Isotopic signatures of H_2 and CO uptake and emissions by soil

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EGU 2016

Intro: H_2 and CO

- **atm. H_2 = 500 ppb**
- **atm. CO = 100 ppb**

- **indirect greenhouse gases**

- **taken up by soil (microbes)**
- **emitted by soil**

Sources

- Industry
- Biomass burning
- CH_4, NMHC oxidation
- ocean, soil

Sinks

- Reaction with OH
- Soil uptake

Intro: H_2 and CO exchange with soil

H_2 exchange with soil

- **Uptake: microbial** 75% of global sink
- **Emission: microbial** 4% of global source

  → emitted by e.g. N_2-fixing bacteria living in symbiosis with legumes (e.g. clover)

CO exchange with soil

- **Uptake: microbial** 10% of global sink
- **Emission: abiotic** 3% of global source

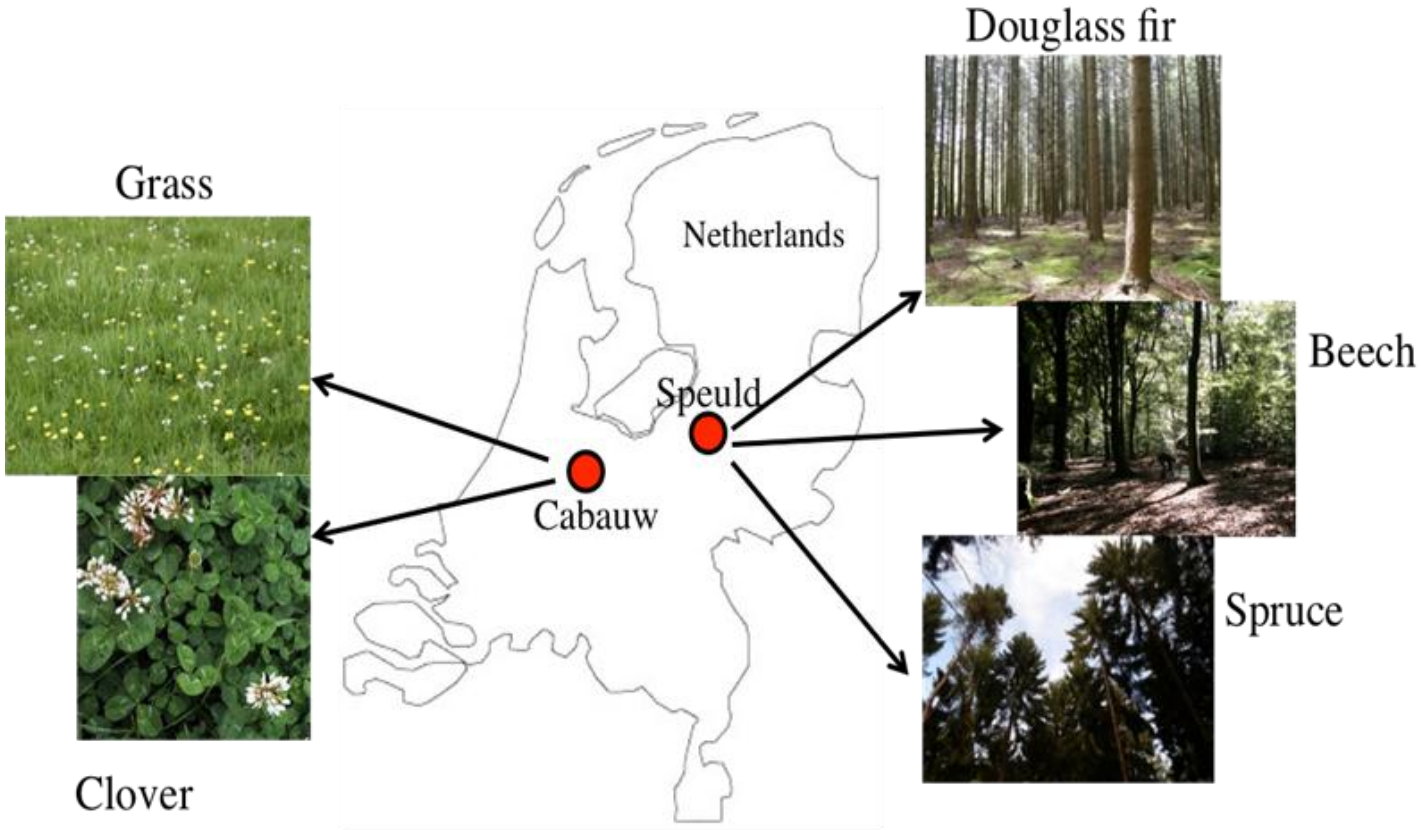
  → thermal or photo- degradation of organic matter

