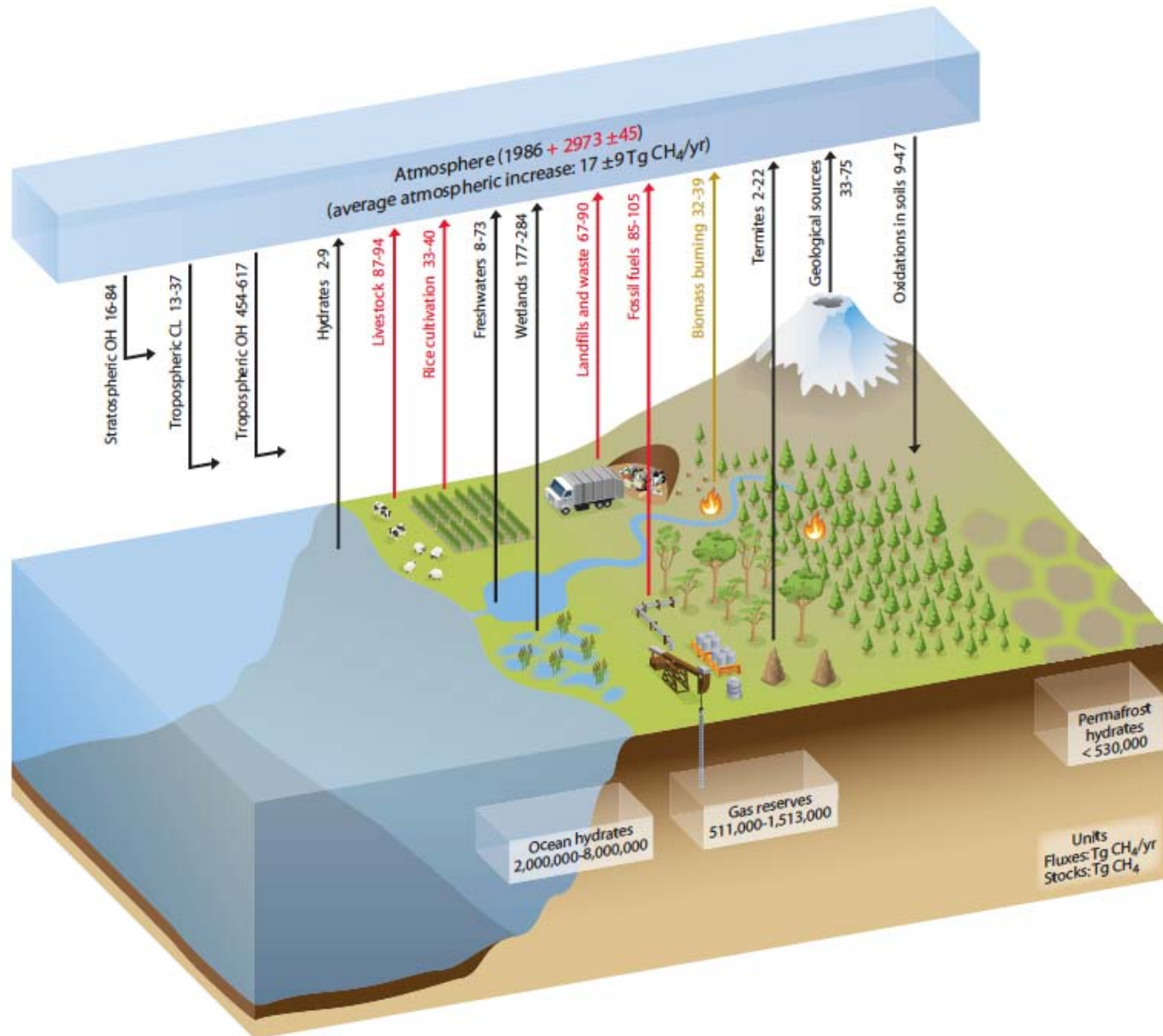
