Trace gas biogeochemistry

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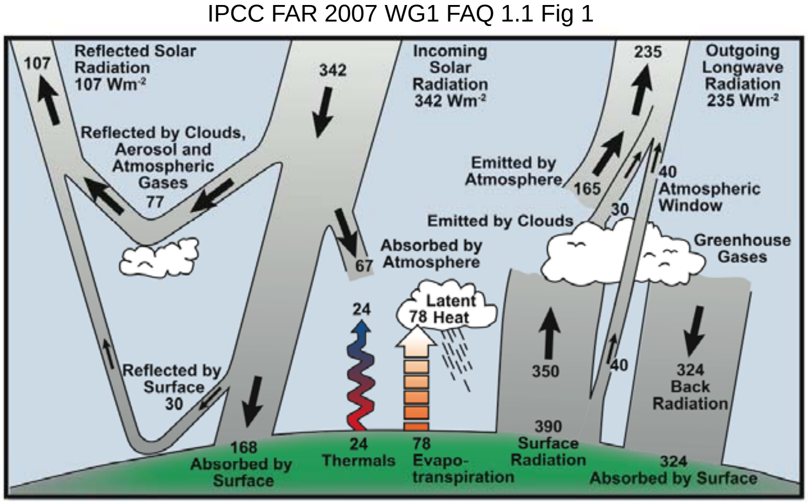
Outline

1. **Greenhouse gases: overview**
2. CH_4 (methane)
3. N_2O (nitrous oxide)
4. Soil diffusivity
5. Field measurements
6. Case study: microbial ecology & greenhouse gases

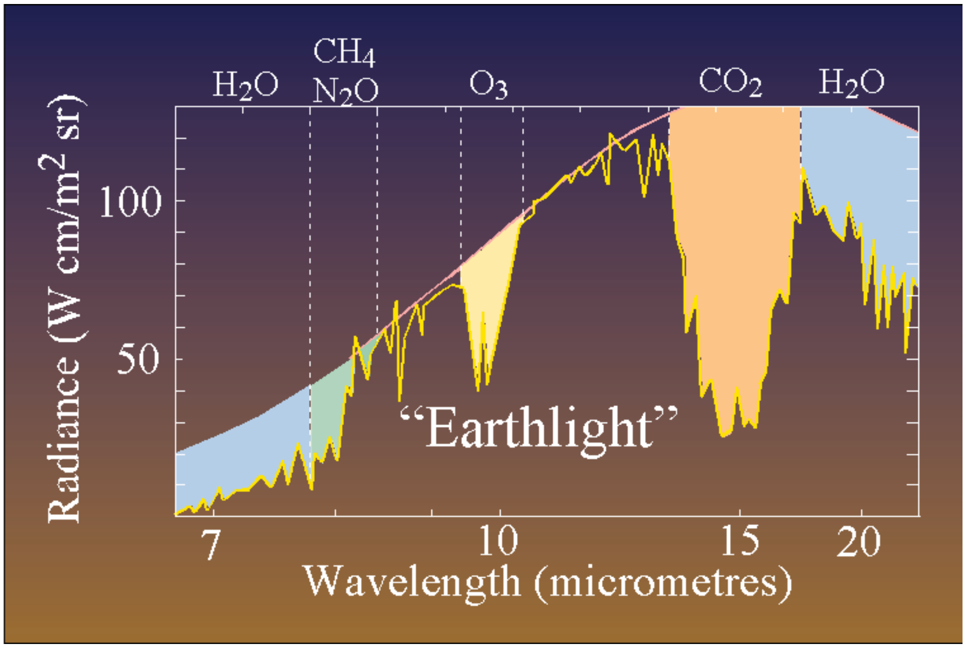
Greenhouse gases

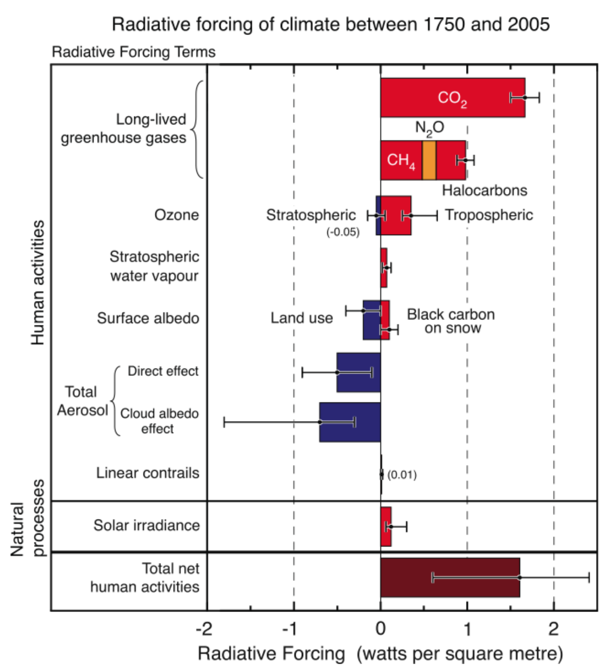
N_2	78%
O_2	21%
H_2O	1 – 4%
Ar	0.93% = 9300 ppmv
CO_2	380 ppmv
Ne	18 ppmv
CH_4	1.75 ppmv
Kr	1.14 ppmv
H_2	550 ppb
N_2O	320 ppbv
Xe	90 ppbv
O_3	Up to 70 ppbv
NO_2 (with NO = NO_x)	20 ppbv

IPCC FAR 2007 WG1 FAQ 1.1 Fig 1



Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transferred to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that is absorbed by clouds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Trenberth (1997).