Use isotopes to constrain atmospheric budgets

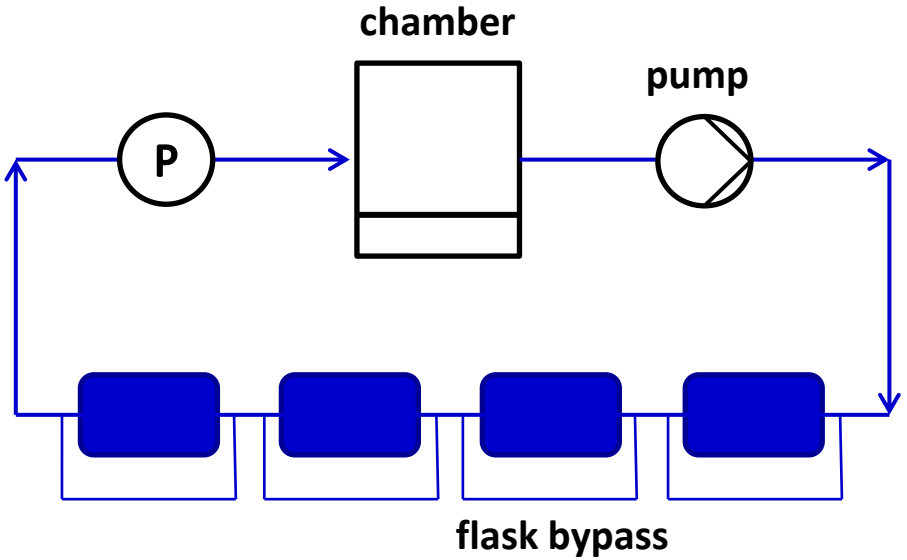
Isotopes of all sources and sinks

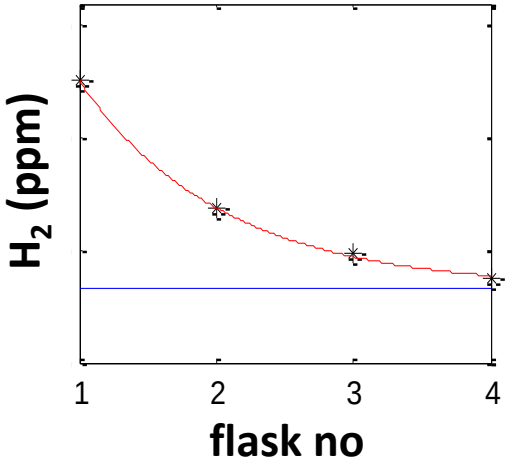
Isotopic signatures of exchange with soil

Methods: Sampling sites



Methods: Sampling





Methods: Calculation

Flux = Source + Sink

$$dc/dt = p - kc$$

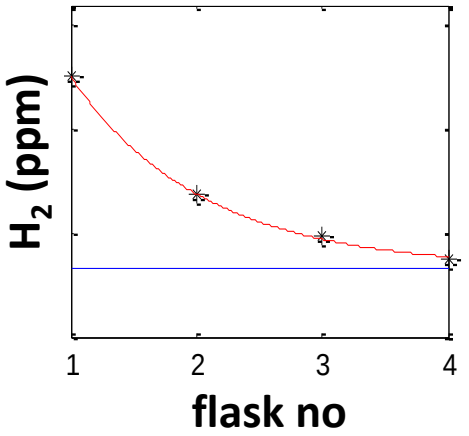
constant source

first order sink

c = concentration
p = gross emission rate
k = gross uptake rate
ci = initial concentration
ce = equilibrium concentration

- integrate → $c(t) = (ci - ce) \exp(-kt) + ce$
- fit to meas. → ce, **k**
- calculate → **p** = k ce

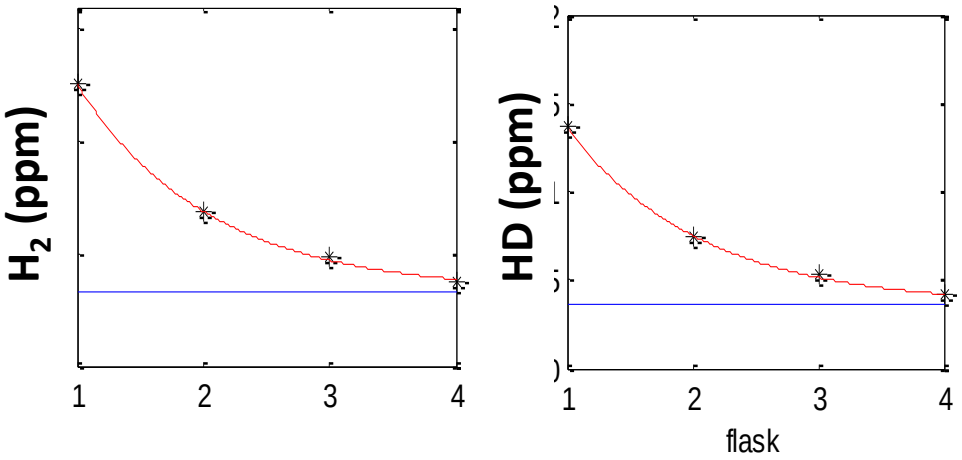
→ **We obtain p and k** (emission and uptake rates)



Methods: Calculation (example H_2)

