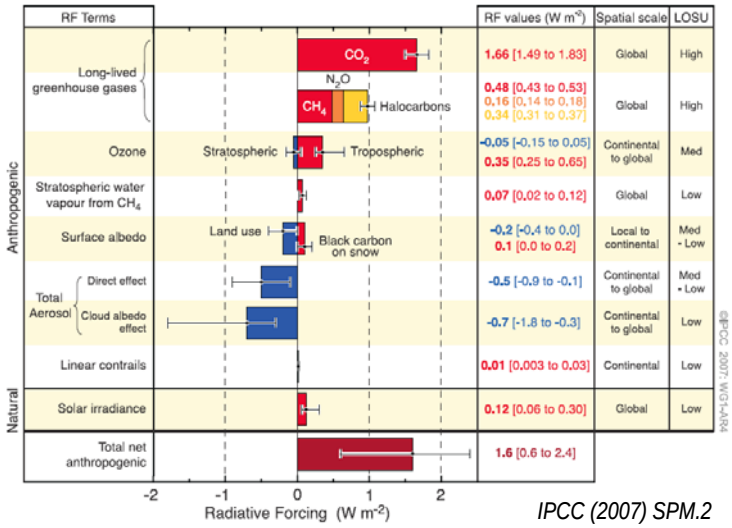
The next 2 weeks

- Th. Jan 15: non-CO_2 greenhouse gases CH_4 and N_2O
- Tu. Jan 20: non-CO_2 greenhouse gases: ozone, halocarbons
- Th. Jan 22: Aerosols and Climate
- Tu. Jan 27: Paper discussion

Reading: IPCC (2007), Chap 7 (sections 7.4 and 7.5)

Centuries
Decades
Months/Weeks
Weeks/Days



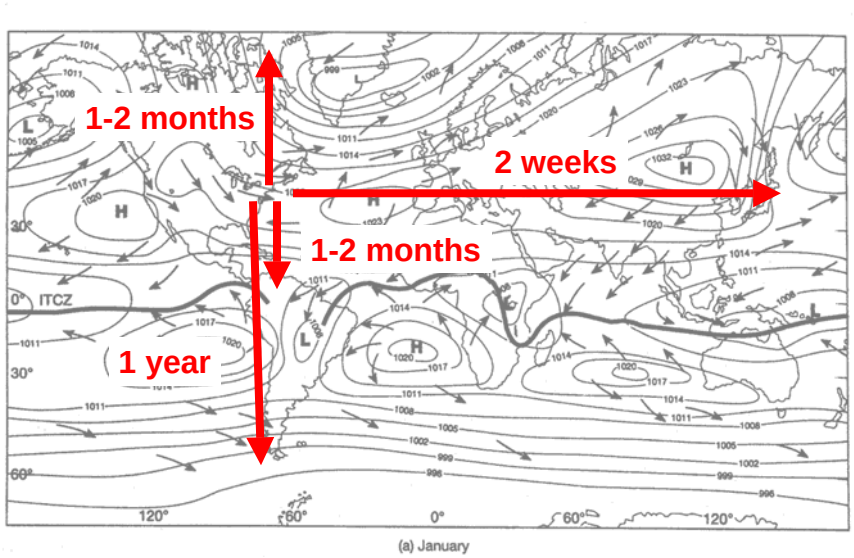
IPCC (2007) SPM.2

Radiative forcing for 2005 relative to 1750:

