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12.842 / 12.301 Past and Present Climate
Fall 2008

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12.842

Climate Physics and Chemistry

Fall 2008

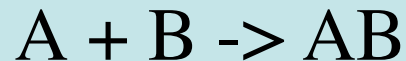
Atmospheric Chemistry I:
Ozone, Chlorofluorocarbons,
Nitrogen Oxides, and Dimethyl Sulfide

A brief history of the atmospheric chemistry of O₃, 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 ozone layer.
- 1971: Crutzen shows that dominant source of NO_x in stratosphere is transport of N₂O released from biosphere.
- Harold Johnston suggests that nitrogen oxides released by supersonic transports might affect ozone layer (but US SST rejected on economic grounds 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. This event was not predicted by Molina-Rowland model.
- Ozone hole intensity continues to increase, with Antarctic ozone virtually disappearing at 15-21 km altitude every spring. 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

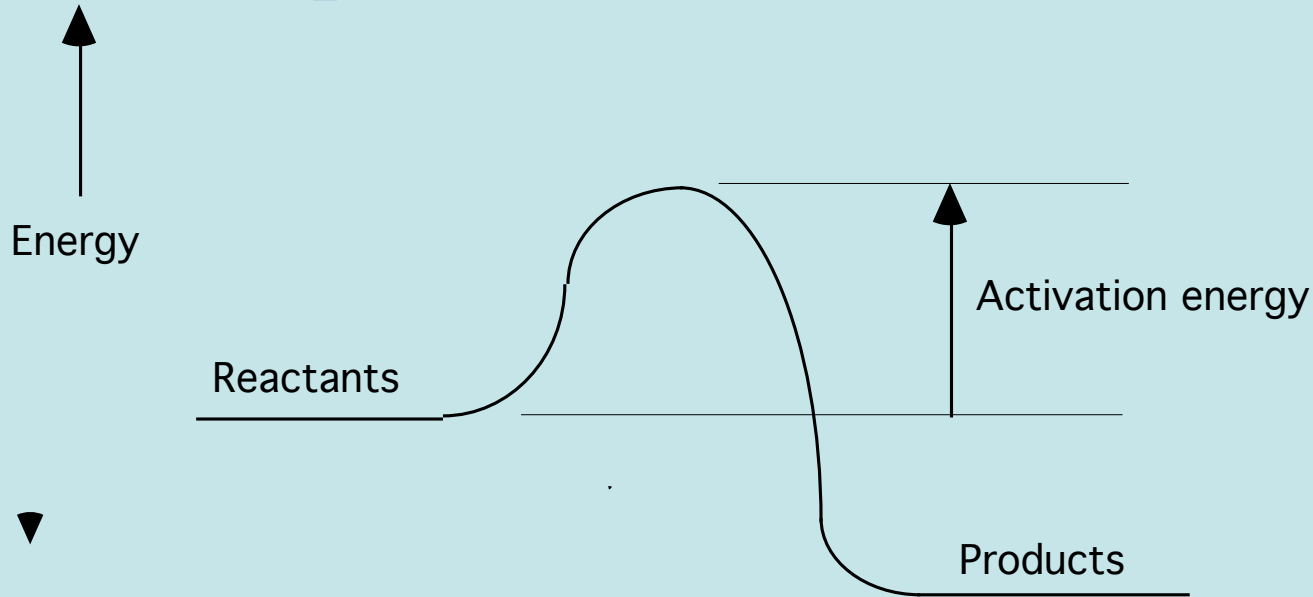
- Elementary bimolecular reaction



- 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

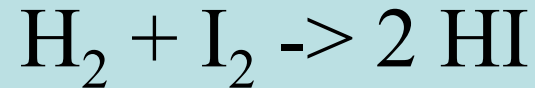


$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

If E_a is constant:

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

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



$$\frac{d \text{HI}}{dt} = [\text{H}_2][\text{I}_2] A e^{-E_a/RT}$$

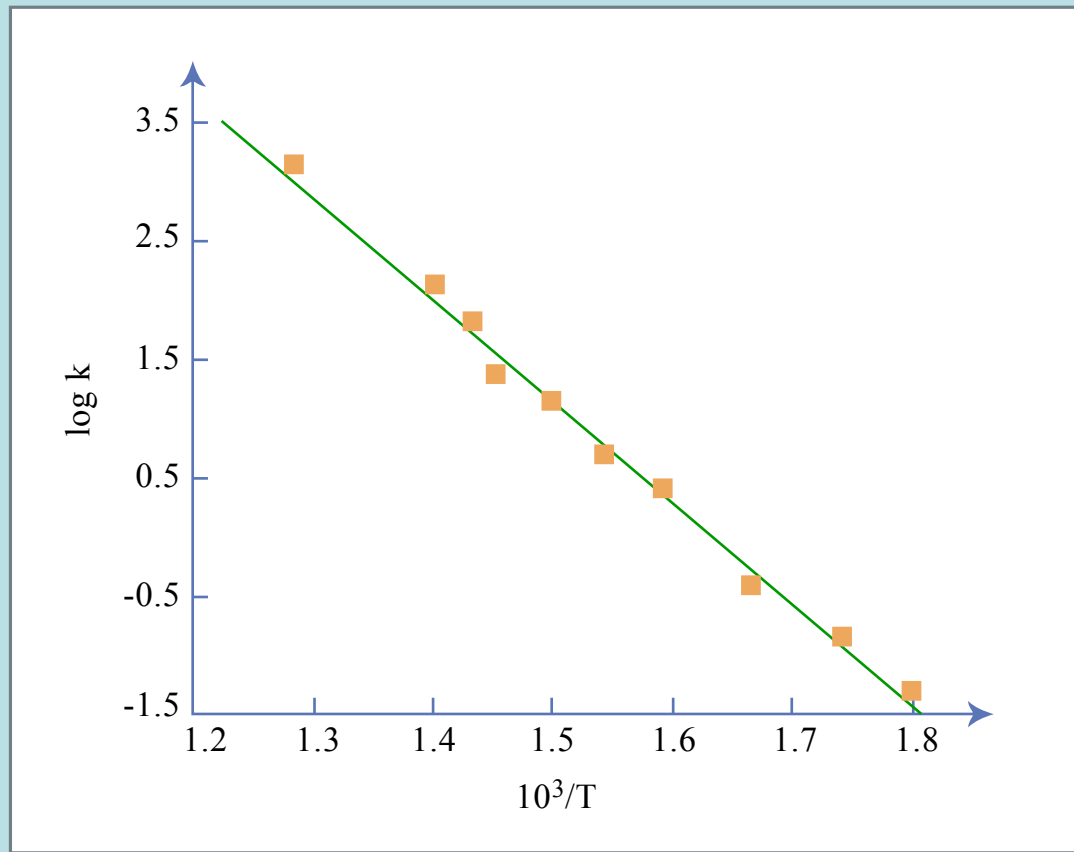
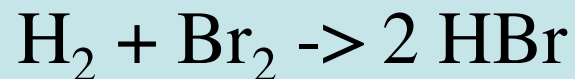


Figure by MIT OpenCourseWare. Adapted from Moore. *Physical Chemistry*. 3rd ed. (1962): 274.

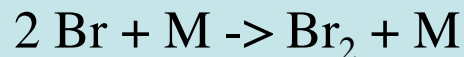
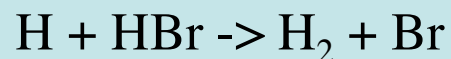
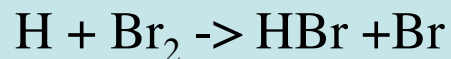
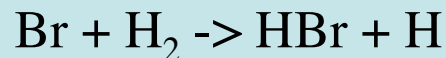
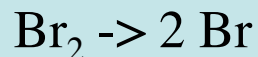
But things can get complicated:
the example of hydrogen bromide



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

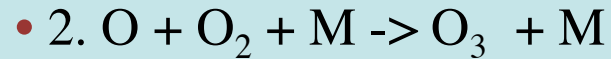
$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2]\sqrt{[\text{Br}_2]}}{M + \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

The reaction actually proceeds by 5 separate reactions:



Stratospheric Ozone - key equations I

A. Ozone production



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

Stratospheric Ozone - key equations II

B. Ozone destruction

- 1. $O_3 + h\nu \rightarrow O_2 + O$
- 2. $O + O_3 \rightarrow 2 O_2$ (A1+A2+B1+B2 are sometimes referred to as the Chapman Cycle)
- 3a. $O_3 + OH \rightarrow HO_2 + O_2$
- 3b. $HO_2 + O_3 \rightarrow OH + 2O_2$ (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. $N_2O + h\nu \rightarrow N_2 + O(1D)$ (most N₂O destruction occurs this way; note that this reaction converts N₂O into forms which do not deplete ozone; O(1D) is an energetically excited oxygen atom)
- 4b. $N_2O + O(1D) \rightarrow 2 NO$ (only 5% of N₂O is destroyed this way - but it leads to products that deplete ozone)
- 4c. $NO + O_3 \rightarrow NO_2 + O_2$ (note: NO, NO₂ and NO₃ are collectively referred to as "NO_x": these plus all oxidized nitrogen species of NO_x on relatively short time scales (e.g. N₂O₅, HNO₃) are referred to as "NO_y")
- 4d. $O_3 \rightarrow O + O_2$
- 4e. $NO_2 + O \rightarrow NO + O_2$
- 5a. $Cl + O_3 \rightarrow ClO + O_2$
- 5b. $O_3 + h\nu \rightarrow O + O_2$
- 5c. $ClO + O \rightarrow Cl + O_2$

Stratospheric Ozone - key equations III

B. Ozone destruction (cont'd)

In the presence of ice clouds:

- 6a. $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$
- 6b. $\text{Cl}_2 + h\nu \rightarrow 2 \text{Cl}$