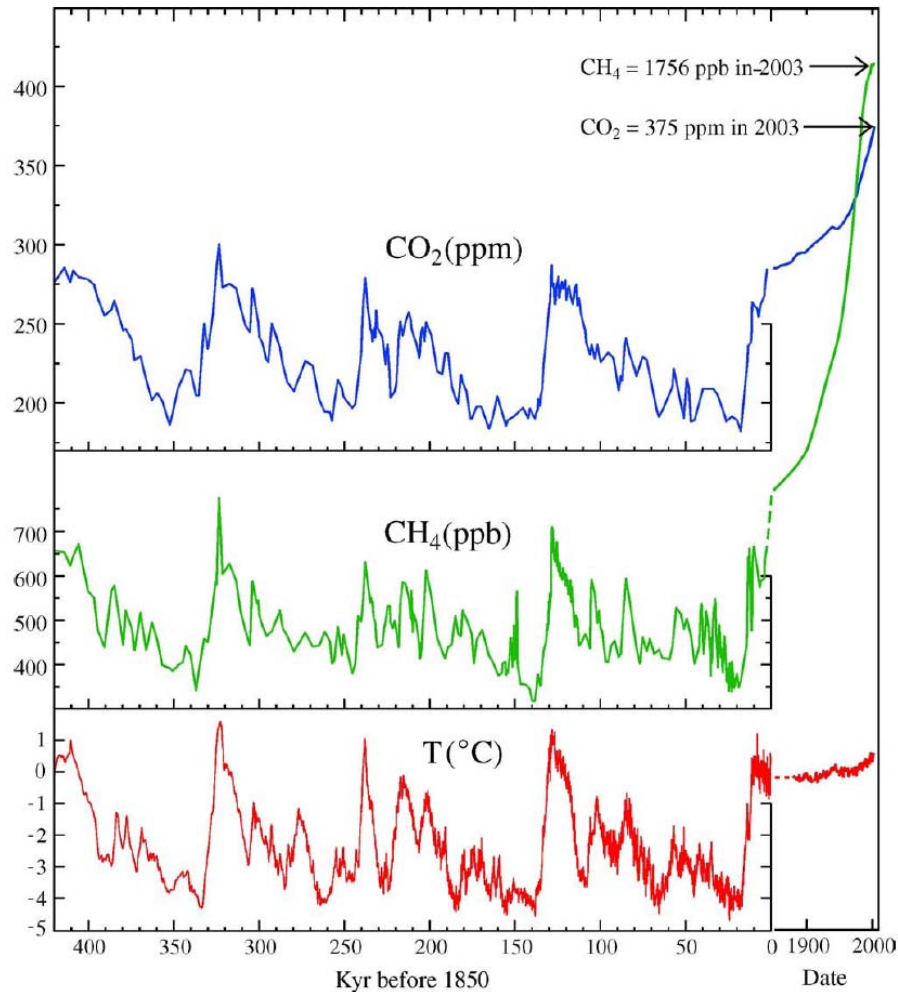