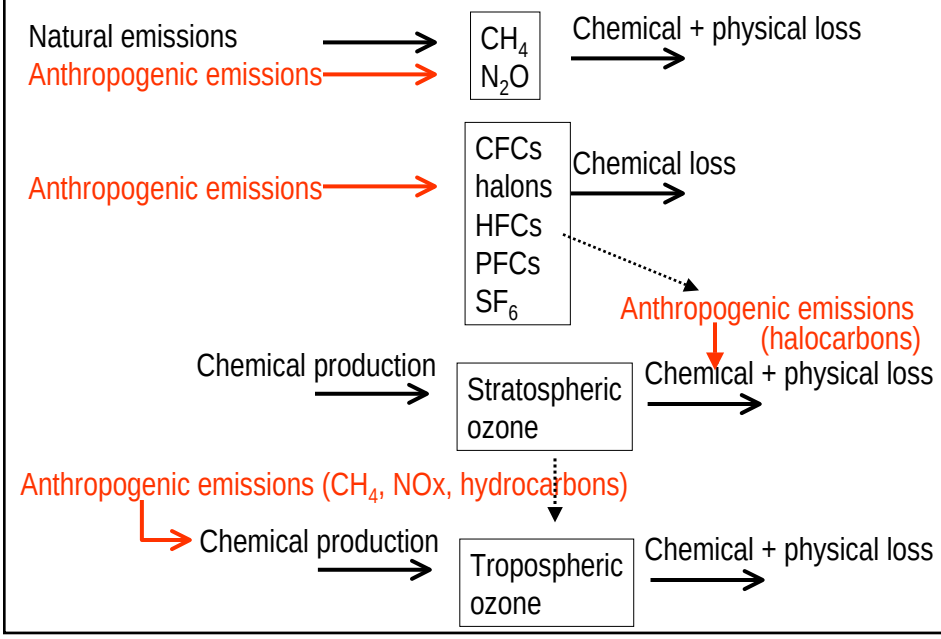
→ CO_2 = 1.66 W/m^2

→ CH_4+N_2O+halocarbons+tropospheric ozone–stratospheric ozone =
0.48 + 0.16 + 0.34 + 0.35 – 0.05 = 1.28 W/m^2

TIME SCALES FOR HORIZONTAL TRANSPORT

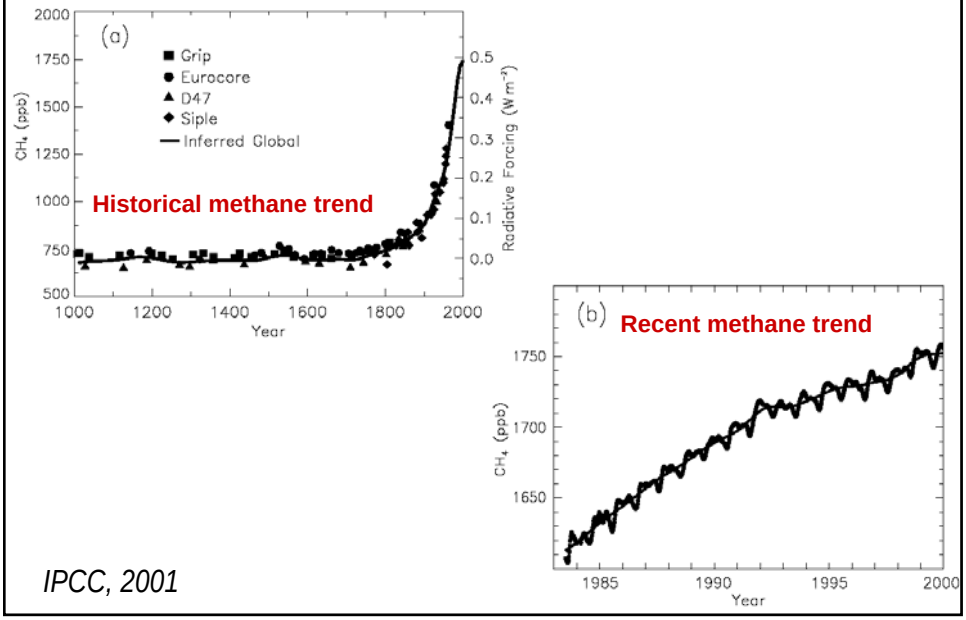


Atmospheric Chemistry and Greenhouse Gases



Human influence on Methane

Increase from 700 ppb → 1770 ppb



IPCC, 2001

Biological formation of methane

- Anaerobic decomposition of organic material by methanogenic bacteria (flooded soils, wetlands, landfills, digestive tracts..)

  $CH_2O \rightarrow ½\ CH_4 + ½\ CO_2$

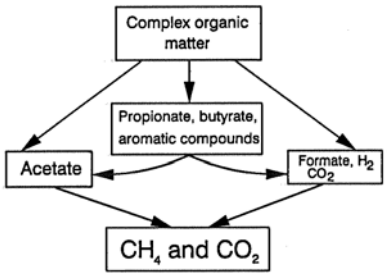


Fig. 1. Organic matter decomposition in methanogenic ecosystems

- Methane production is temperature dependent, with maximum growth 37°-45°C

Present-day global sources of CH_4 (Tg CH_4/yr)