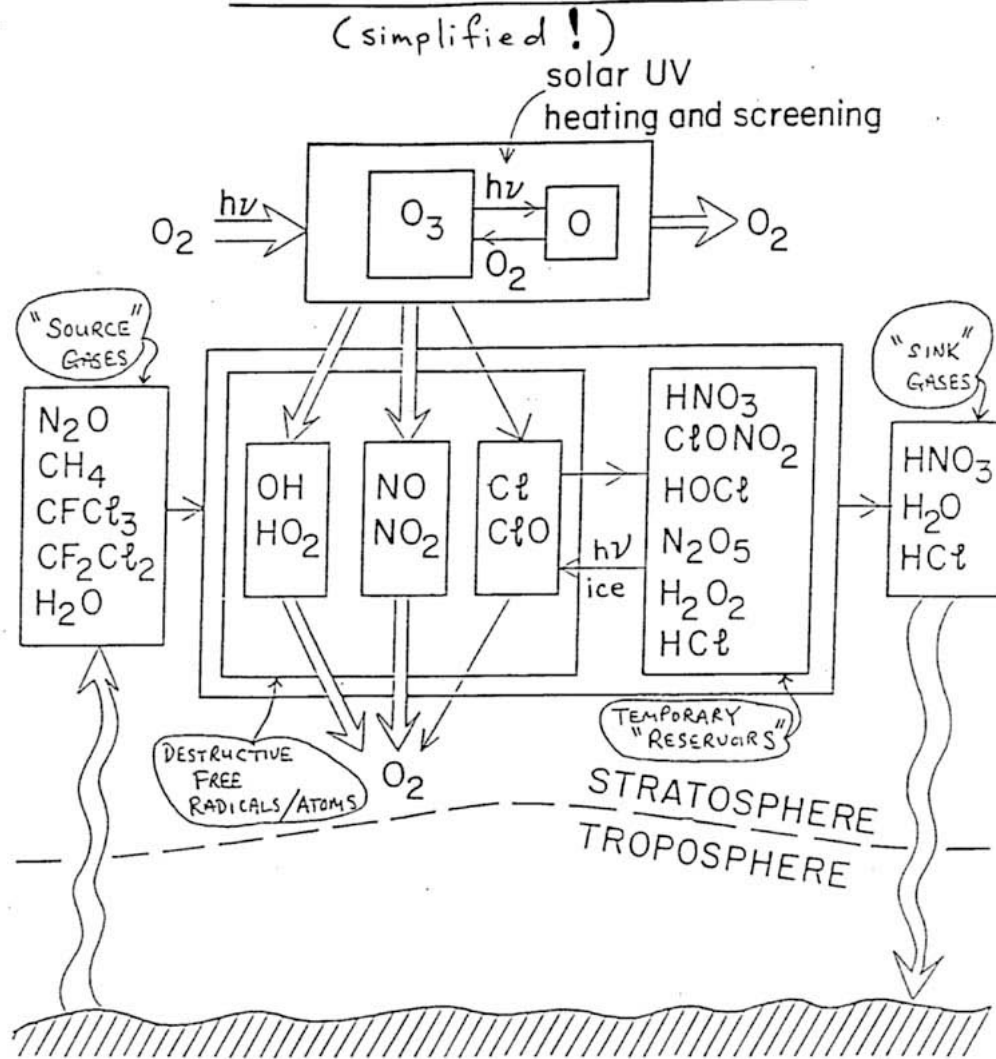
(these are the reactions responsible for the ozone hole)

Source of stratospheric HCl:

- 7. $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$

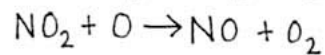
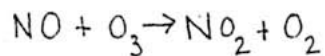
OZONE LAYER CHEMISTRY

(simplified!)

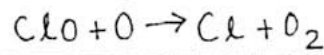
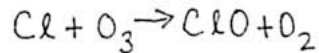


CATALYSTS FOR OZONE DESTRUCTION!

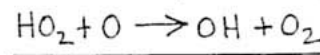
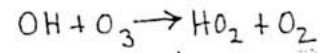
NO_x CYCLE



ClO_x CYCLE



HO_x CYCLE(S)



N₂O (nitrous oxide): Greenhouse gas (and ozone sink)

(no laughing matter)

