

Herausforderungen bei der Messung von N₂O, CH₄ und CO₂ Bodengasflüssen

- Messmethoden
- Probenahme
- Qualitätskontrolle



Ralf Kiese

Karlsruher Institut für Technologie
Institut für Meteorologie und
Klimaforschung (IMK-IFU)
Gramisch-Partenkirchen

Messmethoden

- Chambers
 - the simplest and most common approach
- Eddy covariance
 - applicable to large landscapes with uniform surface sources
- Flux-gradient methods
 - as for eddy covariance, applicable to large landscapes with uniform surface sources
- Mass balance techniques
 - suitable for small bounded areas and heterogeneous surface sources
- Eddy accumulation
 - a fast response system for large uniform landscapes
- Open path lasers / FTIR
 - suitable for point, line and small area sources
- Backward Lagrangian stochastic dispersion
 - suitable for small to medium size landscapes and point and areal sources

Chamber techniques

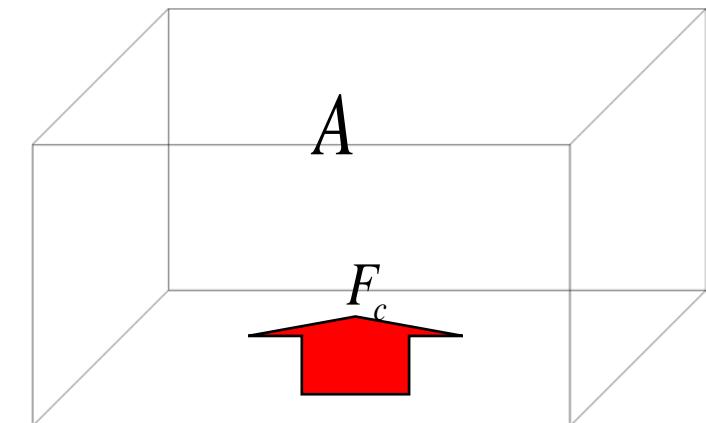
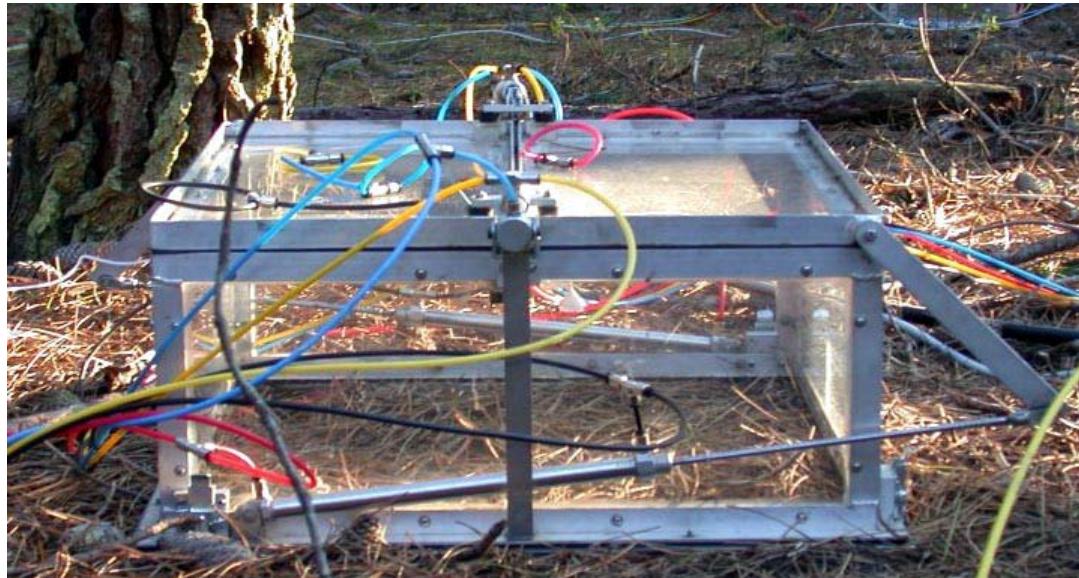
The most common approach for measuring trace gas emissions from soils

- Two types:
 - Closed chambers
 - Dynamic chambers
- Two operation modes
 - Manual
 - Automatic