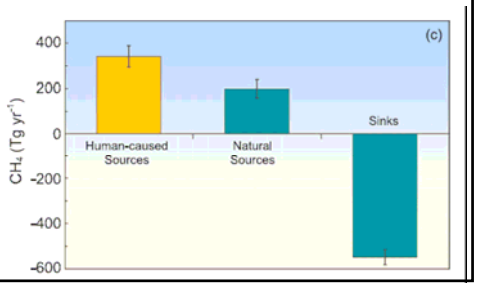
Natural Sources	200(±80)
Wetlands	145-230
Termites	20-30
Ocean	5-15
Hydrates	5
Geological sources	5-15
Wild animals	15
Wildfires	2-5

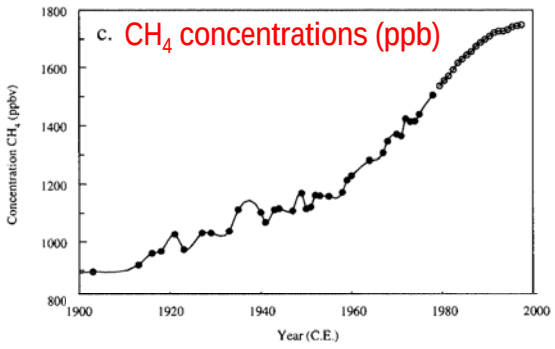
Anthropogenic Sources	330 (±100)
Fossil fuels	100
Landfills & Waste	35-70
Ruminants	70-90
Rice agriculture	30-80
Biomass burning	40-80

60% of present sources are anthropogenic

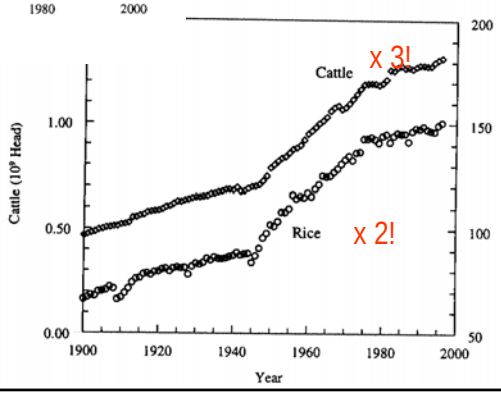
+ direct aerobic emissions from plants (60-240 Tg/yr) [Keppler et al., 2006] – highly controversial…

IPCC, 2008, Chap 7





Changes in methane since 1900



"Atmospheric methane: Its role in the global environment" Khalil (ed.) 2000

Methane sinks

❑Dominant loss (90%) of methane by oxidation in the troposphere:

$CH_4 + OH \rightarrow CH_3 + H_2O \rightarrow \ldots CO_2 + products$

~ 8 year lifetime

❑Minor sinks (~10%)

Soil uptake (biological oxidation in soils)

Chemical reactions in the stratosphere

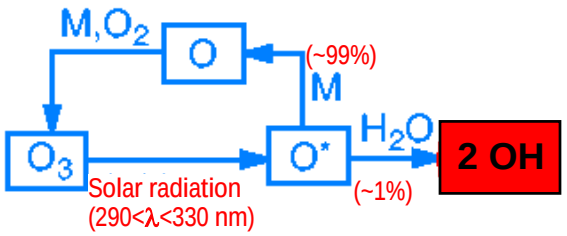
Production of tropospheric OH

$O_3 + sunlight \rightarrow O_2 + O^*$ 290 nm <λ<330 nm

$O^* + M \rightarrow O + M$ M ("third body") = O_2 or N_2

$O + O_2 + M \rightarrow O_3 + M$ O* = Electronically excited oxygen, $O(^1D)$

~1% $O^* + H_2O \rightarrow OH + OH$



Sinks of OH

Reactions with CO and CH_4 are the dominant sinks of OH in the troposphere:

$CO + OH \rightarrow CO_2 + H$

$CH_4 + OH \rightarrow CH_3 + H_2O$ *(~30% of OH sink)*

In the lower troposphere over continents, reaction with non-methane hydrocarbons (NMHCs) is also important:

NMHC + OH → products

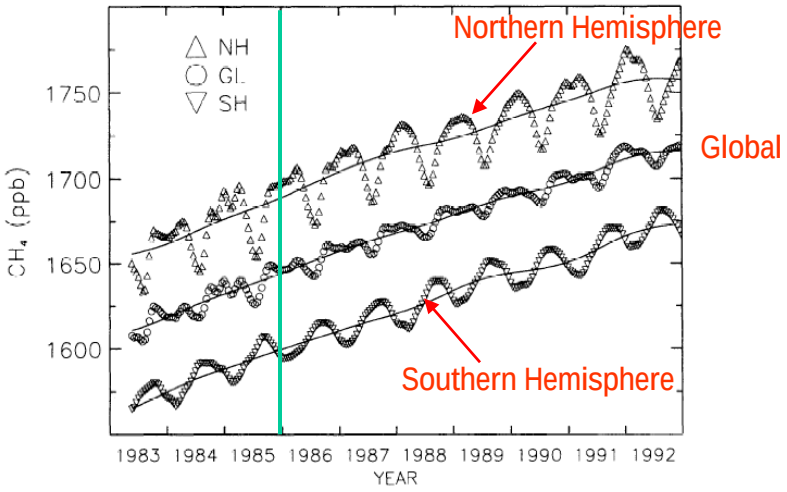
Lifetime of OH ~ 1 second!

Chemical feedback of methane on its lifetime

- Increase in CH_4 emissions → increase in CH_4 concentrations → decrease in OH levels → increase in the lifetime of CH_4 → further increases in CH_4 concentrations (positive feedback)

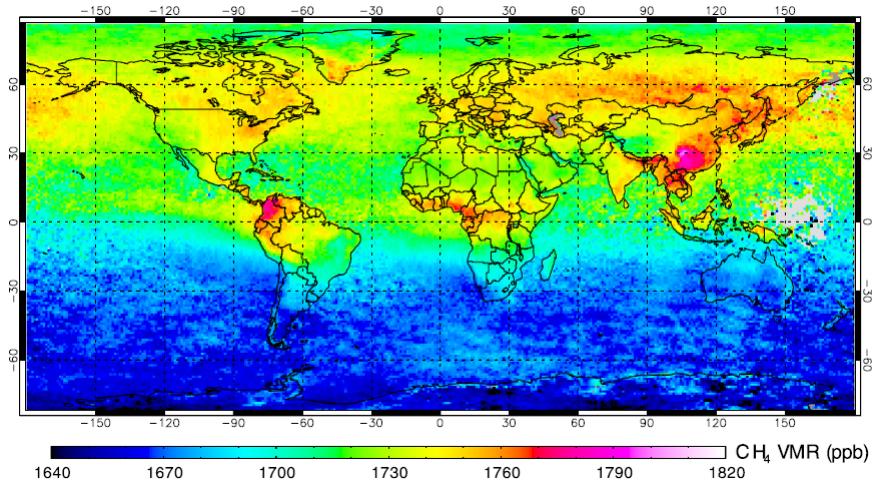
- Example: 1% increase in CH_4 results in a 0.32% decrease in OH → effective CH_4 lifetime ~ 12 years (compared to 8 years without feedback)

Seasonal cycle and interhemispheric gradient



Dlugokencky et al., 1994

Satellite observations of CH_4 (2003-2004)

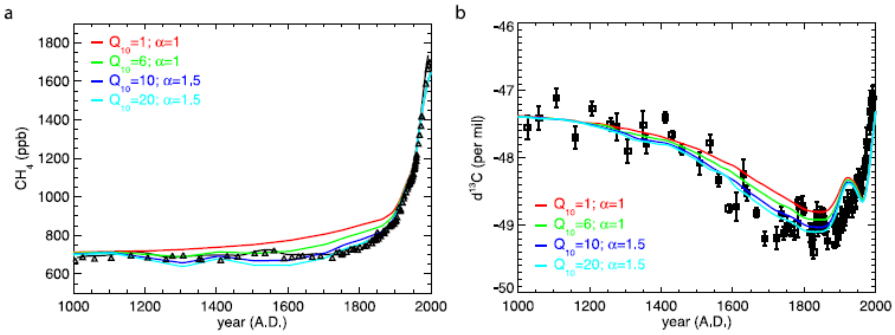


Frankenberg et al., JGR, 2006.

How is the CH_4 budget determined?

