# **CO and H<sub>2</sub> uptake and emission by soil** variability of fluxes from long term soil chamber measurements

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# The idea

#### What we wanted

### To study the soil uptake and release of H<sub>2</sub> and CO

- magnitude
- spatial and temporal variability
- dependence on environmental variables

### What we did

### Long term in-situ measurements with a soil chamber

- high temporal resolution
- various conditions (e.g. temperature, soil moisture)
- different measurement locations
- long term seasons

# The idea



- Variability: time, place
- Influence factors



Uptake and emission fluxes

Note: we always find concurrent uptake and emission

# Contents

- Intro
- <u>Methods</u>
- <u>Results</u>
- <u>Summary</u>



# Intro: H<sub>2</sub> and CO

- indirect greenhouse gases
- taken up by soil (microbes)
- emitted by soil
- atm.  $H_2 = 500 \text{ ppb}$
- atm. CO = 100 ppb
- can be measured together with an RGA

#### Sources

- Industry
- Biomass burning
- CH<sub>4</sub>, NMHC oxidation
- ocean, soil

#### Sinks

- Reaction with OH
- Soil uptake

# Intro: H<sub>2</sub> and CO exchange with soil

## H<sub>2</sub> exchange with soil

- uptake: microbial (75% of the global sink)
- emission: microbial (4% of global source)
  - → emitted by e.g. N<sub>2</sub>-fixing bacteria living in symbiosis with legumes (e.g. clover) – more info

### **CO** exchange with soil

- uptake: microbial (10% of the global sink)
- **emission: abiotic** (3% of global source)
  - $\rightarrow$  thermal or photo- degradation of organic matter

# Methods

go to:

- Sampling sites
- <u>Automatic measurements</u>
- <u>H<sub>2</sub> and CO analysis</u>
- Measurement sequence
- Flux calculation



# Methods: Sampling sites



#### Back to Methods

#### Three data subsets

- Cabauw 2011: Jul Oct (2 locations)
- Cabauw 2012: Apr Jul
- Speuld 2012: Aug Dec

# Methods: Automatic measurements

#### **Gases: calibration, target**

### H<sub>2</sub> and CO analyzer (PP1)



# Methods: H<sub>2</sub> and CO analysis

## Peak Performer PP1 analyser (gas chromatograph) PeakSimple software



- 1 measurement = 4 min
- air dried (Nafion)
- **precision 1 ppb** or better for both H<sub>2</sub> and CO

Back to

**Methods** 

- strong dependence on temperature
  - $\rightarrow$  corrected
- calibrated daily with 2 gas cylinders
- Target gas frequently
- nonlinearity corrected
- memory effects (incomplete line flushing?)
  → corrected

# Methods: Measurement sequence

### Automatic chamber with two positions

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→ this is how the measurement looks like (raw data):



10 x Box 1 - 2 x Target - 10 x Box 2 - 2 x Target.....

# Methods: Flux calculation

Soil chamber closed → evolution of mole fraction



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• Flux = Source + Sink (g

#### (see why we assume this)



- p = production rate
- k = uptake rate

# Methods: Flux calculation

Flux = Source + Sink (see why we assume this)

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dc/dt = p - kc

- integrate  $\rightarrow$  c(t) = (ci ce) exp (-kt) + ce
- fit to meas.  $\rightarrow$  ce, k
- calculate  $\rightarrow p = k ce$ 
  - → We obtain p and k (production and uptake rates) for each soil chamber closing (every ~ 40 min)



p = gross production rate

k = gross uptake rate

ci = initial concentration

ce = equilibrium concentration

## Results

## go to

- <u>H<sub>2</sub> mole fractions</u>
- <u>H<sub>2</sub> fluxes</u>
- <u>CO mole fractions</u>
- <u>CO fluxes</u>
- <u>Correlation of CO and H<sub>2</sub> fluxes</u>

# Results: H<sub>2</sub> mole fractions

- data Cabauw, 2011
- two chamber positions (boxes)
- chamber location 1 (explain)





#### Time (few hours)



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# Results: H<sub>2</sub> mole fractions

- data Cabauw, 2011
- two chamber positions (boxes)
- chamber location 1 (explain)



 Net H<sub>2</sub> emission! – vegetation = glass + clover (see explanation)

- Spatial variability large difference between the two boxes 1 m apart
- diurnal variations emission larger during day
- synoptic variations increase with air / soil temperature



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# Results: H<sub>2</sub> mole fractions

- data Cabauw, 2011
- Sep-11 moved chamber by a few m, no more clover



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Results

# Results: H<sub>2</sub> fluxes

# Concurrent uptake and emission fluxes calculated as shown in methods (go there)

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- spatial variability large difference over few meters
- synoptic variations changes with air / soil temperature;
- soil flooded → uptake stops, emission not
- cold season → uptake does not stop

# Results: CO mole fractions

data Cabauw, 2011

Net flux: uptake during night, often emission during day

 $\rightarrow$  light induced emission from organic matter



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# Results: CO fluxes

Concurrent uptake and emission fluxes calculated as shown in methods (go there)





# Results: CO fluxes

Concurrent uptake and emission fluxes calculated as shown in methods (go there)





- spatial variability not very large
- synoptic variations changes with air / soil temperature;
- day / night variability larger than the long term
- soil flooded → uptake stops, emission not
- cold season → uptake does not stop

# Results: Correlation of CO and H<sub>2</sub> fluxes

Example: data from one soil box, one location

![](_page_21_Figure_2.jpeg)

data Cabauw, 2011

# Results: Correlation of CO and H<sub>2</sub> fluxes

#### Example: all data from Cabauw 2011

The colors correspond to different chamber positions, see here

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![](_page_22_Figure_4.jpeg)

Deposition velocity: all data seem to sit close to the same line

• Emission fluxes of H2 and CO correlated, but differently for each subsite

# Summary

- We can compute the gross uptake and emission fluxes (assuming first order uptake, zero order emission)
- Always both uptake and emission
- H<sub>2</sub> fluxes large variability in both time and space
  → upscaling will be difficult!
- H<sub>2</sub> net emission when clover present (N2 fixation)
- **CO fluxes** less variable in space than H<sub>2</sub>
- CO net emission during day (photo-emission from organic matter)
- CO and H<sub>2</sub> fluxes correlated
- **forest site Speuld** (data not shown)  $\rightarrow$  always strong uptake

Note: work in progress

# From here: More info

![](_page_24_Picture_1.jpeg)

#### soil chamber at Cabauw seen from the Cabauw tower (200m)

# More info: measurements

### RGA

- carrier gas: Zero air
- memory effects (incomplete flushing?) stronger for CO → corrected

#### **Additional measurements**

- soil moisture and temperature
- analyzer box temperature (for temperature correction)

## 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<sub>2</sub> 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)

![](_page_26_Picture_6.jpeg)

## More info: Atmospheric N<sub>2</sub> fixation

Symbiosis: plant (legume) – bacteria (Rhizobium)

![](_page_27_Figure_2.jpeg)

# More info: detail CO fluxes

data: 25 - 26-Sep-2011, Cabauw

![](_page_28_Figure_2.jpeg)

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# More info: soil chamber positions CBW 2011

**Soil chamber position** at Cabauw in 2011: the chamber was moved by about 2 m in Sep-2011; the colors correspond to data plots through the presentation.

![](_page_29_Figure_2.jpeg)

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H2 mole

fractions