IPCC 2007 WG1 Fig FAQ 2.1 Fig 2

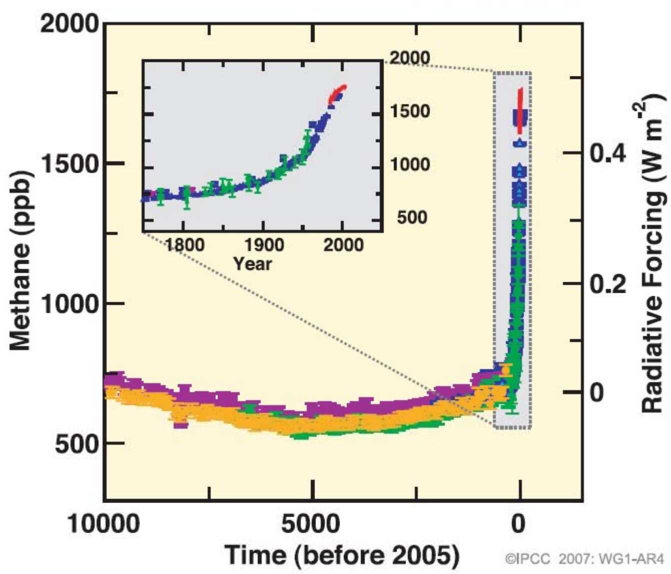
Global CH_4 budget

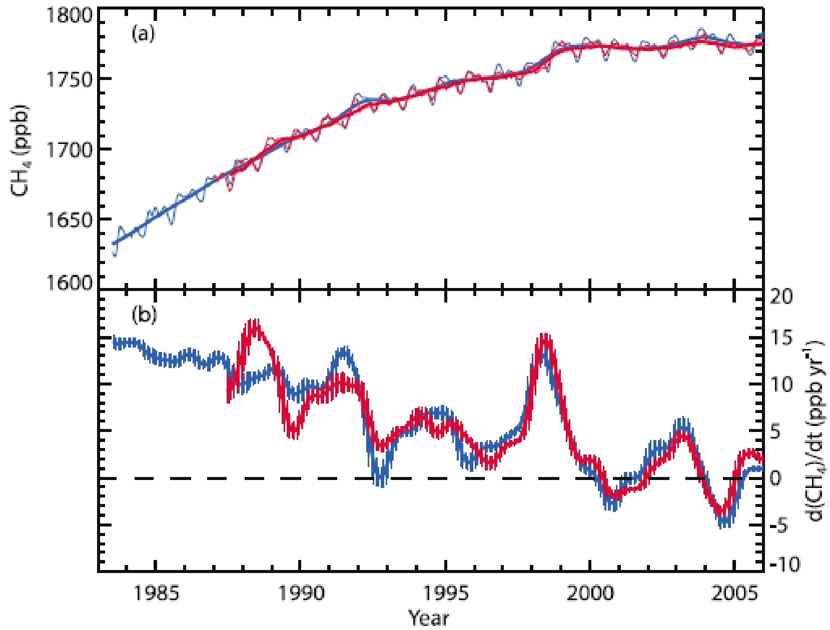
Natural sources	**260**
Wetlands	231
Termites	29
Other*	<10
Human sources	**350**
Ruminants	91
Biomass burning	88
Rice paddies	54
Gas/oil industries	52
Landfills	35
Coal mining	30
Total Sources	**610**