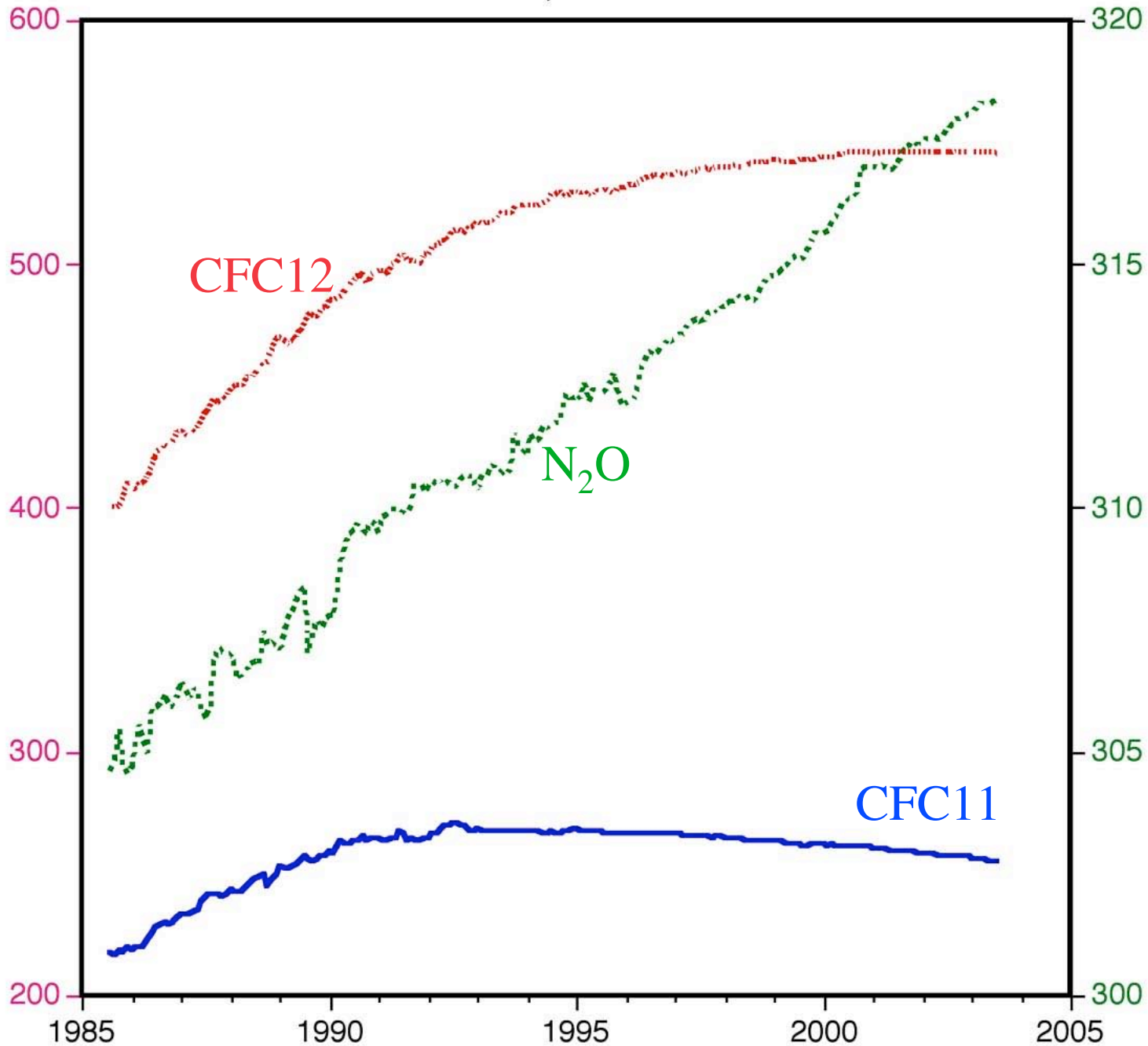
- N₂O is produced from dissolved nitrate by microbes in the earth surface environment:
$$2 \text{ "CH}_2\text{O" } + 2 \text{ NO}_3^- + 2 \text{ H}^+ \rightarrow \text{N}_2\text{O} + 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$$
- Some microbes in the same environment will further reduce N₂O to N₂. However, gaseous N₂O 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 N₂O is the stratospheric photochemistry. It takes about a century for the troposphere to cycle through the stratosphere, so the residence time of N₂O in the atmosphere is about a century.

$\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O} (^1\text{D})$ (most N₂O destruction occurs this way; note that this reaction converts N₂O into forms which do not deplete ozone; O (¹D) is an energetically excited oxygen atom)

$\text{N}_2\text{O} + \text{O} (^1\text{D}) \rightarrow 2 \text{ NO}$ (only 5% of N₂O is destroyed this way - but it leads to products which deplete ozone)

ALE/GAGE/AGAGE data, Barbados 1986-2004

CFC11, CFC12 parts per billion by volume



CFC12

N₂O

CFC11

N₂O is increasing with time

N_2O is increasing with time...