Static chamber

- Gas-tight enclosure of a soil-plant system or e.g. plant part
- Follow the increase/ decrease in concentration of a gaseous compound with time (e.g. N₂O, CO₂, CH₄)
- Kinetics of increase/ decrease is used to calculate the flux



$$F_c = \frac{V}{A} \frac{\partial C_c}{\partial t}$$

Static chamber

Advantages:

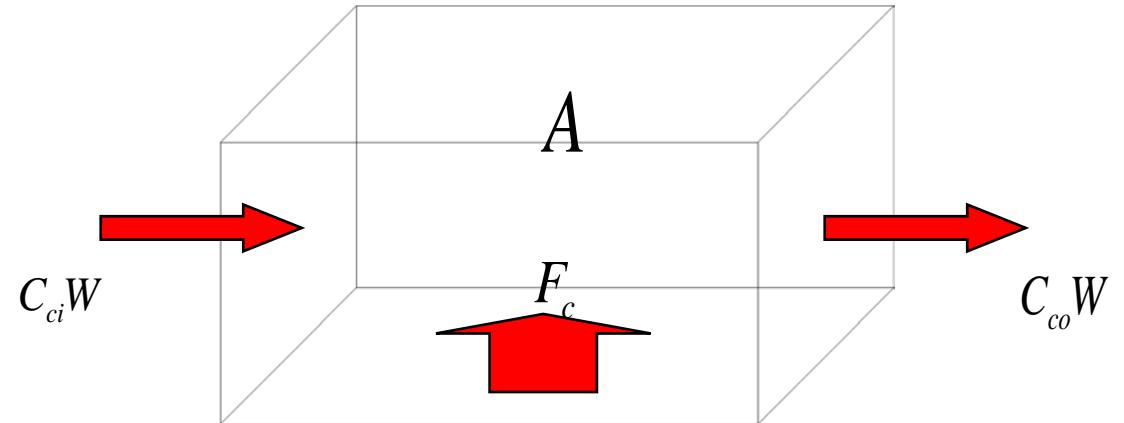
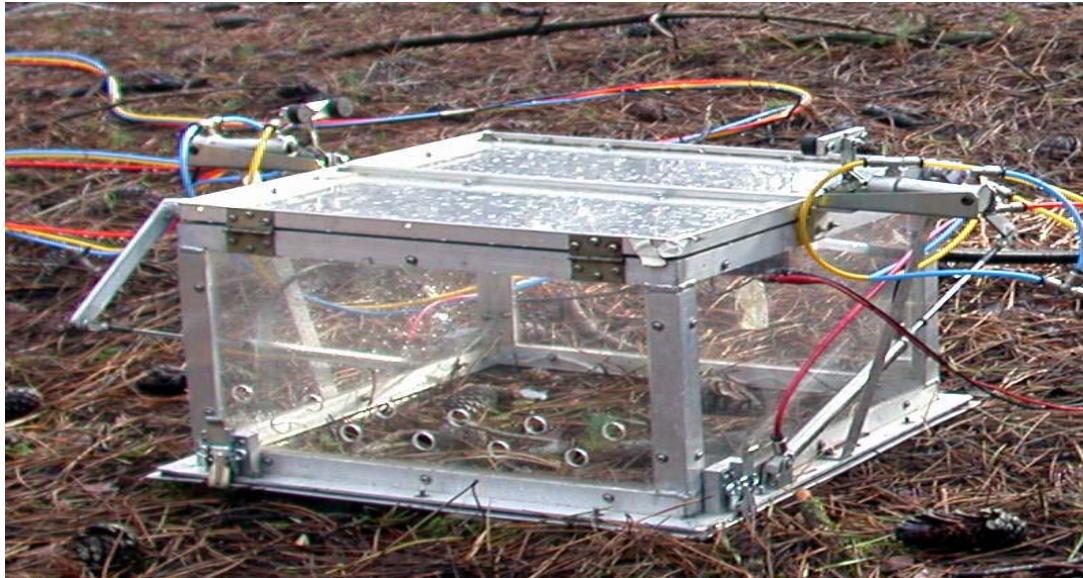
- Low-tech, cheap
- Easy to apply, no power supply, no gas analyzer online
- High sensitivity
- Typically applied for non-reactive substances such as N₂O, CH₄ or CO₂

Disadvantages:

- Alteration of environmental conditions (e.g. temperature, moisture, soil gas concentration profile)
- Biosphere-Atmosphere exchange is a balance of consumption-production processes, this equilibrium may be changed (e.g. for CH₄, NO)