Sinks	**577**
Soil oxidation	30
Tropospheric OH	507
Stratospheric losses	40

Units = 10^{15} g CH_4 y^{-1}

From Mickaloff-Fletcher GBC 2004a



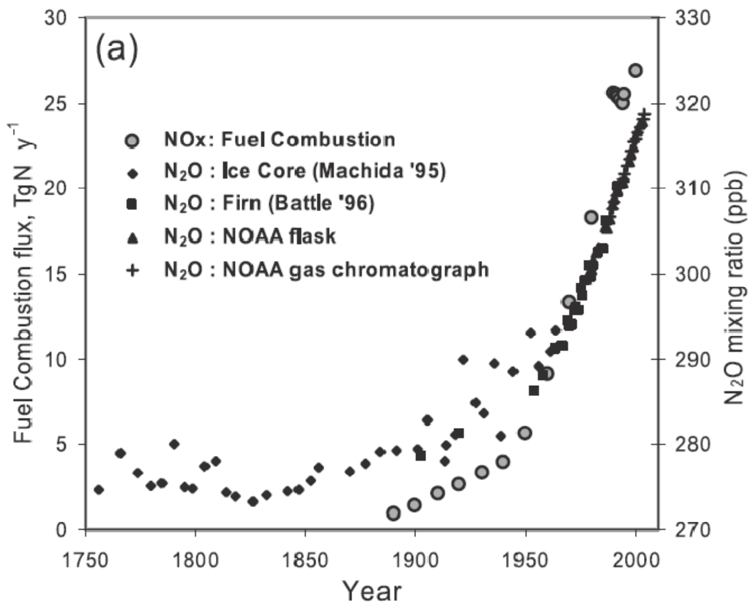


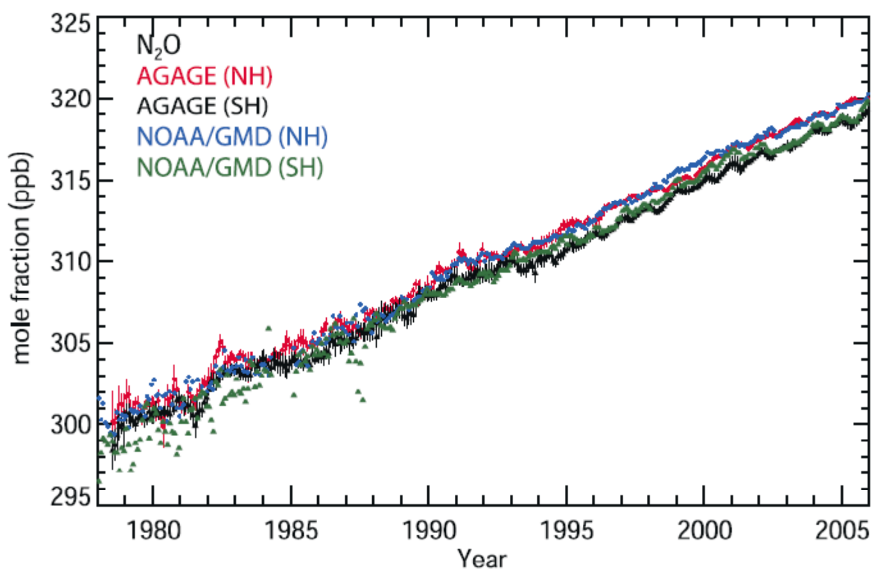
http://ipcc-wg1.ucar.edu/wg1/Report/AR4WG1_Print_Ch02.pdf

Global N_2O budget

Natural Sources	**11**
Soils	6.6
Oceans	3.8
Lightning	<0.1
Atmospheric Chemistry	0.6
Human Sources	**6.7**
Agriculture	2.8
Rivers/Estuaries/Coastal Zones	1.7
Biomass burning	0.7
Internal Combustion	0.7
Atmospheric Deposition	0.6
Total Sources	**17.7**

Sink: atmospheric photolysis


(a)
NOx: Fuel Combustion
N₂O : Ice Core (Machida '95)
N₂O : Firn (Battle '96)
N₂O : NOAA flask
N₂O : NOAA gas chromatograph
Fuel Combustion flux, TgN y⁻¹
N₂O mixing ratio (ppb)
Year
1750
1800
1850
1900
1950
2000


N₂O
AGAGE (NH)
AGAGE (SH)
NOAA/GMD (NH)
NOAA/GMD (SH)
mole fraction (ppb)
Year
1980
1985
1990
1995
2000
2005

Other global TTK*

- New European satellite SCIAMACHY now measuring atmospheric CH_4 from space.
- Keppler *et al.* Nature (2006) reported emission of CH_4 directly from plants.
- Gas concentration data on the Web
  – Ice Cores: www.ncdc.noaa.gov/paleo/icecore.html
  – Atmospheric Sampling (NOAA CMDL) www.esrl.noaa.gov/gmd/

Things To Know

Outline

1. Greenhouse gases: overview
2. **CH_4 (methane)**
   – **Production**
   – **Consumption**
   – **Transport & Ebullition**
3. N_2O (nitrous oxide)
4. Soil diffusivity
5. Field measurements
6. Case study: microbial ecology & greenhouse gases

Methane Production

- Methane production is part of a "syntrophic" system.
  - Metabolic end product of one organism is consumed by another
  - When an organism's end products are consumed, it changes the ΔG, makes process more favorable.
- Anaerobic fermentation of organic material produces acetate and H_2.

Methane Production

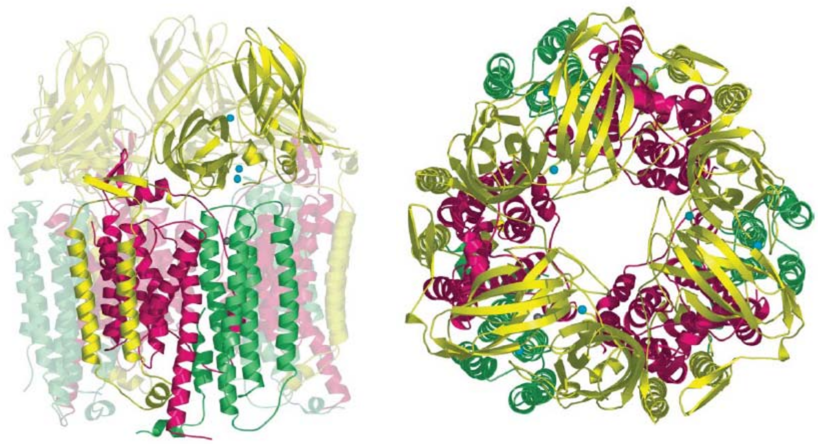
- Acetoclastic methanogenesis
  - $H_3C\text{-}COOH \rightarrow CO_2 + CH_4$
  - $\delta^{13}C$ of CH_4 ~ -60‰
- Hydrogenotrophic methanogenesis
  - $H_2 + CO_2 \rightarrow CH_4$
  - $\delta^{13}C$ of CH_4 ~ -100‰
- Most systems 2/3 acetoclastic, 1/3 hydrogenotrophic
- Ratio constrained by themodynamics & stoichiometry of fermentation

Methane Production TTK

- Methane producers are from the domain Archaea.
  - More phylogenetically different from us than we are from yeast.
- Some other substrates (e.g., methanol, formate) can be used in methane production, but it's rare.
- Methanogens don't switch between pathways. They are "hard wired."