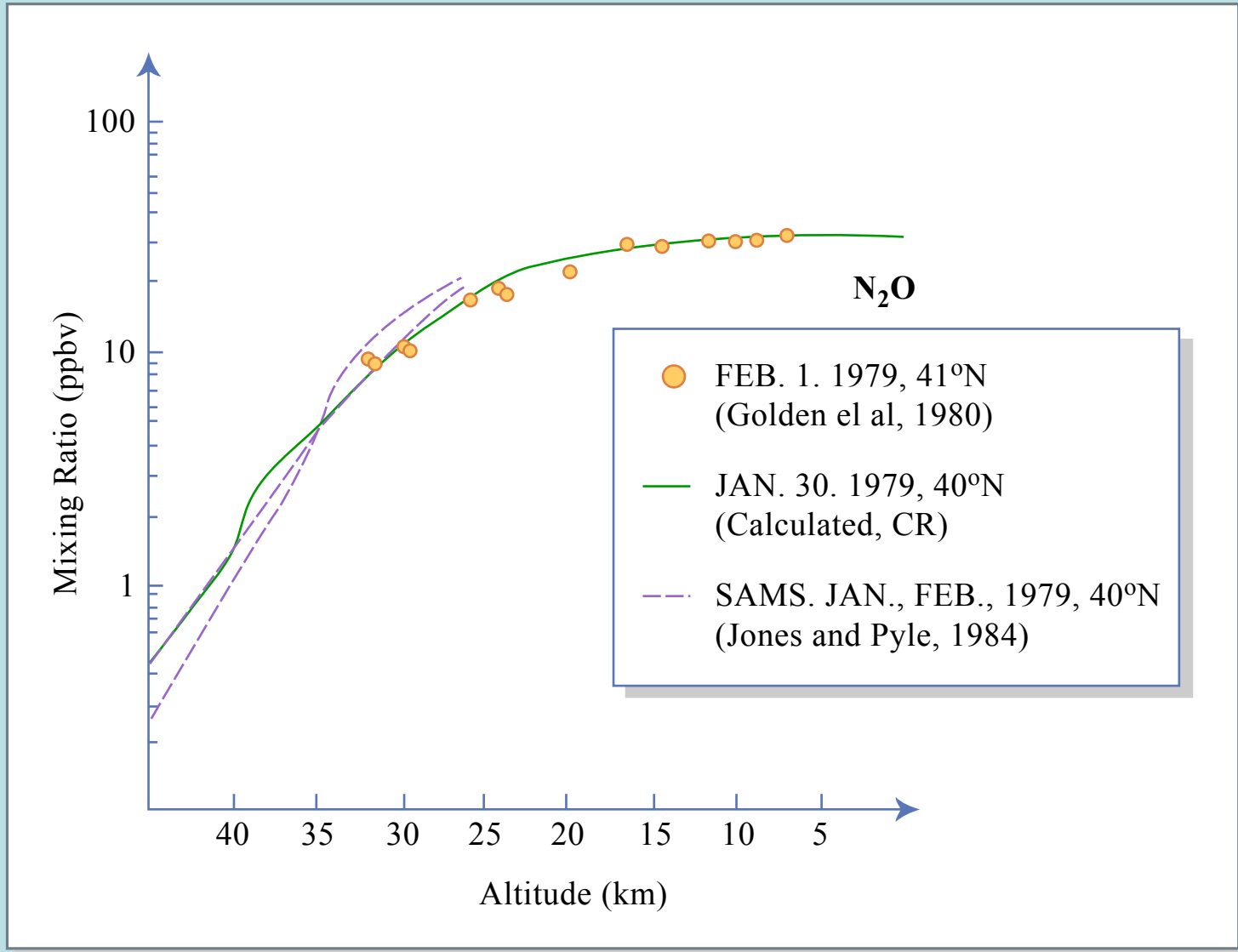
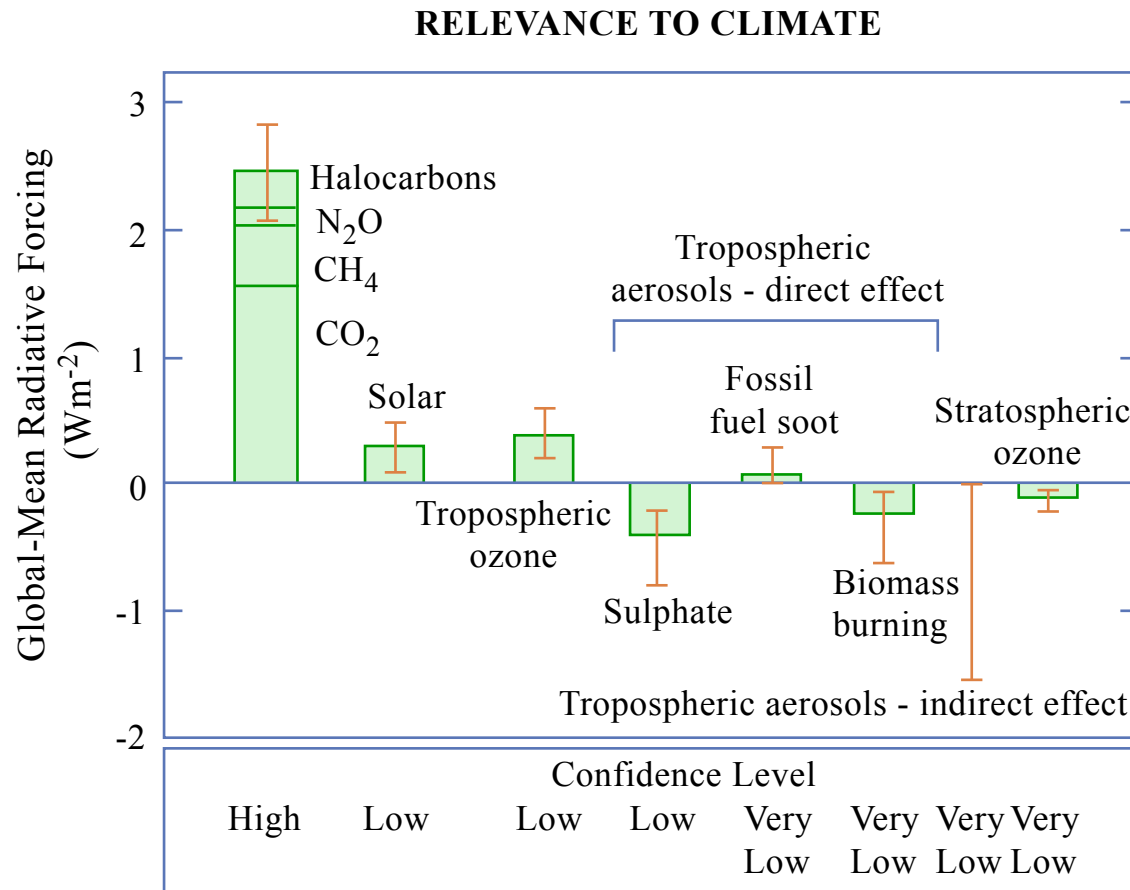