Dynamic chamber

- Gas-flow through a chamber enclosing a soil-plant system or e.g. plant part
- Measurement of the compound concentration at the inlet and at the outlet (e.g. CO₂, NO or NO₂)
- Fluxes are calculated from concentration differences and air mass flow



$$F_c = \frac{W}{A} (C_{co} - C_{ci})$$

Dynamic chamber

Advantages:

- Reduced disturbance of environmental conditions, especially of gas concentrations
- Easy to apply
- Medium to high sensitivity depending on the detector

Disadvantages:

- High exchange rates are applied (pumps and thus power is needed)
- Still environmental conditions are biased

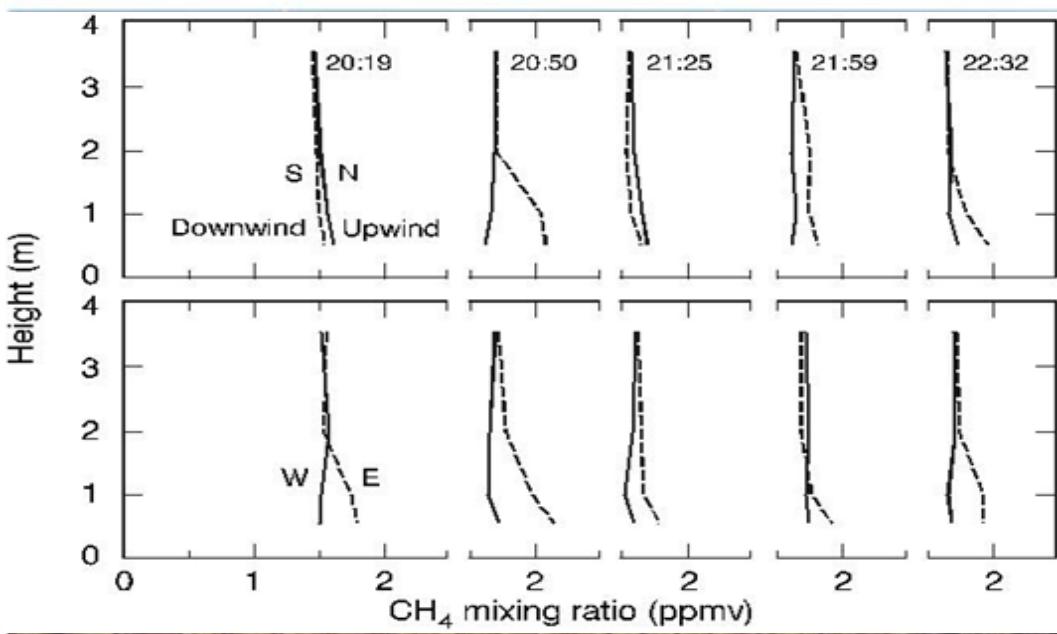
A closed path EC system



(Courtesy Campbell Scientific Australia)

T. Denmead, CSIRO Land and Water

Mass balance for closed systems

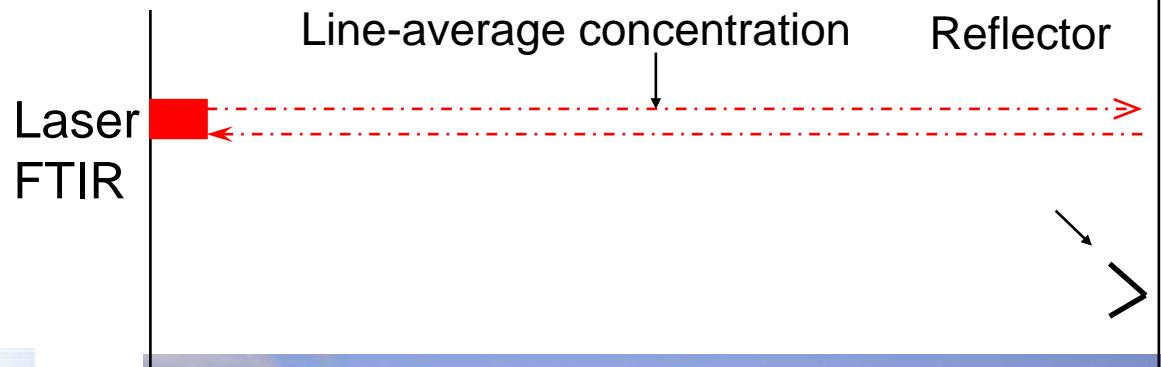


- Measuring CH₄ production with a closed mass balance method
- Animals enclosed in a plot 24m x 24m
- 4 sampling tubes on each boundary, at heights of 0.5, 1, 2 and 3.5m
- Top sampling arm high enough to be above the plume from the test area
- Air drawn continuously into the 16 sampling tubes
- The 16 airstreams pass in turn through a CH₄ gas analyser
- Anemometers measure $u(z)$