Obtain p and k

- for HH
- for HD



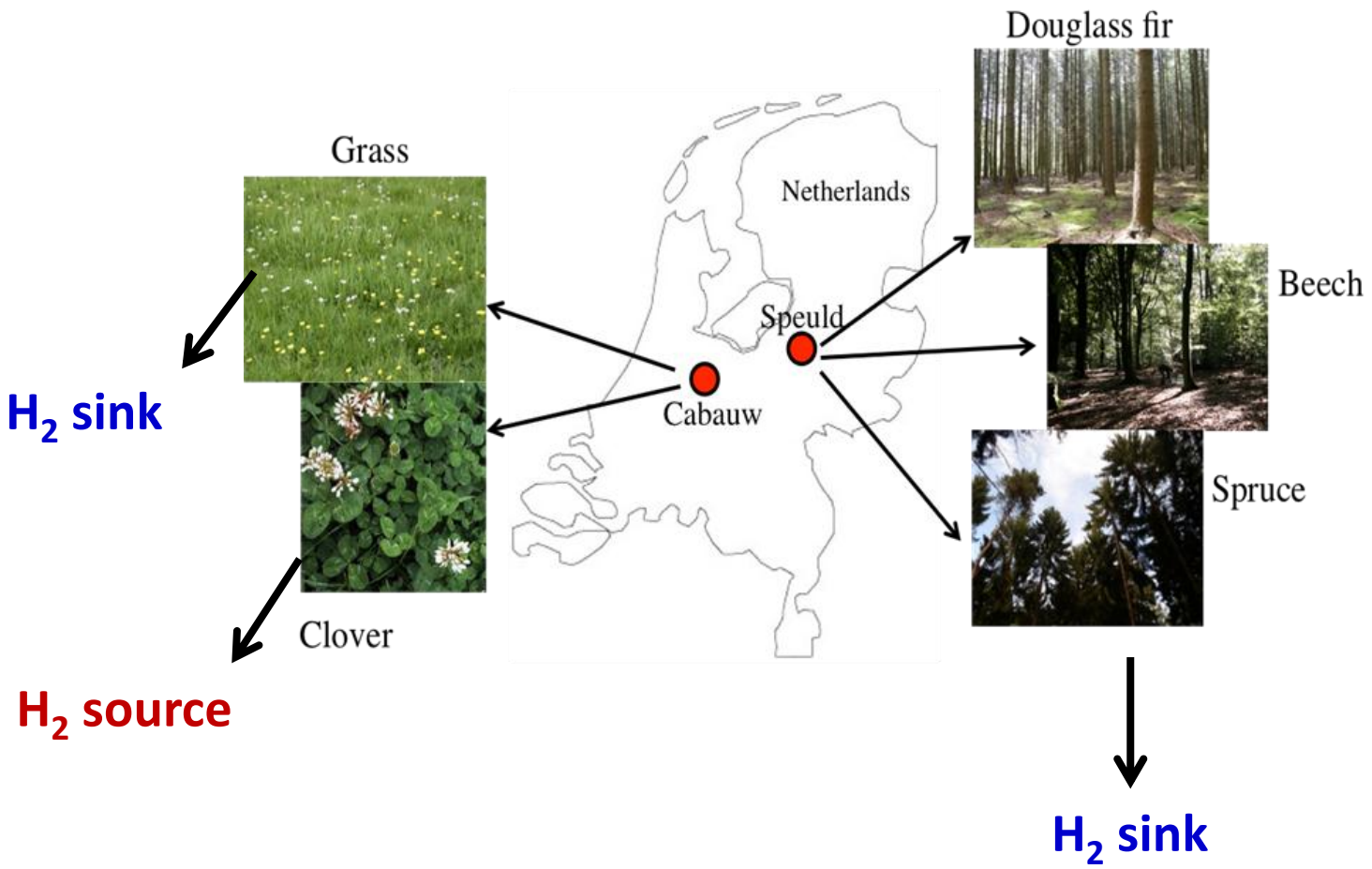
k_{HH}, k_{HD} → Fractionation during uptake: $\alpha = k_{HD} / k_{HH}$

$\varepsilon = \alpha - 1$

p_{HH}, p_{HD} → Emission signature: $\delta D = (p_{HD} / p_{HH}) / R_{ref} - 1$

p = gross emission rate
k = gross uptake rate

Results: H_2 isotopes



Q. Chen et al., 2015: Isotopic signatures of production and uptake of H_2 by soil

Results: H_2 isotopes

1. Soil uptake fractionation

$$\alpha_{soil} = k_{HD}/k_{HH} = 0.945$$

→ no difference between grassland and forest sites

→ no dependence on deposition velocity

→ α_{soil} similar to previous studies in US
(Gerst & Quay, 2001; Rahn et al., 2002; Rice et al., 2011)

→ for comparison: $\alpha_{H2+OH} = 0.57$ (Talukdar et al., 1996)