Figure by MIT OpenCourseWare.

Methane is a strong greenhouse gas and contributes to global warming



Estimates of the globally and annually averaged anthropogenic radiative forcing (in Wm⁻²) due to changes in concentrations of greenhouse gases and aerosols from pre-industrial times to the present day and to natural changes in solar output from 1850 to the present day.

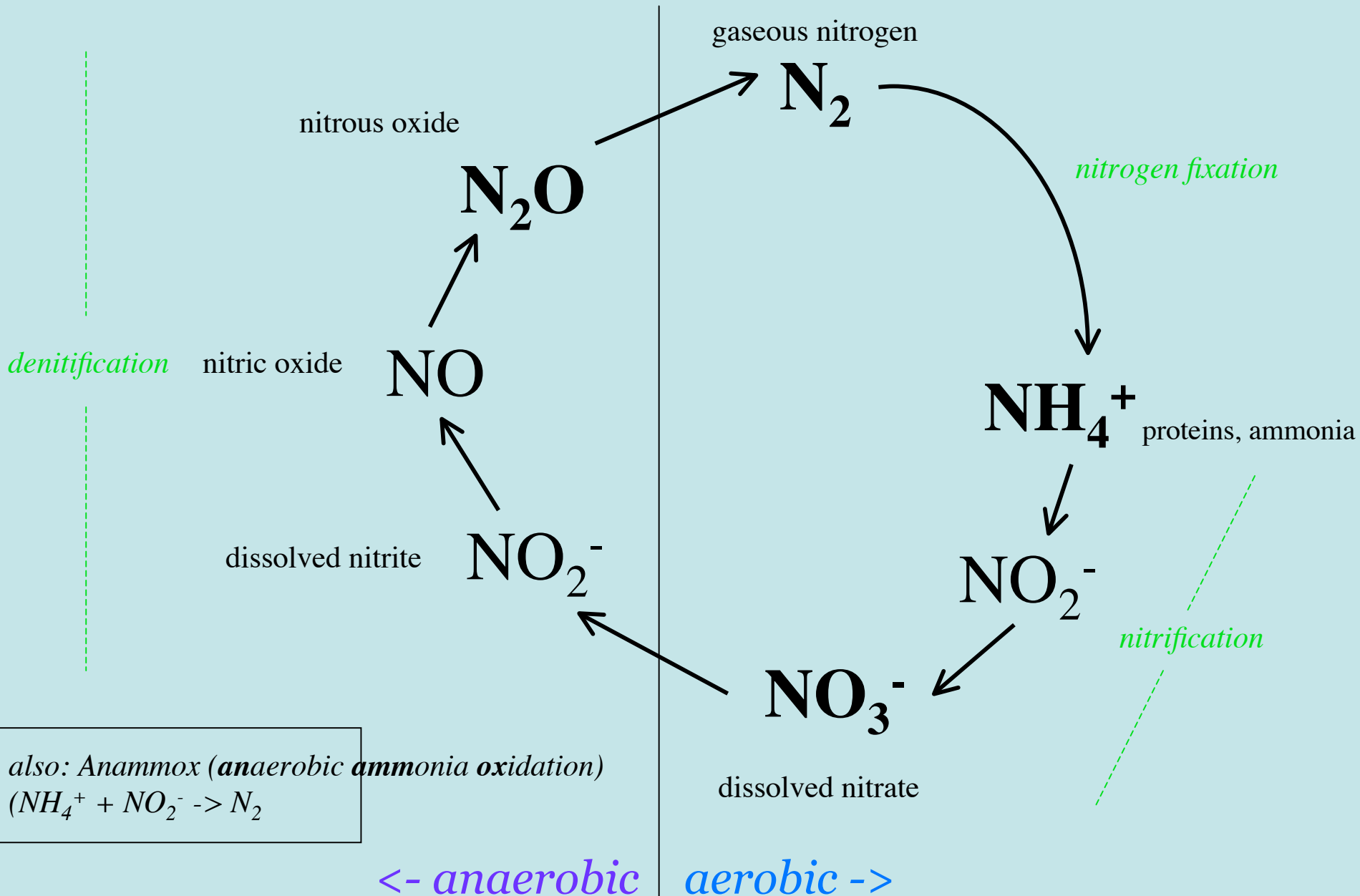
But it has also
changed before large-
scale human
activities:

N₂O 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



The nitrogen cycle

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

Image removed due to copyright restrictions.