What is the ideal habitat for methane production?

methane mono-oxygenase enzyme



From Lieberman & Rosenzweig

Methane Consumption

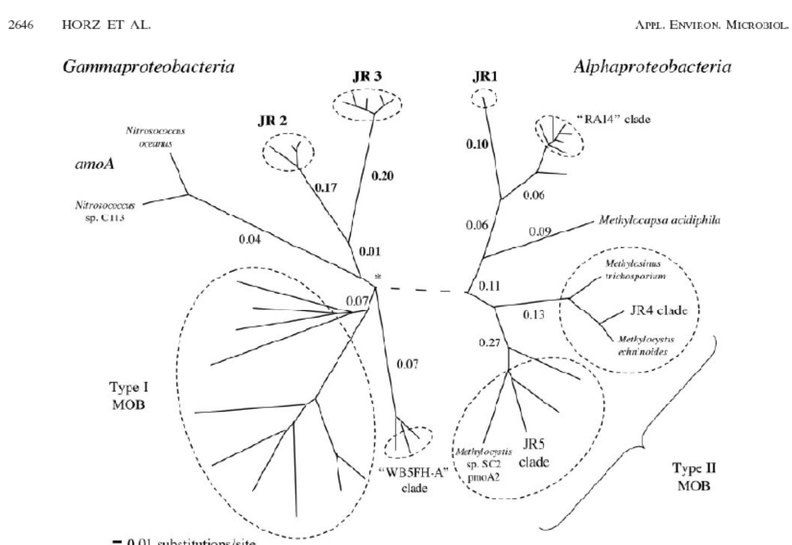
- Methanotrophic bacteria consume methane, oxidizing it with O_2.
- The enzyme that binds to methane is Methane Monooxygenase (MMO) and it is usually in a particulate form (pMMO).
- MMO is very similar to Ammonium Monooxygenase.
  - CH_4 oxidizers are closely related to bacterial nitrifiers
- High soil ammonium inhibits methane oxidation (competitive inhibitor of MMO)

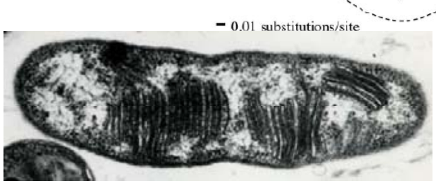
Methane Consumption

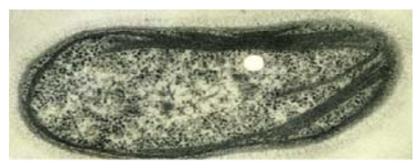
- MMO enzymes differ in affinity for CH_4, following Michaelis-Menten kinetics.

$$\frac{dC}{dt} = V_{\max} \frac{[C]}{K_M \cdot [C]}$$

  - Low affinity (high K_M) where $[CH_4]$ is high
  - Having low affinity means it's harder to bind CH4 at low concentrations, but it allows V_{max} to be higher.
- Methane consumption fractionates against ^{13}C by about 20‰.







Methane Consumption TTK

- Methanotrophic bacteria used to be divided into two groups (Type I and II).
- As molecular tools become more common, we are finding more types all the time.
- Cultured types differ in ecophysiological traits
  - Optimal pH, response to temperature, enzyme kinetics, ability to form resting stages

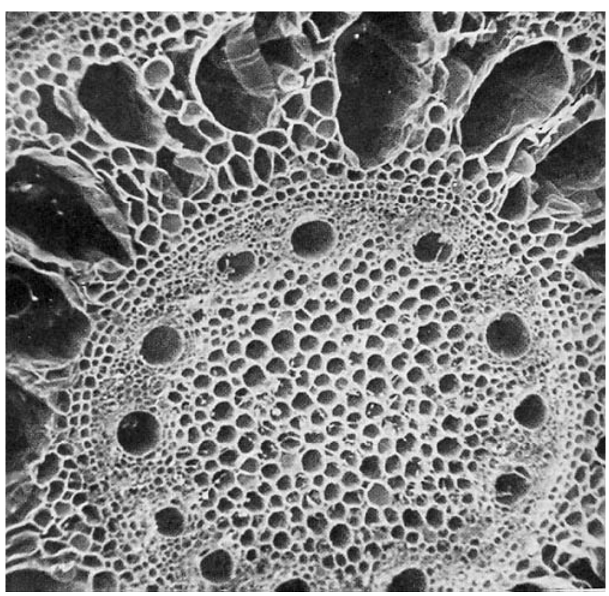
What is the ideal habitat for methane consumers?

Methane Transport

- Upland soils: gas transport is by diffusion.
- Wetland soils are different.

Wetland Methane Transport

- Many vascular wetland plants includes "aerenchyma" (tiny tubes, like empty xylem vessels) that conduct O_2 from the atmosphere to the roots, allowing root respiration.
- These tubes also allow methane to be transported to the atmosphere.
- Transport can be via active pumping or diffusion
  - Which mechanism fractionates methane isotopes?