T. Denmead, CSIRO Land and Water

Open-path lasers and FTIR

Instruments measure line-averaged concentrations up to 1km, FTIR less



Open-path FTIR ($\text{CO}_2, \text{CH}_4, \text{N}_2\text{O}, \text{NH}_3$)

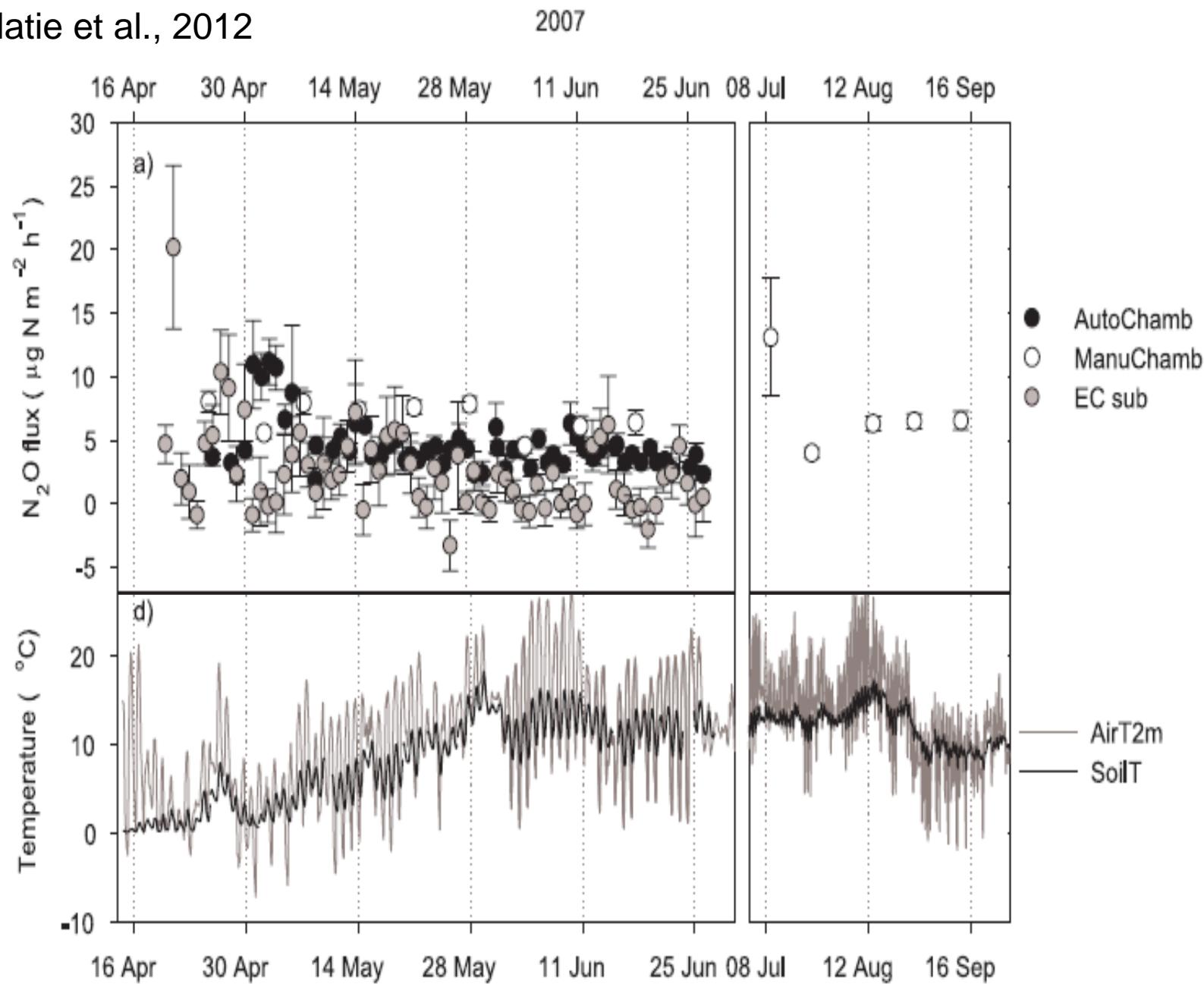


Open-path laser ($\text{CO}_2, \text{CH}_4, \text{NH}_3$)