Q. Chen et al., 2015: Isotopic signatures of production and uptake of H_2 by soil

Results: H_2 isotopes

2. Soil source signature

$$\delta D_{soil} = (-530 \pm 40\ )\ ‰$$

→ less negative than expected

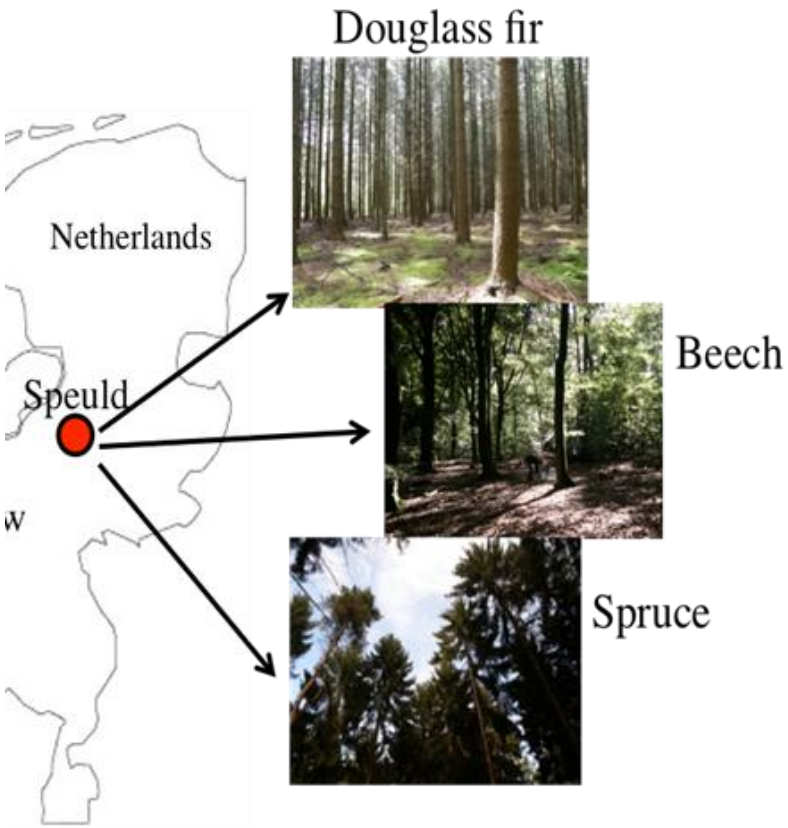
For comparison

- measured microbial H_2 -570 … - 650
  (Luo et al., 1991; Walter et al., 2012)

- isotopic equilibrium with water -700

Q. Chen et al., 2015: Isotopic signatures of production and uptake of H_2 by soil

Results: CO isotopes



Samples only from Speuld

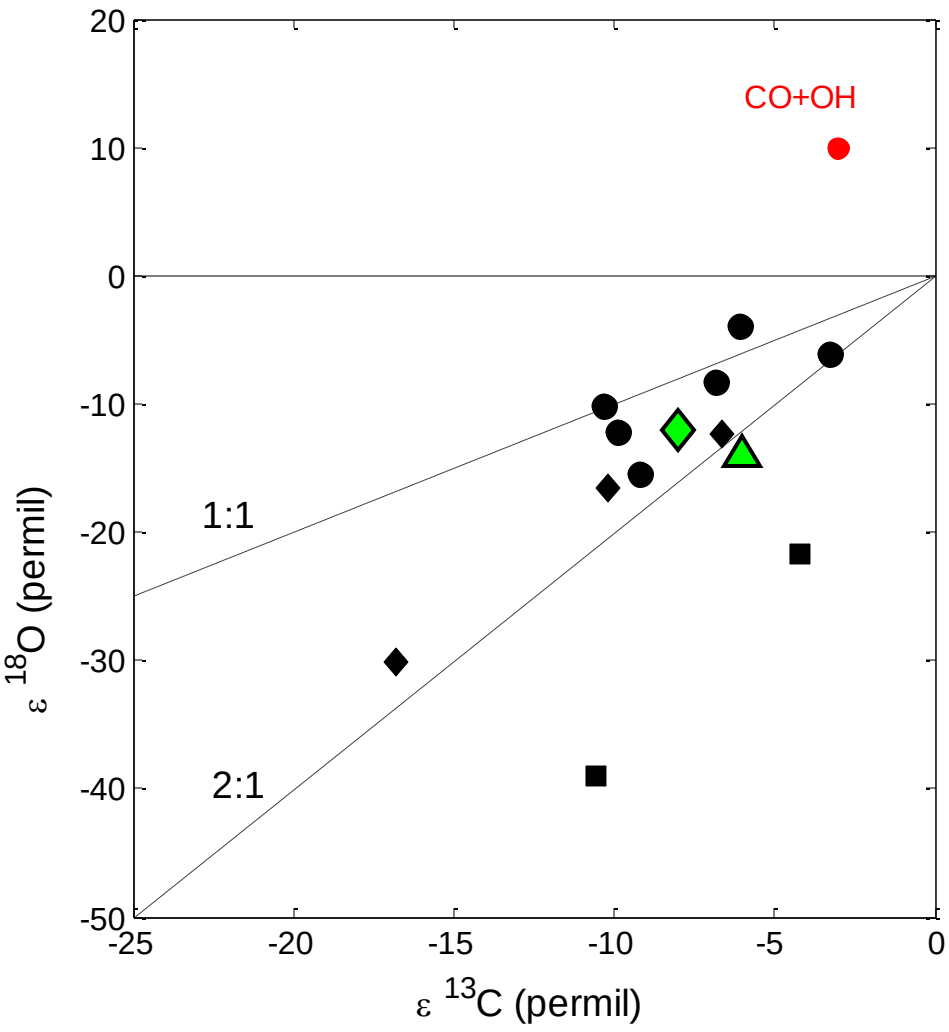
- **2012: CO and H_2 isotopes**
- **2014: ~~CO~~ and CO_2 isotopes**