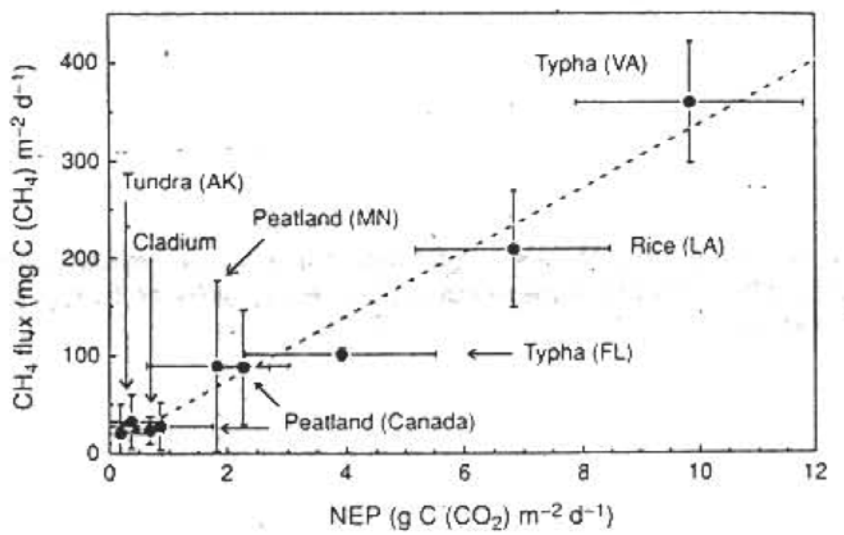


Wetland Methane Transport

- Two factors create an unusual transport phenomenon in methane
  - Solubility of methane is very low
  - Diffusive transport to the atmosphere can be very low.
- What happens when a gas becomes super-saturated?
- Ebullition is

Wetland methane questions

- How would methane biogeochemistry & transport be different in Sphagnum (moss) dominated vs. Carex (sedge)?
- Is it easy or hard to measure ebullition fluxes? Why?



Whiting & Chanton (1993) Nature

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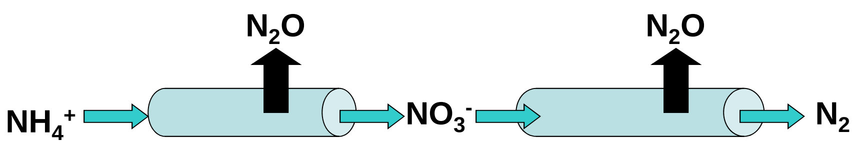
   - Hole in the pipe model
4. Soil diffusivity
5. Field measurements

Hole in the Pipe Model



Firestone & Davidson (1989) "Microbiological basis of NO and N2O Production and consumption in Soil" in Exchange of **Trace Gases Between Terrestrial Ecosystems and the Atmosphere**.
Andrae & Schimel, eds.

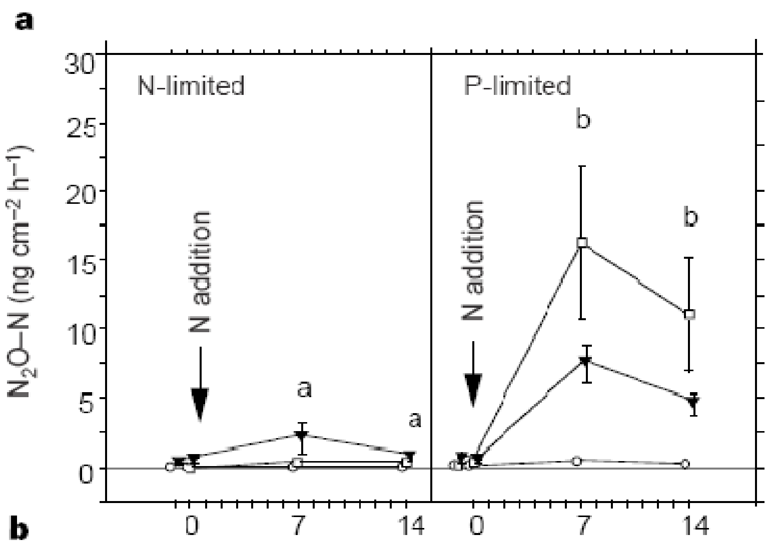
Hole in the Pipe Model

- N_2O is a biochemical intermediate in nitrification & denitrification.
- The pipe "leaks" N_2O, meaning it leaks through bacterial cell membranes.
- Rate of leakage is proportional to rate that N flows through each pipe.
- In very wet soils, N_2O is an important electron acceptor, so little leakage escapes to atmosphere.

N_2O TTK

- We used to think that all nitrifiers were bacteria, but it is becoming clear that much (most?) of the nitrification is done by Archaea.
- Most denitrifiers are facultative, so the link between functional gene and activity is weak.

What conditions favor coupled nitrification & denitrification?



Hall & Matson (1999) Nature

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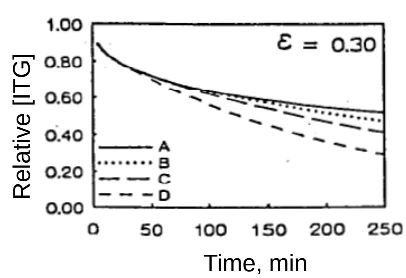
Gas diffusion in soils

- Gas molecules move by random diffusion from regions of high concentration to low concentration.
- In soil, this movement is through the soil pores.
- "Diffusivity" is the conductance of the soil to diffusive gas movement (high values = fast diffusion). Soil diffusivity < Free air diffusivity.
- Free air diffusivity varies with molecular weight.
  - CH_4: 0.195 cm^2 $second^{-1}$
  - N_2O: 0.144 cm^2 $second^{-1}$

Measuring Soil Diffusivity

- Rolston et al. SSSAJ (1991) describes a method for measuring soil diffusivity using flux chambers
- Add an inert tracer gas to the headspace & monitor changes in concentration over time.