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

Image removed due to copyright restrictions.

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

Human perturbations of the nitrogen cycle:

- High temperature (and sometimes pressure) combustion converts N_2 into nitrogen oxides
- Production of nitrogen fertilizers, release into the environment
- Sewage inputs of fixed nitrogen
- High-nutrient environments lead to oxygen depletion (eutrophication), e.g. “dead zone” on Mississippi coast; this environment leads to denitrification.

Image removed due to copyright restrictions.

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

Fertilizer production

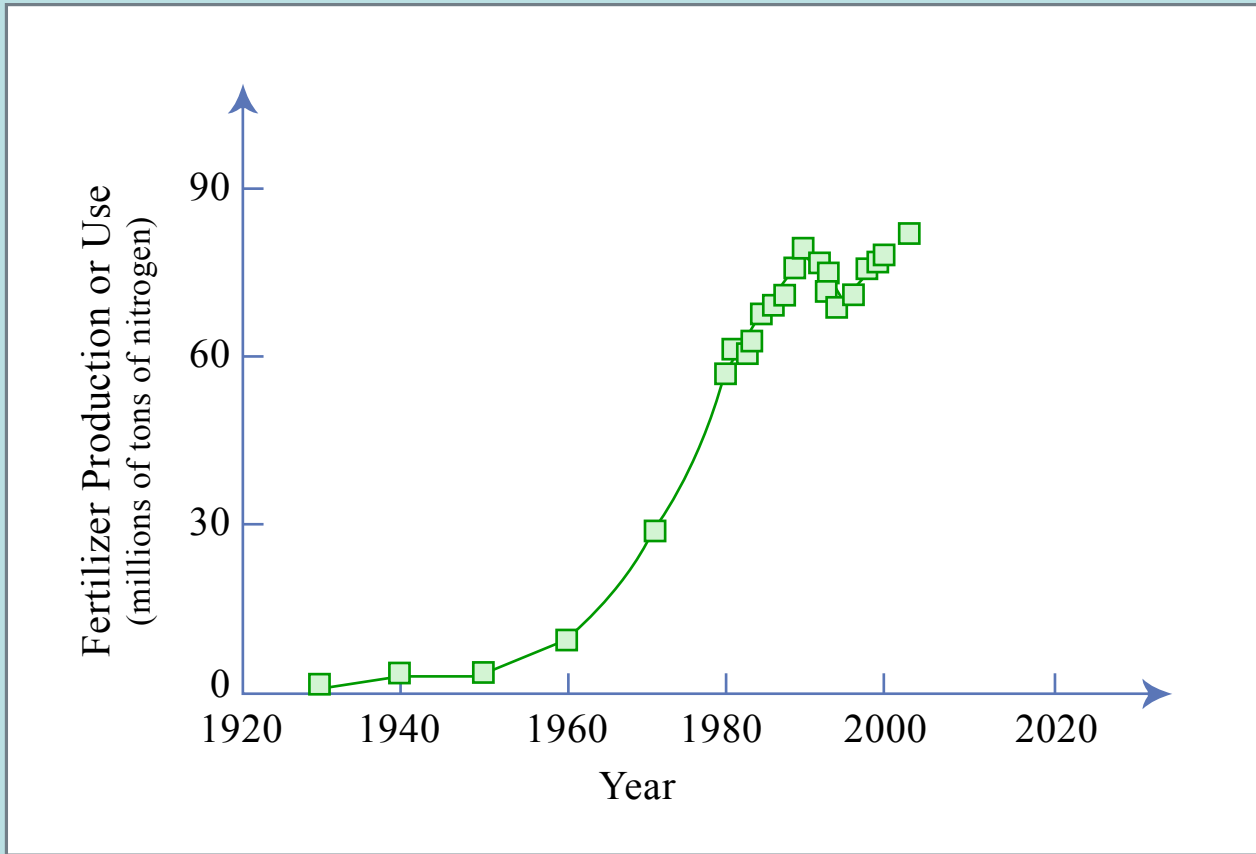


Figure by MIT OpenCourseWare based on *Physics Today*

Nitrate in a Greenland ice core

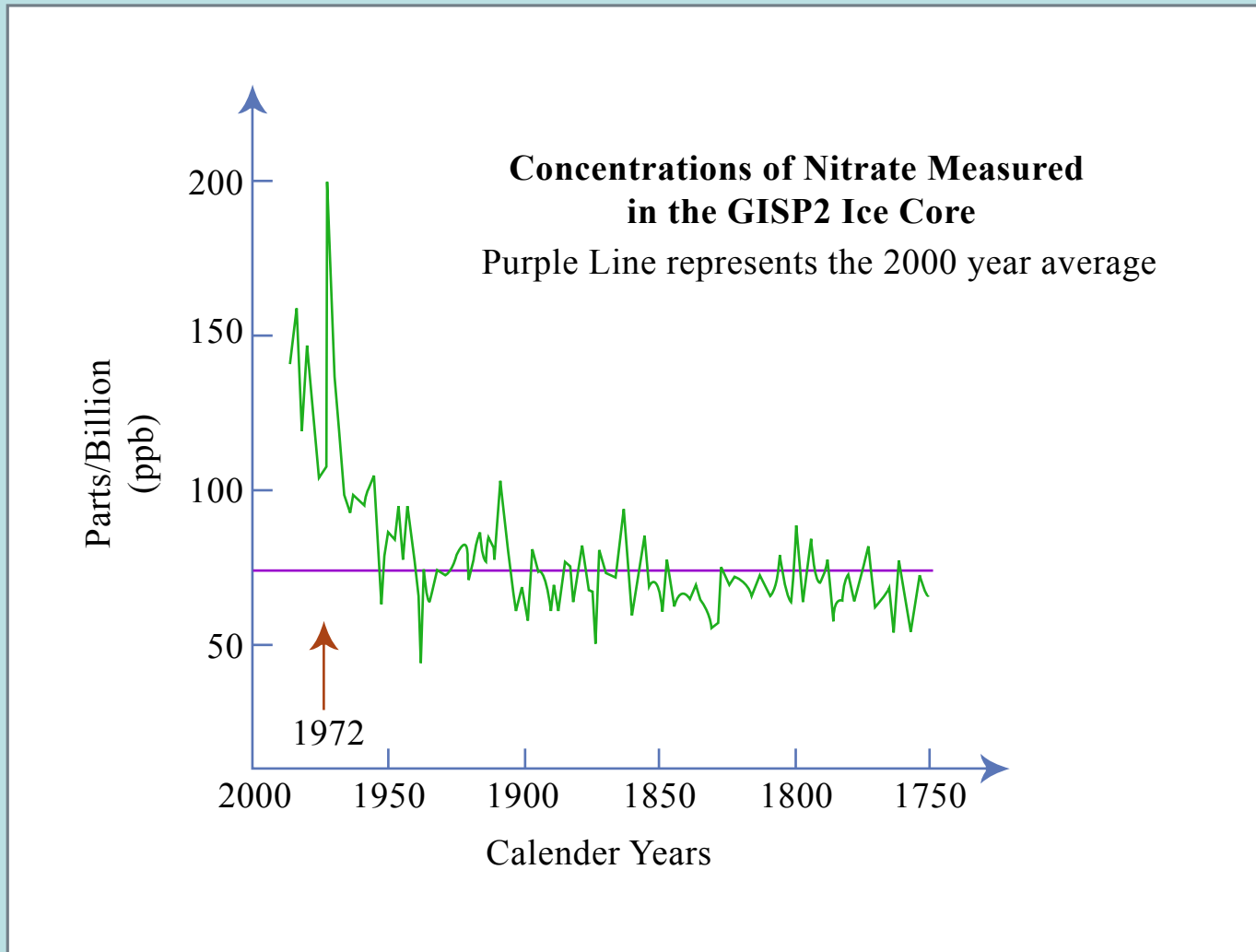


Figure by MIT OpenCourseWare based on Mauwewski et al., 1990 and Zielinski et al., 1994.