CO in flask unstable

→ get more samples, 2016

Results: CO soil uptake fractionation

$\varepsilon^{13}C = (k^{13}C/k^{12}C - 1) = \alpha - 1$



- Douglas fir
- Beech
- Spruce
- Bergamaschi 2000 model
- Tsunogai 2002 measurements
- CO + OH [1]

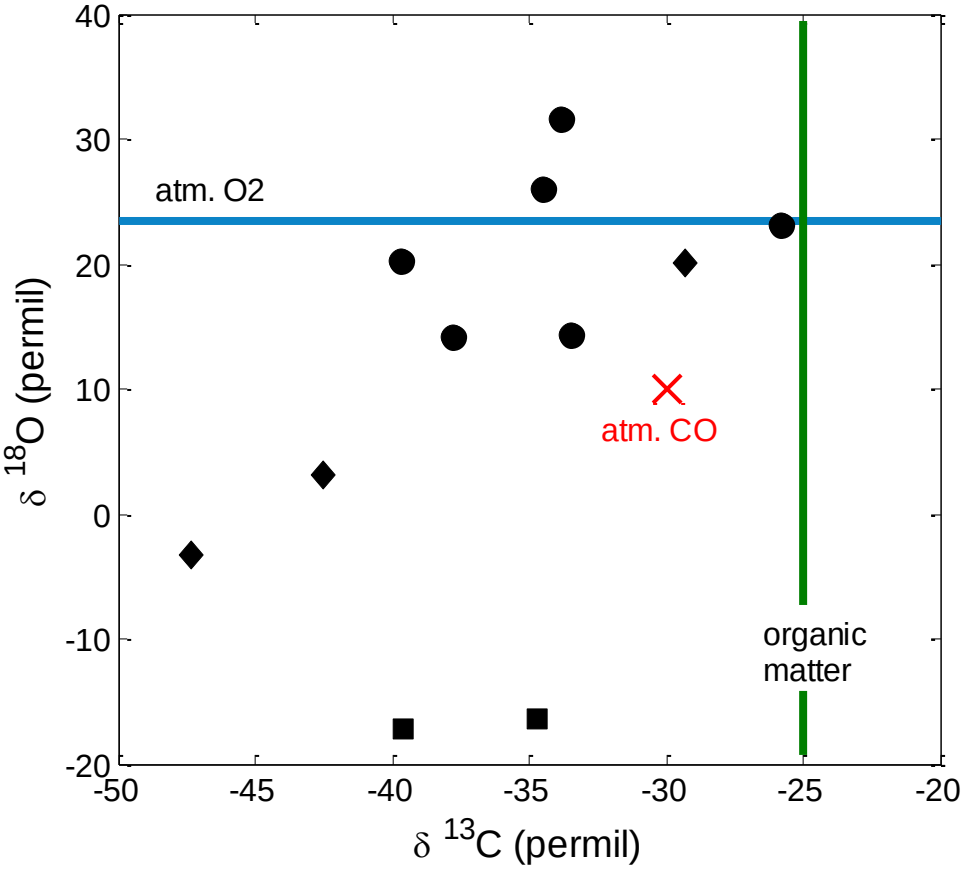
$\varepsilon^{13}C$ median = -9.5 ‰

$\varepsilon^{18}O$ median = -14 ‰

- **Soil sink = large fractionation**
  → large influence on atmospheric CO
- **^{18}O – fractionation opposite to the CO + OH reaction**

[1] **from** Roeckmann et al., 1998; Stevens and Wagner, 1989

Results: CO source signature



$\delta^{13}C$ median = -34.6 ‰ (VPDB)

$\delta^{18}O$ median = +17.2 ‰ (VSMOW)

- Soil emission = large variability
- ^{13}C, ^{18}O – strongly depleted relative to C and O source