Lecture: Atmospheric CH<sub>4</sub> and  
N<sub>2</sub>O: Phenomenology and controls

# CH<sub>4</sub> Sources and Sinks



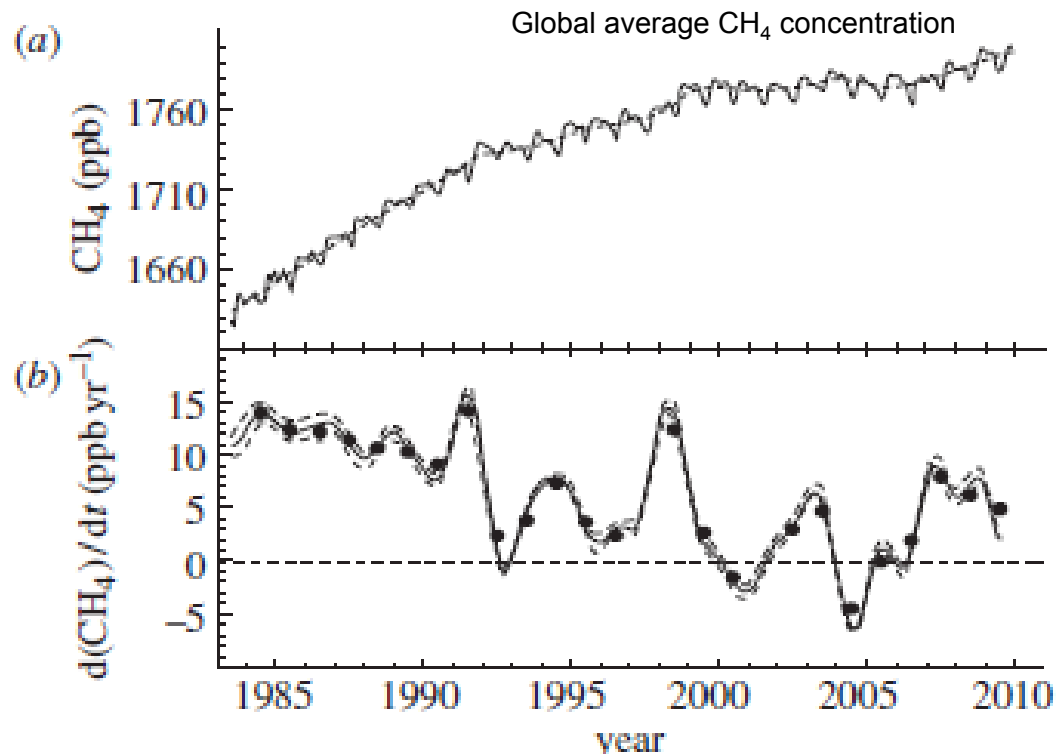
## Methane from ice core records



Glacial-Interglacial CH<sub>4</sub> changes are believed to be controlled mostly by changes in wetland area, e.g. associated with changes in the Asian Monsoon.

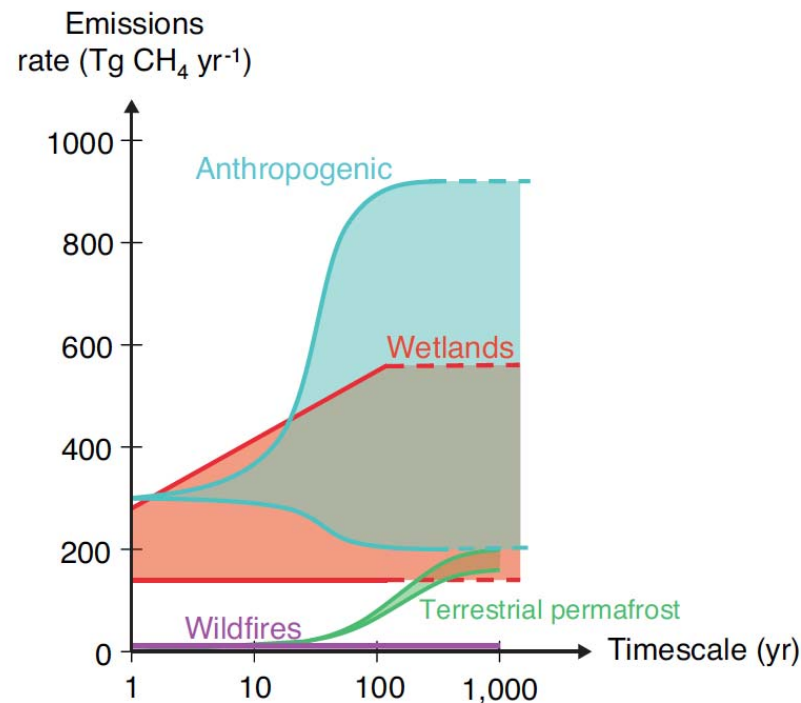
**Figure 15.** CO<sub>2</sub>, CH<sub>4</sub> and temperature records inferred from Antarctic ice core and recent in situ measurements (reference 6). Time scale after 1850 is expanded to allow changes of the past century to be seen. The indicated global temperature anomaly, relative to the 1880-1899 mean, is estimated to be half of the Antarctic temperature anomaly.

Methane growth rate slowed for nearly a decade, but has started increasing again of late



Cause of slowing is unknown, but may be due to reduced fossil-fuel CH<sub>4</sub> emissions from countries of the former Soviet Union in early 1990s.

# Future CH<sub>4</sub> emissions trends are hard to predict:



**Figure 6.36** | Schematic synthesis of the magnitude and time scales associated with possible future CH<sub>4</sub> emissions (adapted from O'Connor et al., 2010). Uncertainty in these future changes is large, and so this figure demonstrates the relative magnitude of possible future changes. Anthropogenic emissions starting at a present-day level of 300 Tg(CH<sub>4</sub>) yr<sup>-1</sup> (consistent with Table 6.8) and increasing or decreasing according to RCP8.5 and RCP2.6 are shown for reference. Wetland emissions are taken as 140 to 280 Tg(CH<sub>4</sub>) yr<sup>-1</sup> present day values (Table 6.8) and increasing by between 0 and 100% (Section 6.4.7.1; Figure 6.37). Permafrost emissions may become important during the 21st century. CH<sub>4</sub> release from marine hydrates and subsea permafrost may also occur but uncertainty is sufficient to prevent plotting emission rates here. Large CH<sub>4</sub> hydrate release to the atmosphere is not expected during the 21st century. No quantitative estimates of future changes in CH<sub>4</sub> emissions from wildfires exist, so plotted here are continued present-day emissions of 1 to 5 Tg(CH<sub>4</sub>) yr<sup>-1</sup> (Table 6.8).