NH_4^+ (ammonium) in an Alpine ice core

Image removed due to copyright restrictions.

Citation: Figure 1a. Alpine NH_3 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 N₂O TYPICAL OF THE LAST DECADE (Tg(N)/yr)

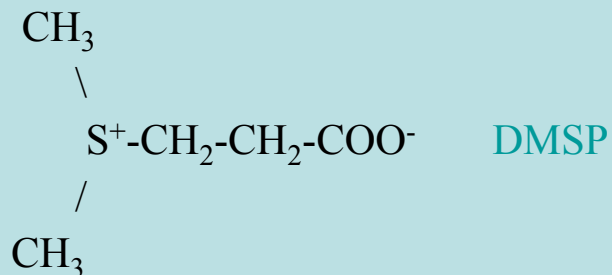
	Range of Estimates	Most Likely Value
Increase in Atmosphere	3.1 - 4.7	3.9 [#]
Sinks		
Stratosphere (N ₂ O + h → N ₂ + O)	9 - 16	12.3
Soils	?	
Total Sinks	9 - 16	12.3
Implied Total Sources (atmospheric increase + total sinks)	13 - 20	16.2

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.

Dimethyl sulfide and climate

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



This compound is converted to DMS $[(\text{CH}_3)_2\text{S}]$ 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: $\text{CH}_3\text{SO}_3\text{H}$). 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.

Image removed due to copyright restrictions.

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