→ fractionation during CO production

- large effect on atmospheric CO

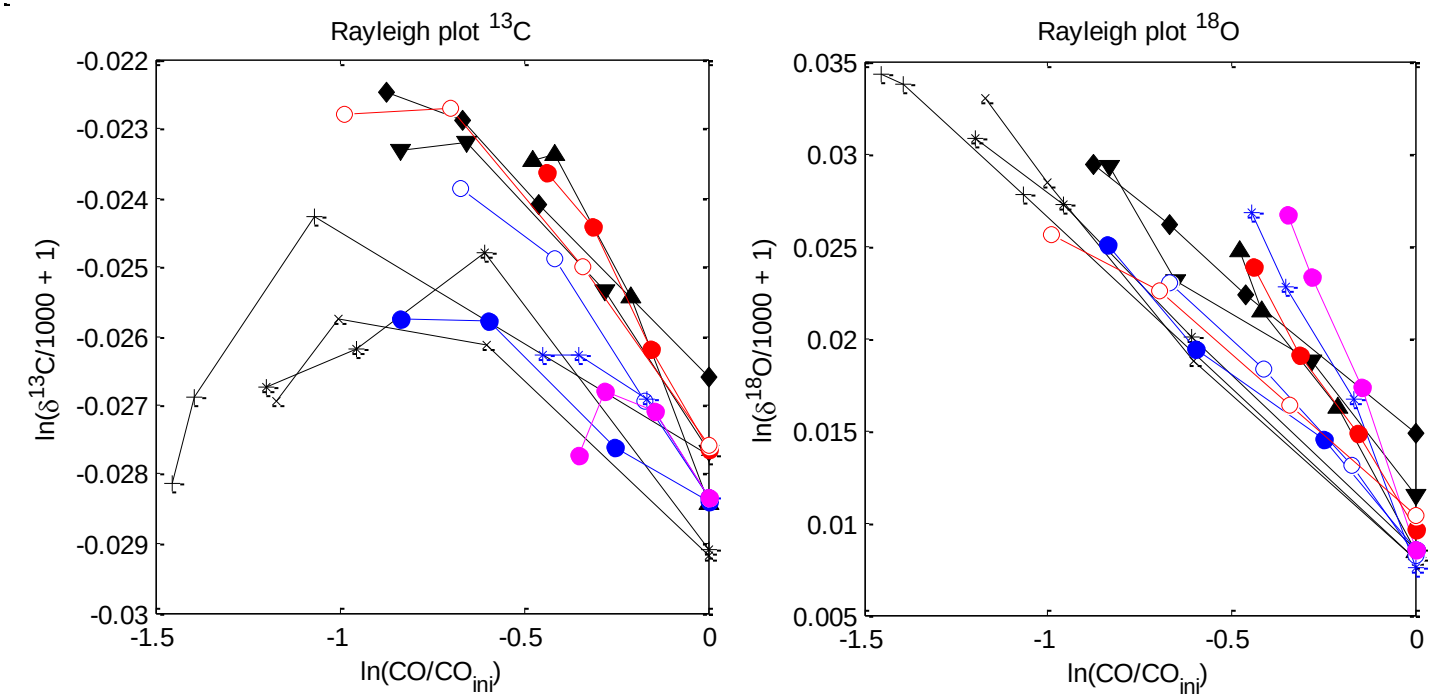
Summary

- **H_2 soil uptake fractionation** — $\alpha_{soil} = 0.945 \pm 0.004$
- **H2 soil emission signature** — $\delta D_{soil} = (-530 \pm 40)$ ‰
- **CO soil uptake fractionation** — $\varepsilon^{13}C$ median = -9.5 ‰; $\varepsilon^{18}O$ median = -14 ‰
- **CO soil emission signature** — $\delta^{13}C$ median = -34.6 ‰; $\delta^{18}O$ median = +17.2 ‰

Thank you

More results: Always source AND sink

Rayleigh fractionation plot



Rayleigh plot

→ should be linear, if only sink (slope = fractionation)

→ NOT linear → SOURCE present !

More info: concurrent source and sink

We assume that we always have **concurrent source and sink**, based on:

- **Mole fraction** evolution– e.g., the mole fraction does not decrease to zero when the net flux is uptake

- **Isotope** evolution: additional measurements of CO and H_2 stable isotope (in flask sampled from the soil chamber) indicate the presence of both source and sink