# How do we know the CH<sub>4</sub> lifetime?

The main sinks are reaction with OH and uptake by soils.  
The overall equation can be written:

$$\frac{dX_{CH_4}}{dt} = -k \cdot X_{CH_4} + S(t)/M_{air} \quad (1)$$

$$= -k_{OH} \cdot X_{CH_4} - k_{soil} \cdot X_{CH_4} + S(t)/M_{air}$$

$$= X_{CH_4} / \tau_{OH} - X_{CH_4} / \tau_{soil} + S(t)/M_{air}$$

$$= -(1/\tau_{OH} + 1/\tau_{soil})X_{CH_4} + S(t)/M_{air} \quad (2)$$

Which shows that the overall lifetime can be computed by combining the separate lifetimes for soils and reaction with OH radicals.

$$\tau = (1/\tau_{OH} + 1/\tau_{soil})^{-1} \quad (3)$$

To estimate the lifetime for  $\text{CH}_4$  with respect to reaction with OH, we need to consider the fundamental bi-molecular reaction mechanism:

$$\frac{d[\text{CH}_4]}{dt} = -k_{\text{OH}+\text{CH}_4}[\text{OH}][\text{CH}_4] \quad (4)$$

Here  $[\text{CH}_4]$  and  $[\text{OH}]$  are the number densities in molecules per cubic cm. It is easily shown that,  $k_{\text{OH}+\text{CH}_4}$  has units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . This equation holds in each  $\text{cm}^3$  of air.

The lifetime for reaction of  $\text{CH}_4$  with OH is related to the fundamental reaction rate according to

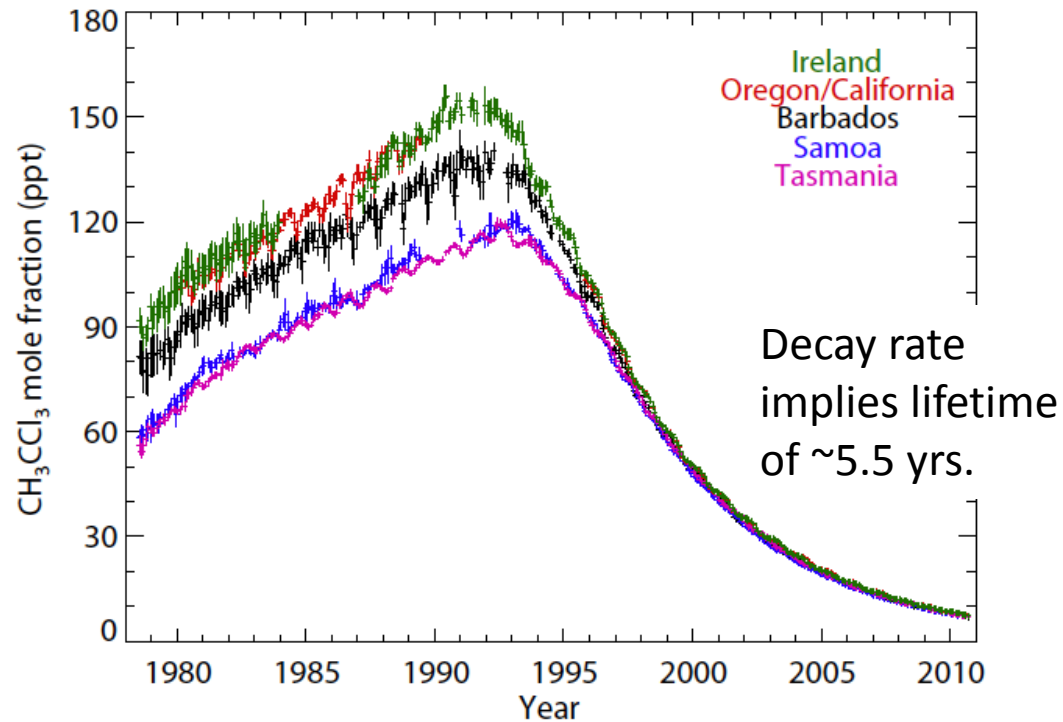
$$1 / \tau_{\text{OH}} = k_{\text{OH}+\text{CH}_4}[\text{OH}] \quad (5)$$

Eq. (5) actually gives a measure of the “local” lifetime. You must average  $k_{\text{OH}+\text{CH}_4}[\text{OH}]$  over the atmosphere to get the global lifetime.

$$1 / \tau_{\text{OH}} = \langle k_{\text{OH}+\text{CH}_4}[\text{OH}] \rangle$$

A challenge here is that OH is hard to measure directly and varies rapidly with time of day and location.