A) Infinitely deep chamber base
B) – **D)** 25, 15 or 10cm deep bases

Lesson: keep chamber flux time <20 minutes or ITG will diffuse Horizontally.

Other diffusivity TTK

- The diffusivity of soil declines with soil moisture, as pore spaces get filled with water.
- Soil diffusivity varies among soils, depending on pore structure. Large pores allow faster gas movement.
- Heat and pressure gradients can induce advective movement of gases, that is often much faster than diffusion.

Other diffusivity TTK

- Diffusivity is well-correlated with the soil's % Water-filled pore spaces (%WFPS)
- As a rule of thumb, field capacity of upland soils is around 60%.
- Below 60% WFPS, soil respiration increases with water content, as water limitation is alleviated.
- Above 60% WFPS, soil respiration declines with additional water due to O_2 limitation

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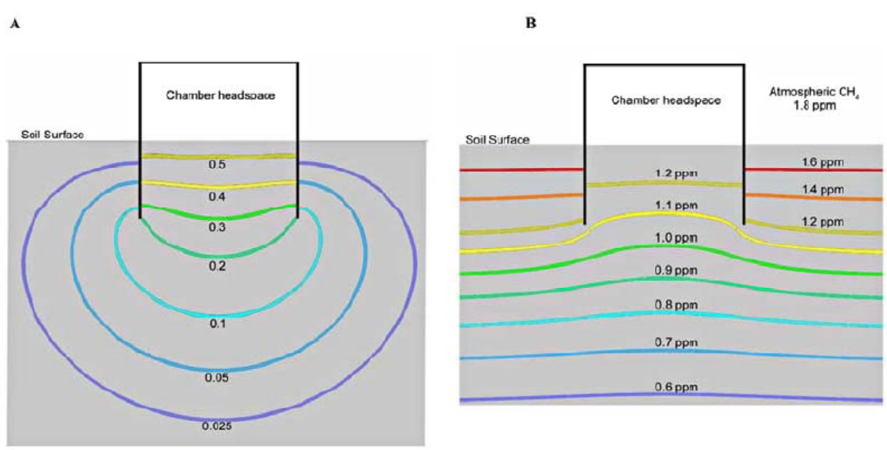
Flux Chambers

<u>Pros</u>
- Easy to deploy
- Captures finer scale features
- Gives reasonable results

- Cons
- Artifacts from
  - Chamber base insertion to ground
  - Gas accumulation in chamber
  - Temperature inside chamber

Nice review in book <u>Biogenic Trace Gases: Measuring Emissions from Soil & Water</u> (1995) by P.A. Matson & R.C. Harriss.
Chapter 2 (Livingston & Hutchinson) on flux chambers.



From von Fischer et al. JGRB 2009

Eddy Flux Towers

- Swirls of air pass over the land surface
- This interaction alters: temperature, humidity, and gas concentrations in the air parcel
- Coincident measure of wind speed & direction with 10Hz measures of air properties allows measurement of flux rate

Flux Towers

Pros

- Larger spatial scale (function of tower height)
- Less tedious
- Longer temporal scale

Cons

- Expensive to set up towers
- Electronics require TLC
- More sophisticated data analysis

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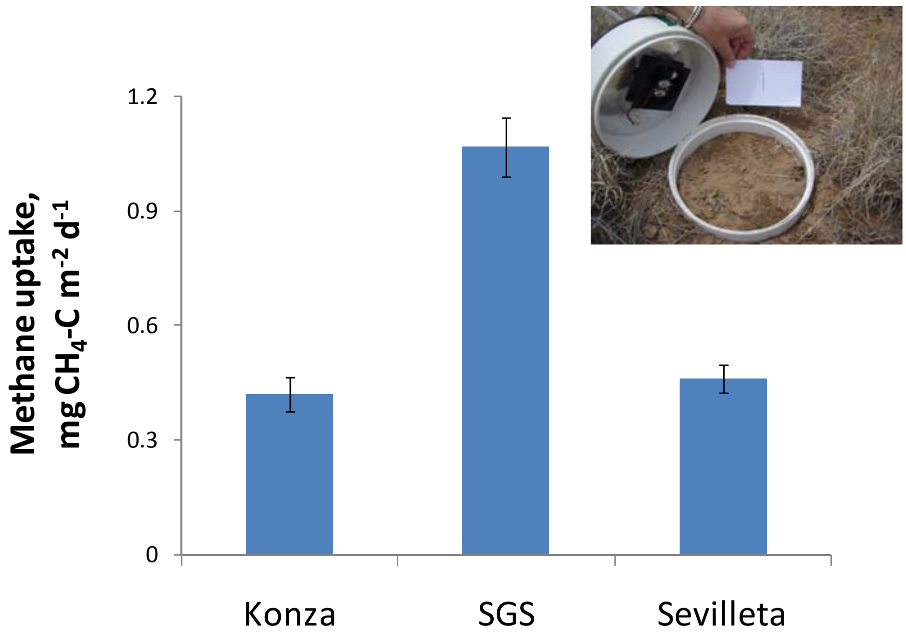
Cross-Site Comparison: May 2008