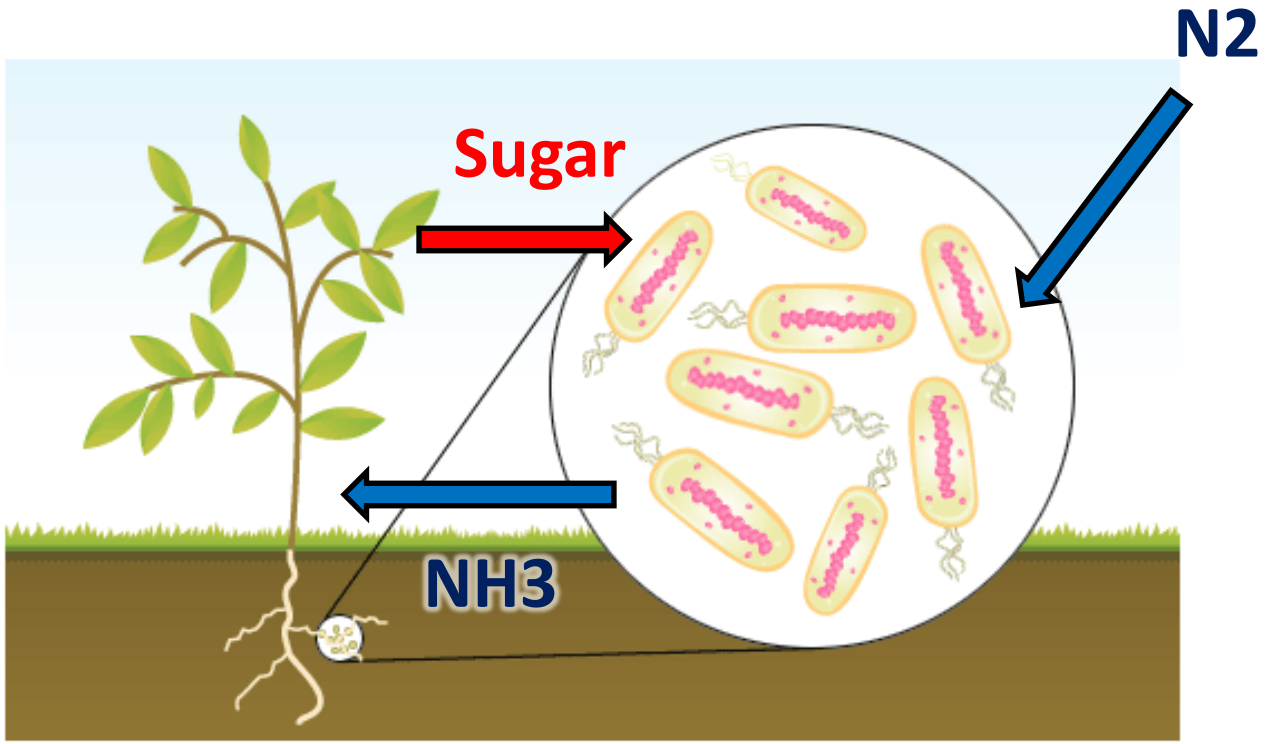
  - H_2 isotope results published:

  Chen et al., 2015: Isotopic signatures of production and uptake of H_2 by soil

  - for CO isotopes, paper in preparation (Popa et al)

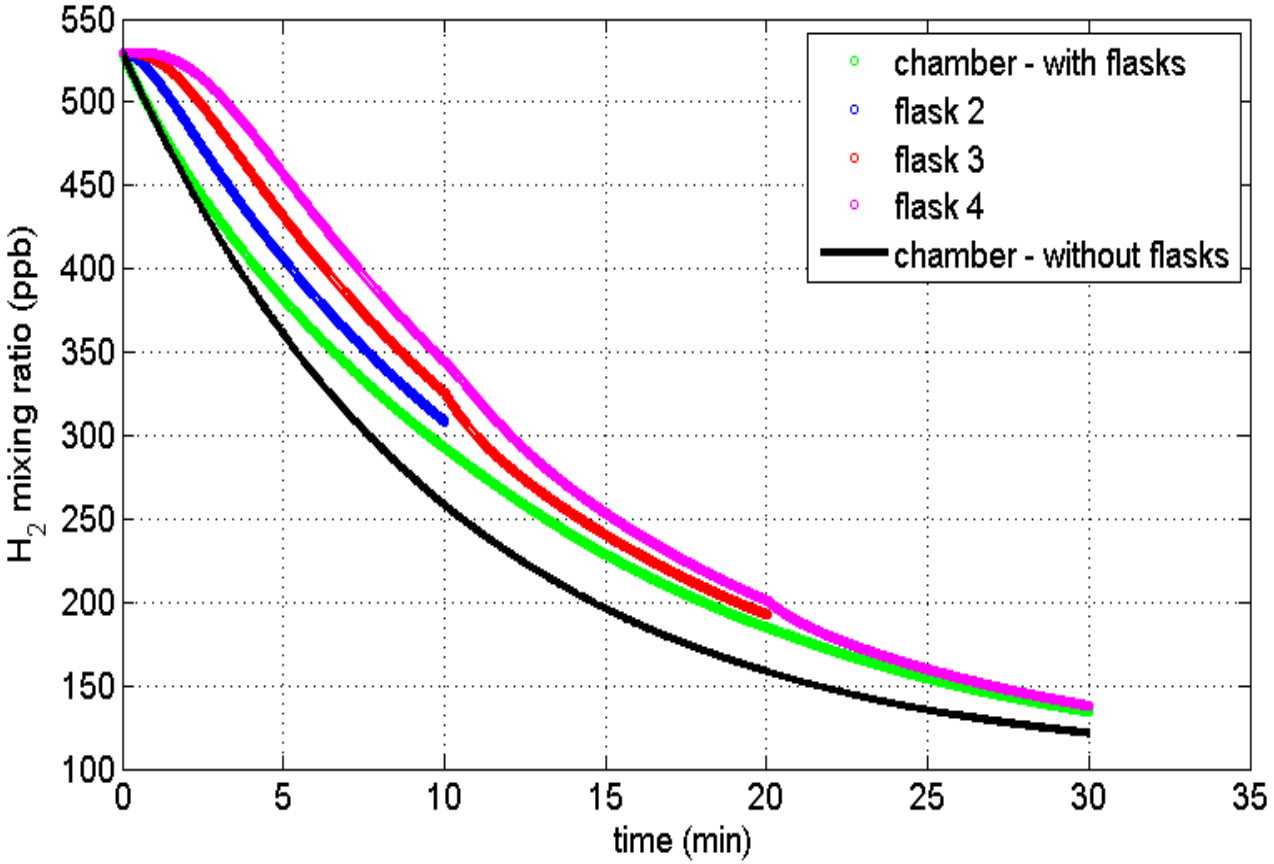
More info: Atmospheric N_2 fixation

Symbiosis: plant (legume) – bacteria (Rhizobium)