The uncertainty in OH can be overcome by reference to the lifetime of methyl chloroform, a man-made compound that was banned under the Montreal Protocol. Since 1997 it has been undergoing almost pure exponential decay in the atmosphere due to reaction with OH:





Methyl chloroform reacts analogously with OH

$$\frac{d[CH_3CCl_3]}{dt} = -k_{OH+CH_3CCl_3}[OH][CH_3CCl_3]$$

$$1/(5.5yr) = \langle k_{CH_3CCl_3}[OH] \rangle$$

$$\begin{aligned} [OH] &= \frac{1}{k_{CH_3CCl_3} \cdot 5.5yr} \\ &= \frac{1}{(6.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \cdot (5.5yr) \cdot (3.15 \times 10^7 \text{ s yr}^{-1})} \\ &= 9 \times 10^5 \text{ molecule cm}^{-3} \end{aligned}$$

Here we have used a rate constant for reaction of OH with methyl chloroform from lab experiments at 252K, an appropriate average temperature for the troposphere.

You can compare the OH abundance to the number of molecules in a  $\text{cm}^3$  of air (or any other ideal gas) at STP. This can be calculated from Avagadro's number and the ideal gas constant and is  $2.7 \times 10^{19}$  molecule  $\text{cm}^{-3}$ . This constant is also known as Loschmidt's number.

Returning to the calculation of CH<sub>4</sub> lifetime, we now can compute  $\tau_{OH}$  according to

$$\begin{aligned}\tau_{OH} &= \frac{1}{k_{OH+CH_4}[OH]} \\ &= \frac{1}{(3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})(9 \times 10^{-5} \text{ molecule cm}^{-3})(3.15 \times 10^7 \text{ s yr}^{-1})} \\ &= 10.0 \text{ yr}\end{aligned}$$

The CH<sub>4</sub> uptake rate with respect to soils can be measured by putting chambers over the ground and measuring the CH<sub>4</sub> loss rate. These studies yield an estimate of  $\tau_{soil} = 150$  yrs.

So the overall CH<sub>4</sub> lifetime is then

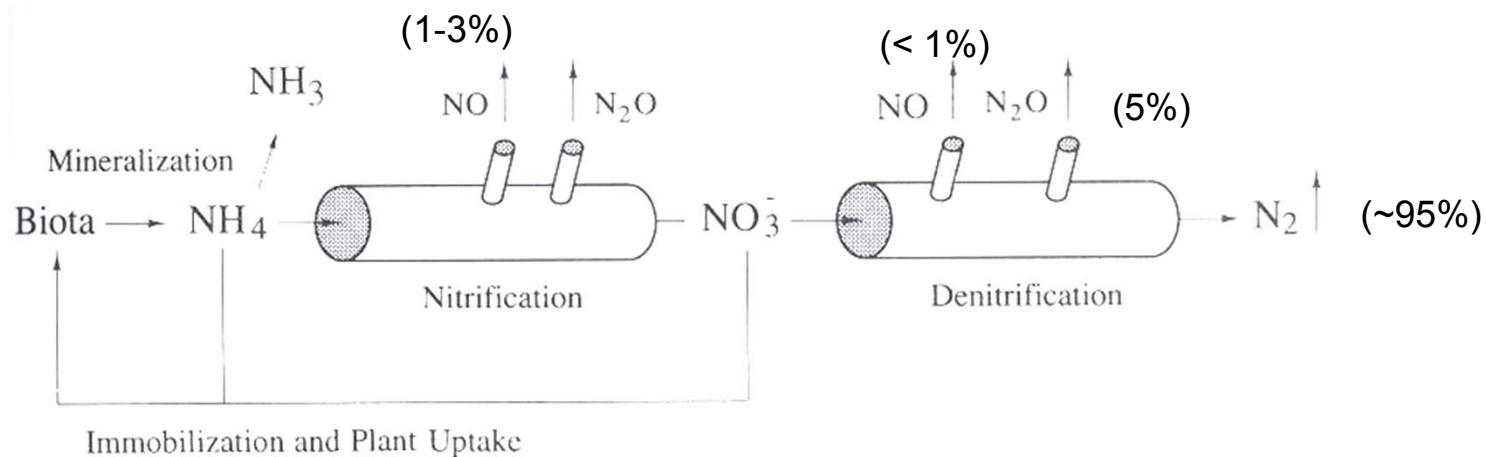
$$\begin{aligned}\tau &= \left(1/\tau_{OH} + 1/\tau_{soil}\right)^{-1} \\ &= (1/10 + 1/150)^{-1} = 9.3 \text{ yr}\end{aligned}$$

Reference on above calculation:

Finlayson-Pitts et al (1992) GRL **19**): 1371-1374.