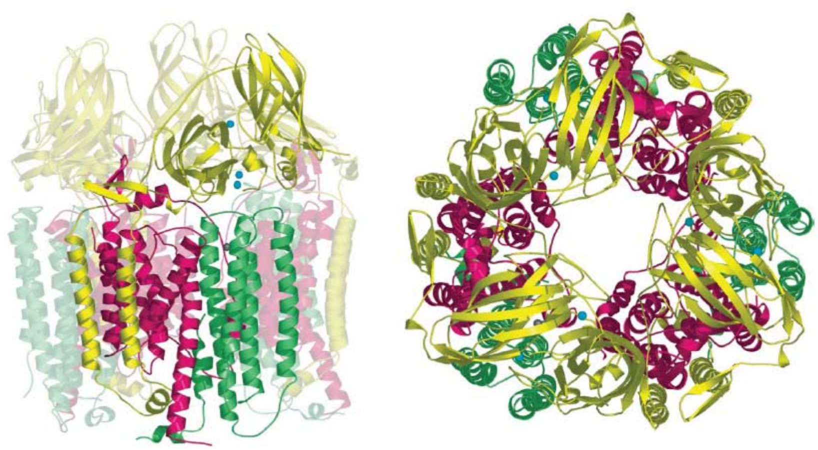
	Konza	Shortgrass Steppe	Sevilleta
Precip, mm	835	320	255
Soil moisture, % gravimetric	30.3%	7.7%	4.3%
Soil pH	6.3	6.4	8.2
Soil [CH_4]	low	low-med	med
Inorganic N (NH_4^+ + NO_3^-), mg/L	1.75	1.65	0.78