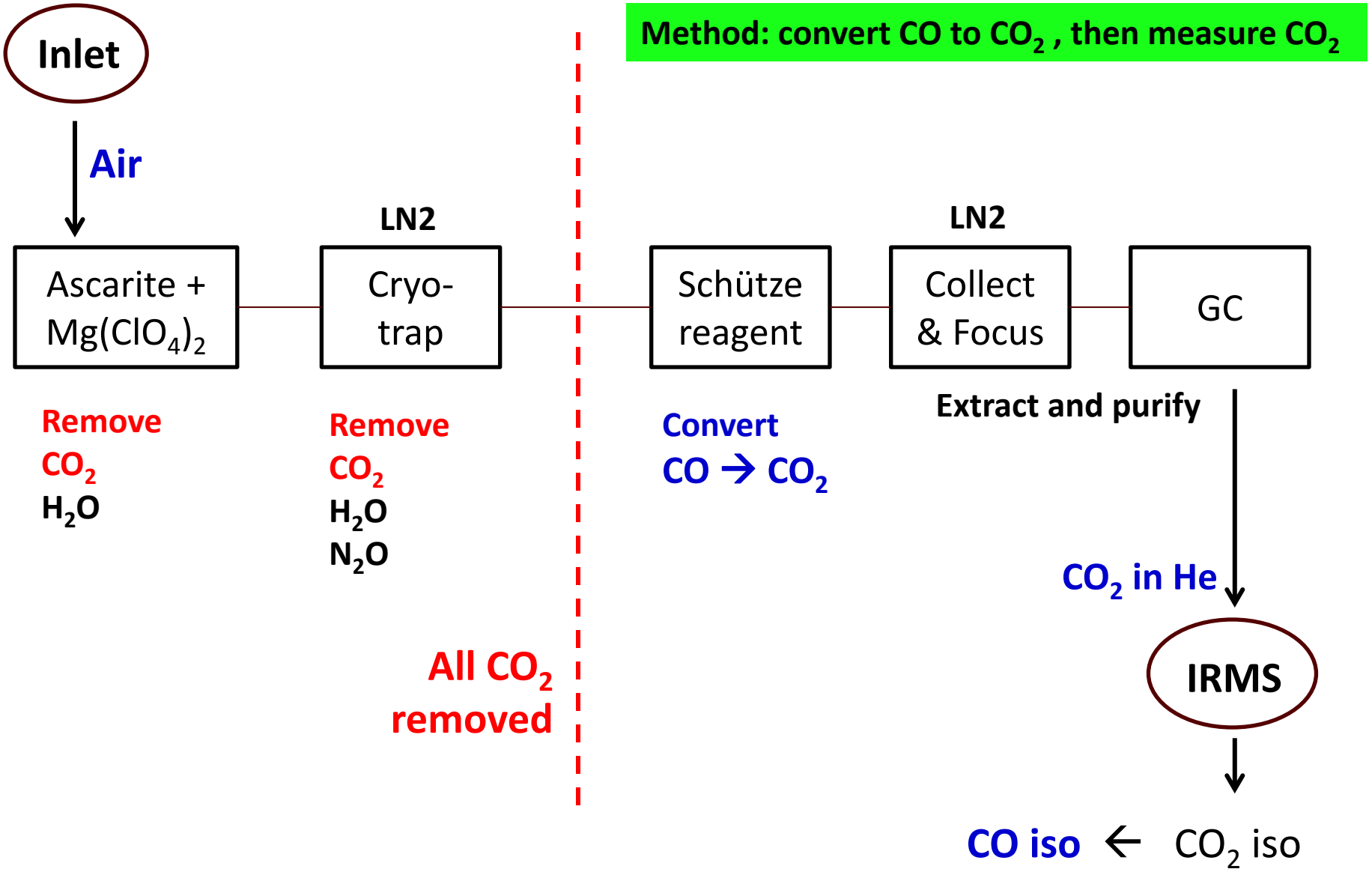


$$N_2 + 8\,H^+ + 8\,e^- \rightarrow 2\,NH_3 + H_2$$

More info: Mole fraction evolution



More info: CO isotope measurements



Atmospheric air: CO_2 = 400 ppm, CO = 0.1 ppm

More info – Work on CO isotopes

Vehicle emissions
- tunnel: Popa 2014
- individual veh. – ongoing, Stijn

Plant emissions
- ongoing, Sem, Selma

Reactor – chemistry
- CO + OH
- CH4, NMHC → Form → CO, H2

Soil exchange
- student, summer 2016

Sampling
- Cabauw
- Korea (starting)
- Amazon (future)

Continuous measurements IMAU
CO-iso, H2:CO, CH4, CO2