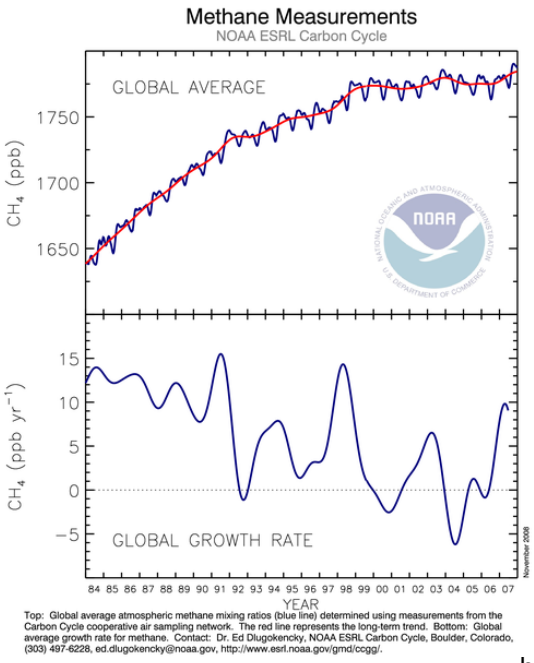
- Ice-core record → assess human influence
- Bottom-up studies:
  - ❑ Extrapolate direct flux measurements and observations
  - ❑ Process-based models (1,2,3-box models or global chemical transport models)
- Inverse modeling (top-down approach):
  - ❑ Spatial distribution of observations→ latitudinal distribution of sources
  - ❑ Use temporal evolution of CH_4 → sources
  - ❑ Use observations of isotopes: Separate fossil fuel and biomass burning from bacterial sources
    - ^{13}C-CH_4: enriched = natural gas, biomass burning vs. depleted = bacterial sources
    - ^{14}C -CH_4: enriched (modern) vs. depleted (fossil)

Atmospheric $^{13}CH_4$ over the last millennium



Houweling et al., GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 22, 2008

- ^{13}C-CH_4: enriched = natural gas, biomass burning vs. depleted = bacterial sources



IPCC A1B projection (1840 ppb)

Recent trends in CH_4

...decreasing rate of increase?

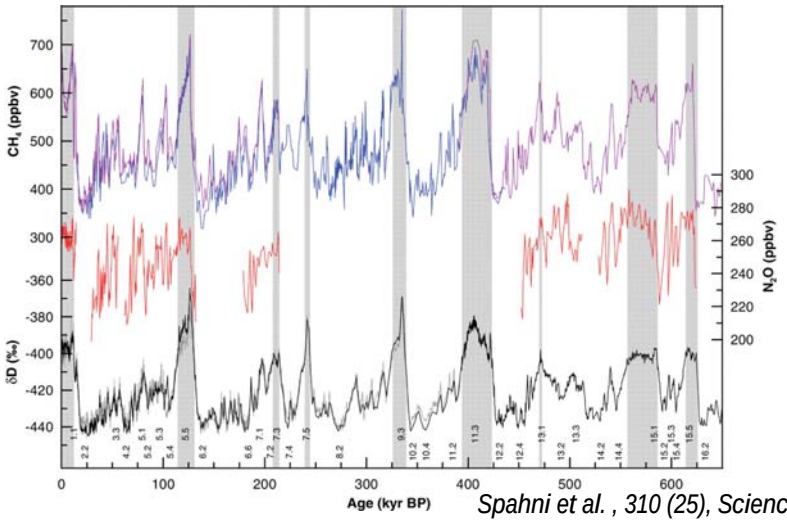
... large interannual variability

http://www.esrl.noaa.gov/gmd/ccgg/

Effects of climate of CH_4 emissions

- Effect of climate on biogenic CH_4 emissions from natural (wetlands) and anthropogenic (landfills, rice agriculture, biomass burning): temperature and moisture
- Wetlands: in a warmer+wetter world → increase extent of wetlands and their CH_4 emissions (30-80% increase for a 2.5-4.5°C warming) [IPCC, 2007]
- Climate affects stability of methane hydrates in ocean sediments… highly uncertain but potentially large

Learning from the past…
The ice core record of CH_4 : glacial-interglacial cycles



Spahni et al. , 310 (25), Science, 2005.

Rapid variations between 350 ppbv and 700 ppbv during glacial-interglacial + remarkable correlation with temperature proxy

How can we explain the changes in CH_4 between glacial and interglacial periods?