Prather et al (2012) GRL **39**.

# N<sub>2</sub>O source in relation to nitrification and denitrification



**Figure 6.12** Microbial processes that yield nitrogen gases during nitrification and denitrification in the soil. Modified from Firestone and Davidson (1989).

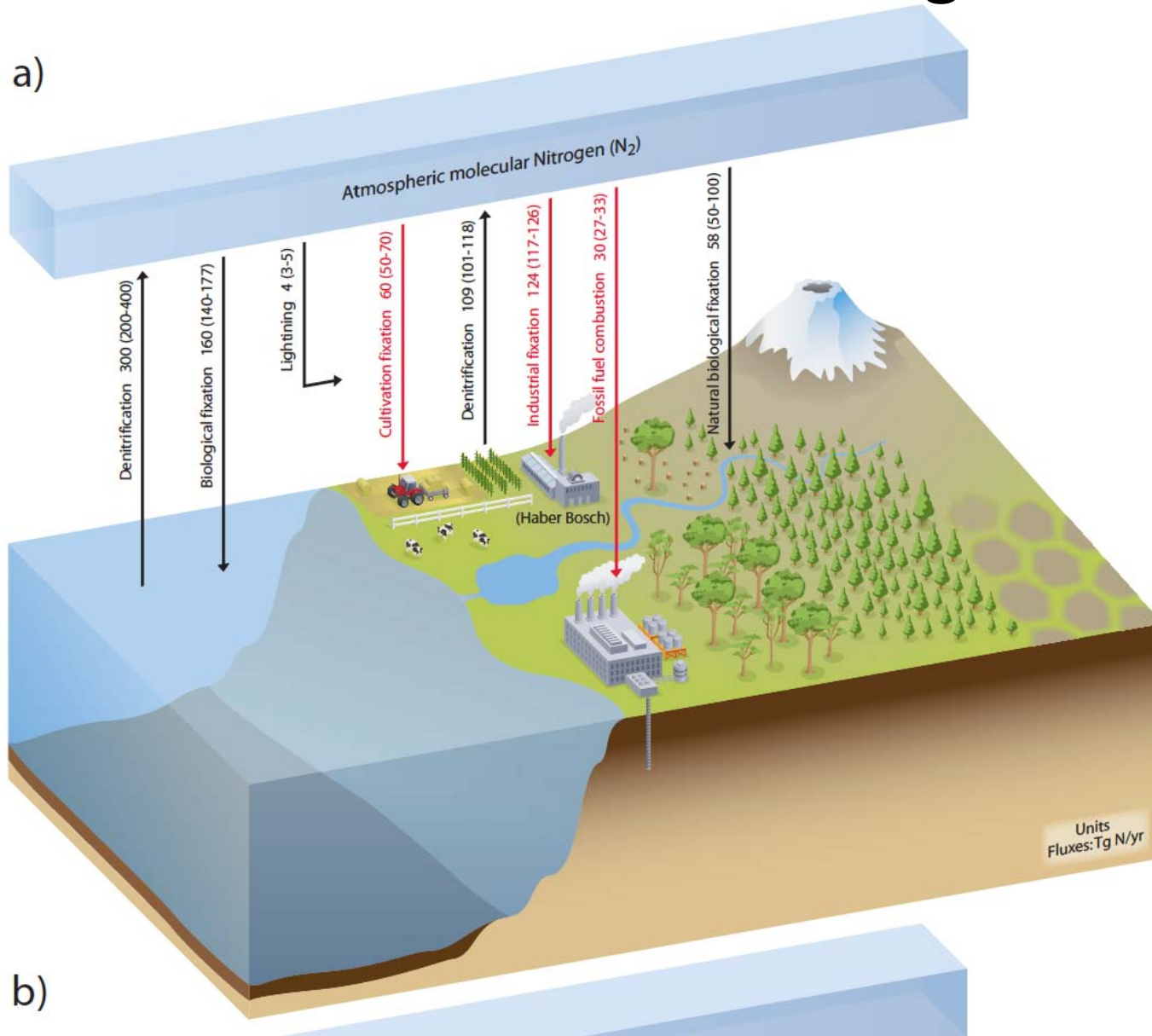
Nitrification rates more important in dry soils

