Tg(N)/yr.

Figure by MIT OCW.

Dimethyl sulfide and climate

- A. Marine organisms (e.g. coccolithophorids, single-celled plants) produce DMSP (dimethylsulfoniopropionate):



$$(CH_3)_2S^+\text{-}CH_2\text{-}CH_2\text{-}COO^-$$

DMSP

  This compound is converted to DMS $[(CH_3)_2S]$ when the cell is destroyed and the cell contents are degraded.
- B. DMS is volatile and moves into the atmosphere by gas exchange.
- C. DMS is oxidized in the atmosphere to two byproducts with a "branch ratio": sulfuric acid (H_2SO_4) and methanesulfonic acid (MSA: CH_3SO_3H). Cycle is complex with many intermediates; branch ratio appears to depend mainly on temperature (low MSA:nss$SO_4^=$ at warmer temperatures)
- D. The products are transported to ice cores and recorded there as non-sea-salt sulfate (nss $SO_4^=$) and MSA.
- E. The non-sea-salt sulfate, (initially sulfuric acid but later reacted with sea salt particles and mineral aerosols) forms particles that act as cloud condensation nuclei (CCN). In areas that are far from land, these CCN can be an important factor regulating cloud formation and rainfall. Some people have hypothesized a feedback between DMS and climate.

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Citation: See the image about concentration of DMS in seawater published on Woods Hole Notes by John W. H. Dacey, Woods Hole Oceanographic Institution.