Judd et al. in prep



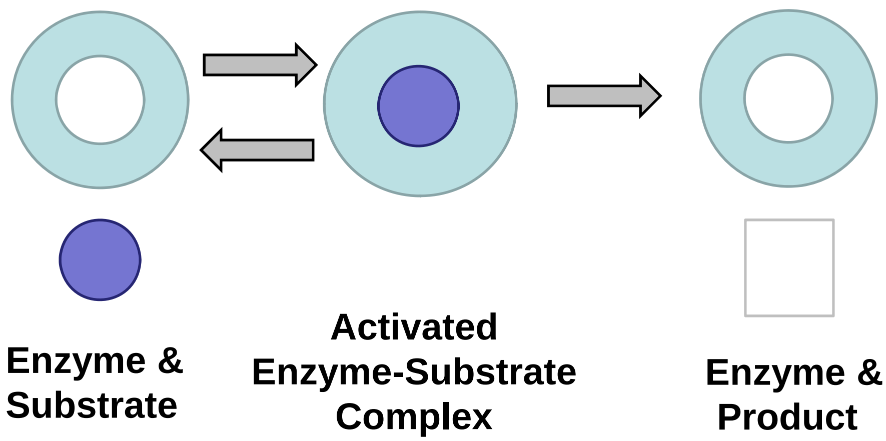
Judd et al. in pre

methane mono-oxygenase enzyme

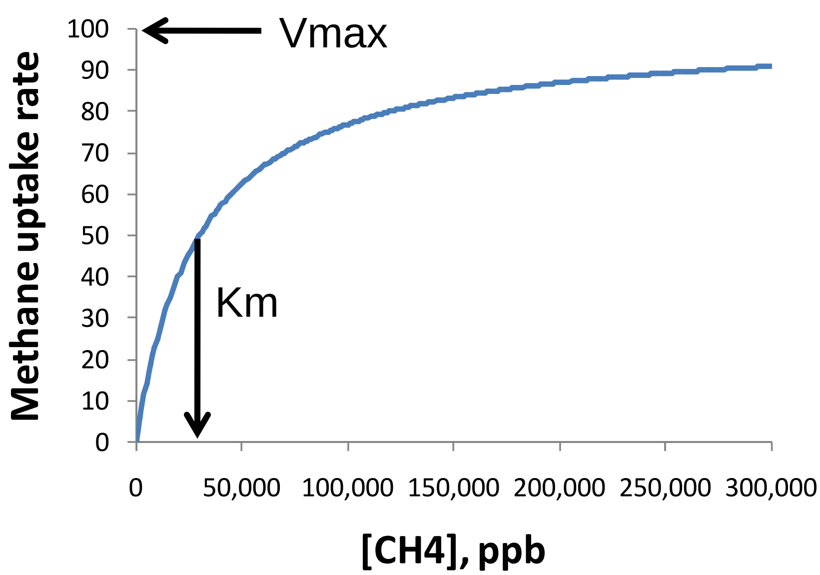


From Lieberman & Rosenzweig

Enzyme kinetics

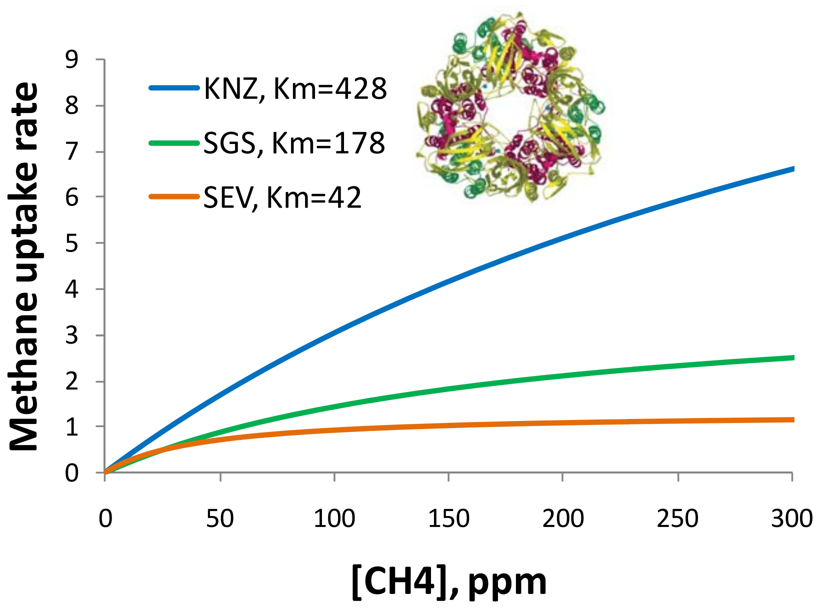


Michaelis-Menten kinetics

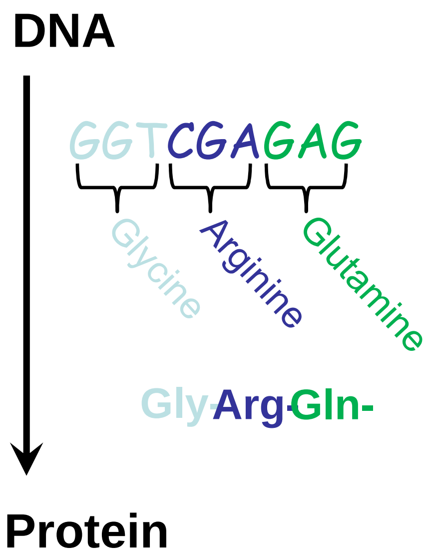


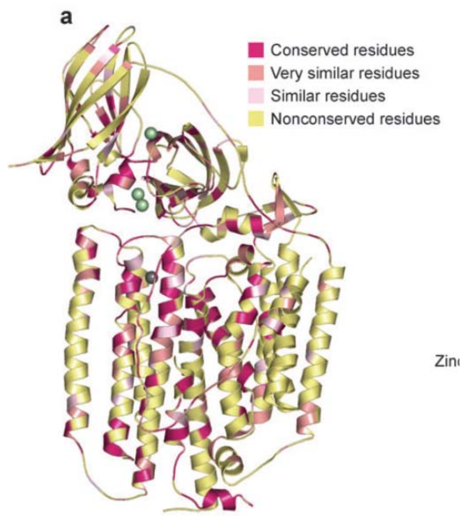
Micahelis-Menten kinetics

- Km reflects affinity of enzyme for substrate
  - Lower value = better at low [CH_4]
- Tradeoff between Km and Vmax
  - Tight binding to substrate slows Vmax
- Spoon or fork?
  - Low [CH_4] soil = low Km
  - High [CH_4] soil = high Km



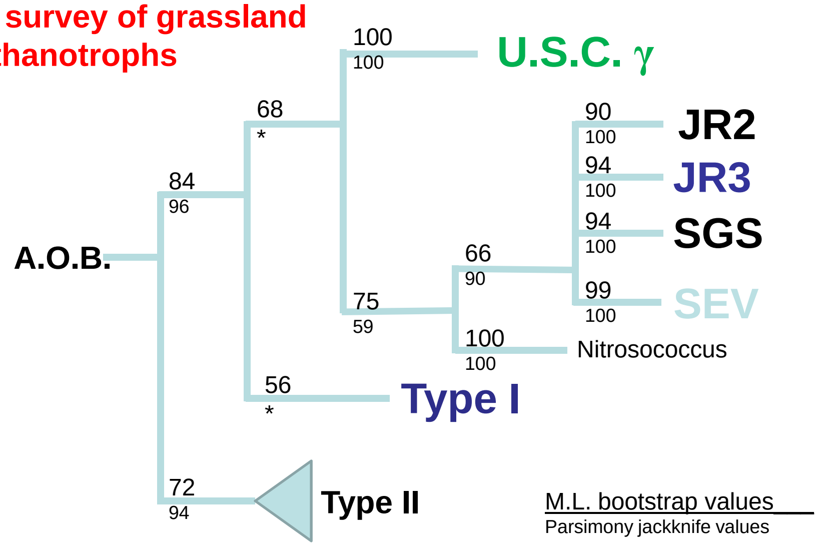
Judd et al. in prep





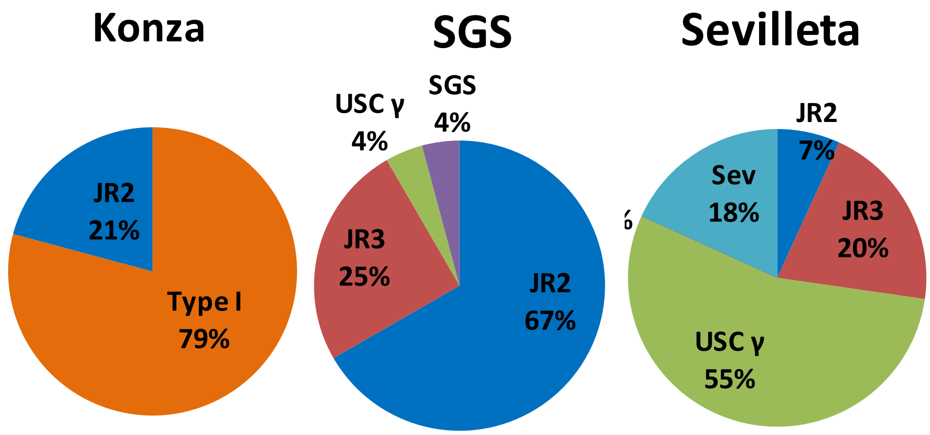
From Hakeman & Rosenzweig 2007

We found red clades in our survey of grassland methanotrophs



Judd et al. in prep

* Indicates branch is not supported by parsimony



Judd et al. in prep