Denitrification more important in moist soils (tied to O<sub>2</sub> availability)

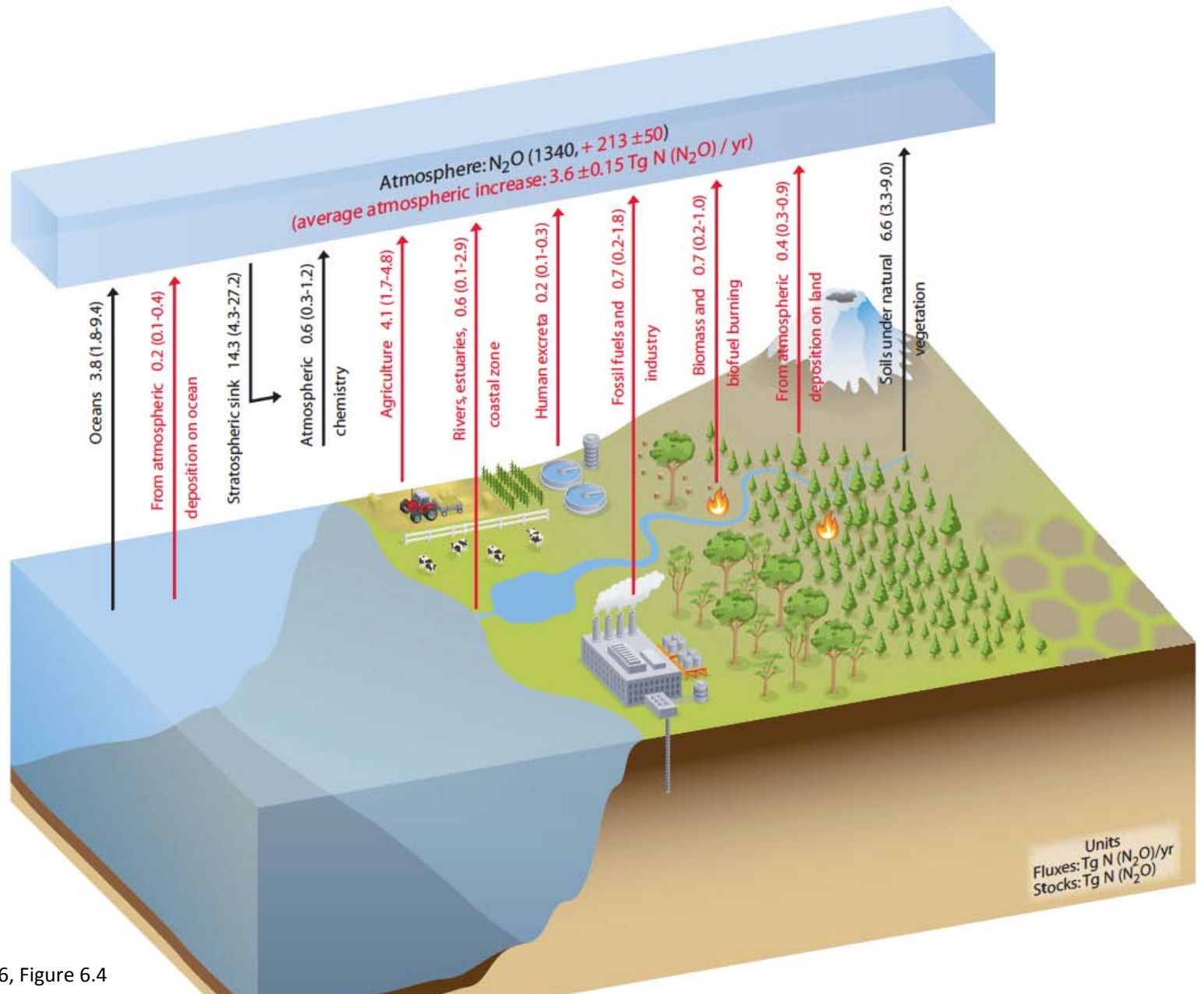
Denitrification can proceed in anoxic “microsites”