- Change in wetland area and productivity caused by changes in temperature and precipitation
- Changes in CO_2
- Changes in the sink of CH_4, the hydroxyl radical

Changes in wetlands

CH_4 emissions from wetlands

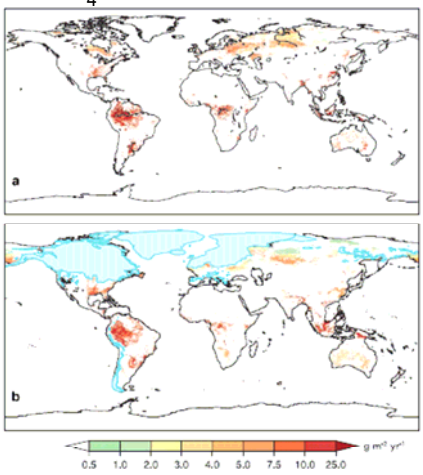


Plate 1. Potential natural wetlands and CH_4 emission simulated for (a) the present day and (b) the LGM.

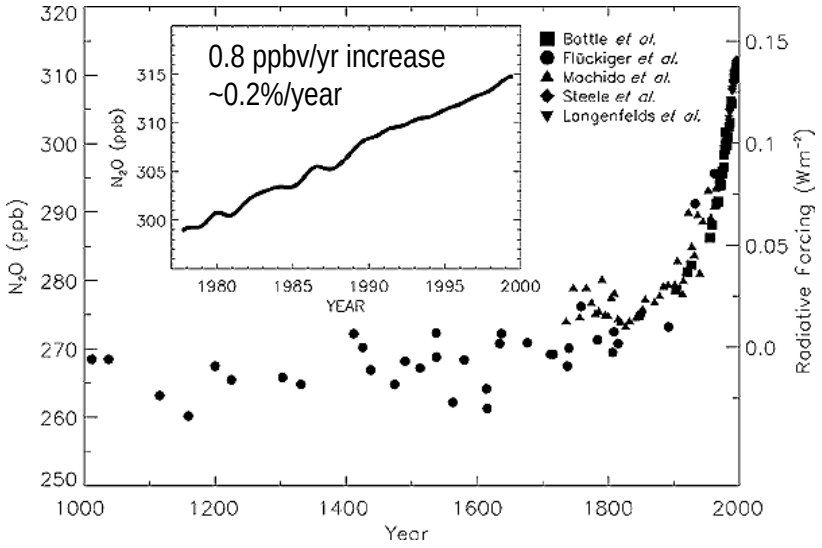
Present day

Last Glacial Maximum
15% larger wetland area but
24% lower CH_4 emissions

… explains only half of the 50% decrease between present day and LGM… did OH change too?

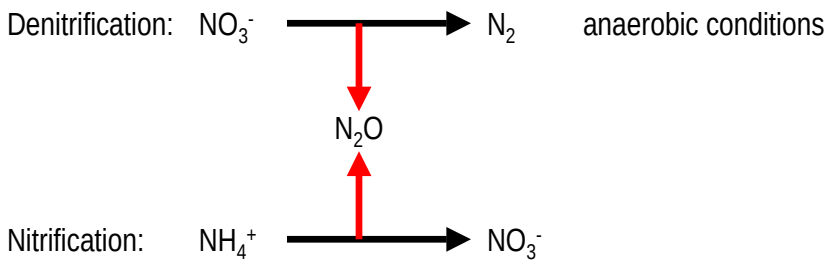
Kaplan, Geophys. Res. Lett., 29, 2002.

Nitrous oxide (N_2O)



~15% increase since pre-industrial times

Nitrification and denitrification: microbial source of N_2O in soils and oceans



Oceans: nitrification ~ 4 TgN/yr
Soils: nitrification and denitrification ~7 TgN/yr

Global budget of N_2O (TgN/yr)

Anthropogenic sources	**6.7**
Fossil Fuel Combustion & Industrial processes	0.7 (0.2-1)
Agriculture	2.8 (1.7-4.8)
Biomass and biofuel burning	0.7 (0.2-1)
Rivers, estuaries, coastal zones	1.7 (0.5-2.9)
Atmospheric deposition	0.6 (0.3-0.9)

Natural Sources	**11**
Soils (undisturbed)	6.6 (3.3-9)
Oceans	3.8 (1.8-5.8)
Atmospheric chemistry	0.6 (0.3-1.2)

Sink: N_2O photolysis in stratosphere (120 year lifetime)

IPCC, 2007, Chap 7