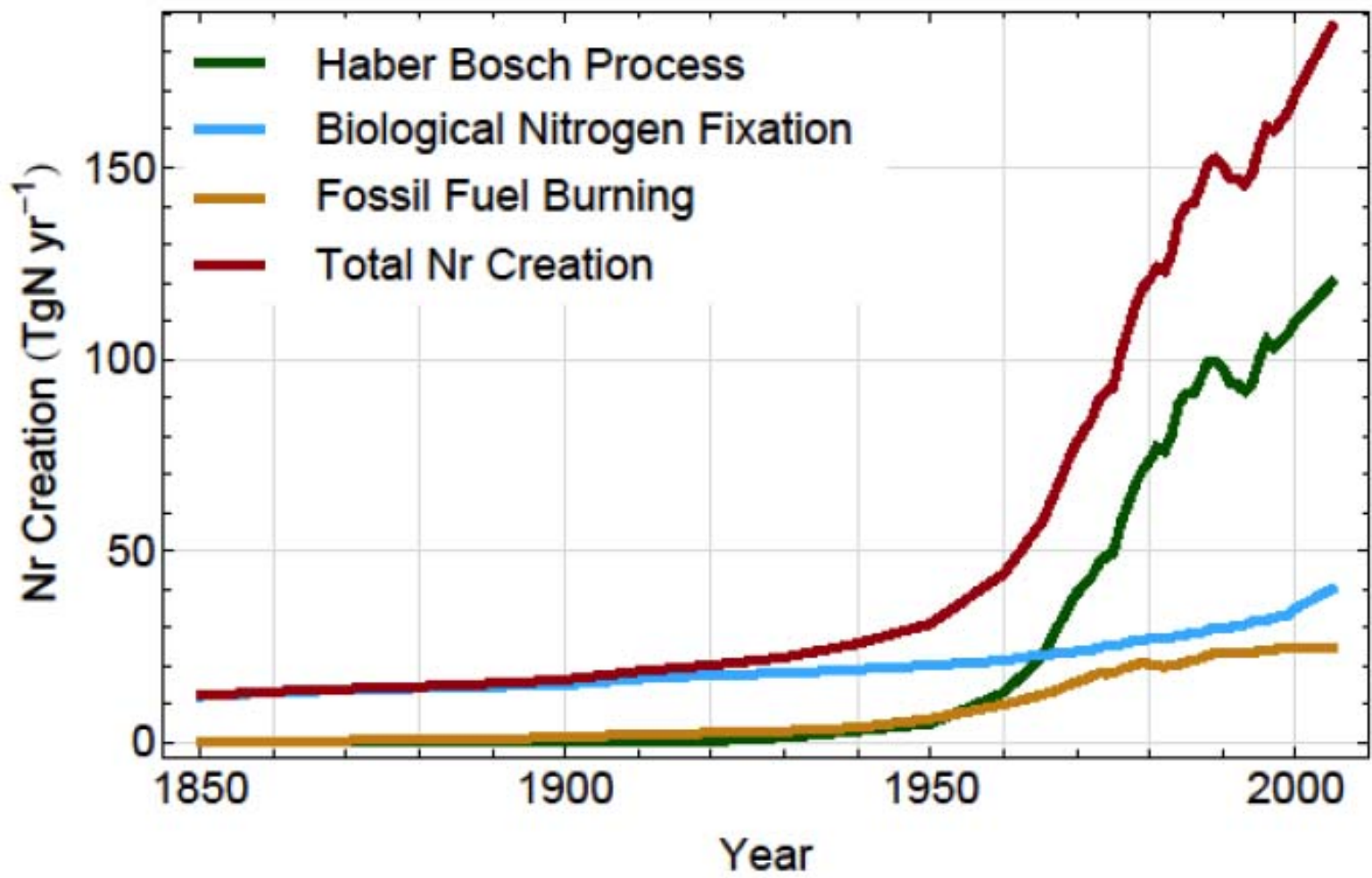
NO & N<sub>2</sub> also released by fires: “pyro-denitrification”

# Sources and Sinks of Fixed Nitrogen



# Sources and Sinks of N<sub>2</sub>O





# N<sub>2</sub>O loss mechanisms

Main source of N<sub>2</sub>O loss is photolysis and reaction with O(<sup>1</sup>D) in the stratosphere.

Loss rate must be calculated with dynamic and photochemical model. No simple scaling rule (e.g. as true for CH<sub>4</sub>).

N<sub>2</sub>O budget is more uncertain than CH<sub>4</sub> budget because neither the global source nor sink is well pinned down (only the difference, which is the atmospheric growth rate).