T. Denmead, CSIRO Land and Water

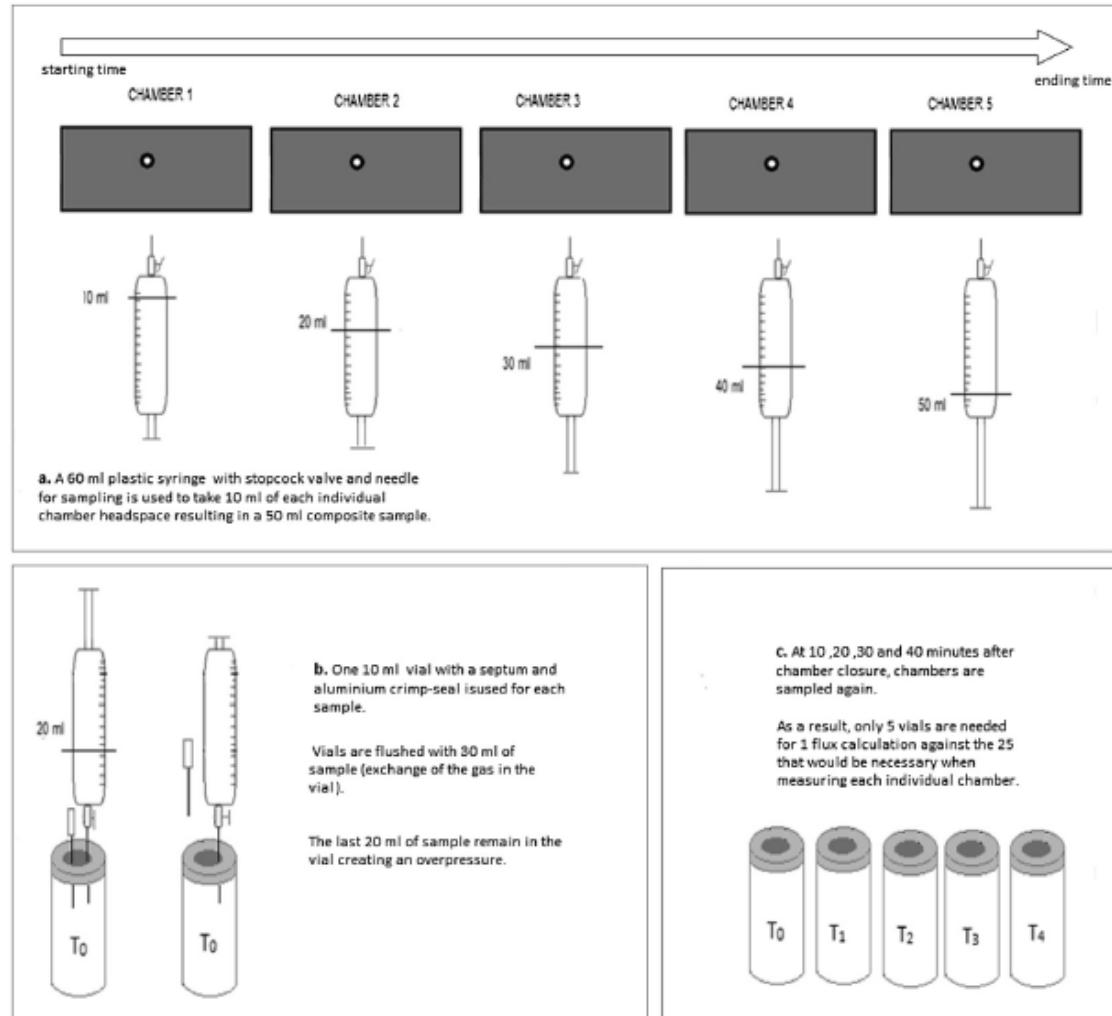
Chambers vs. micromet

Pihlatie et al., 2012



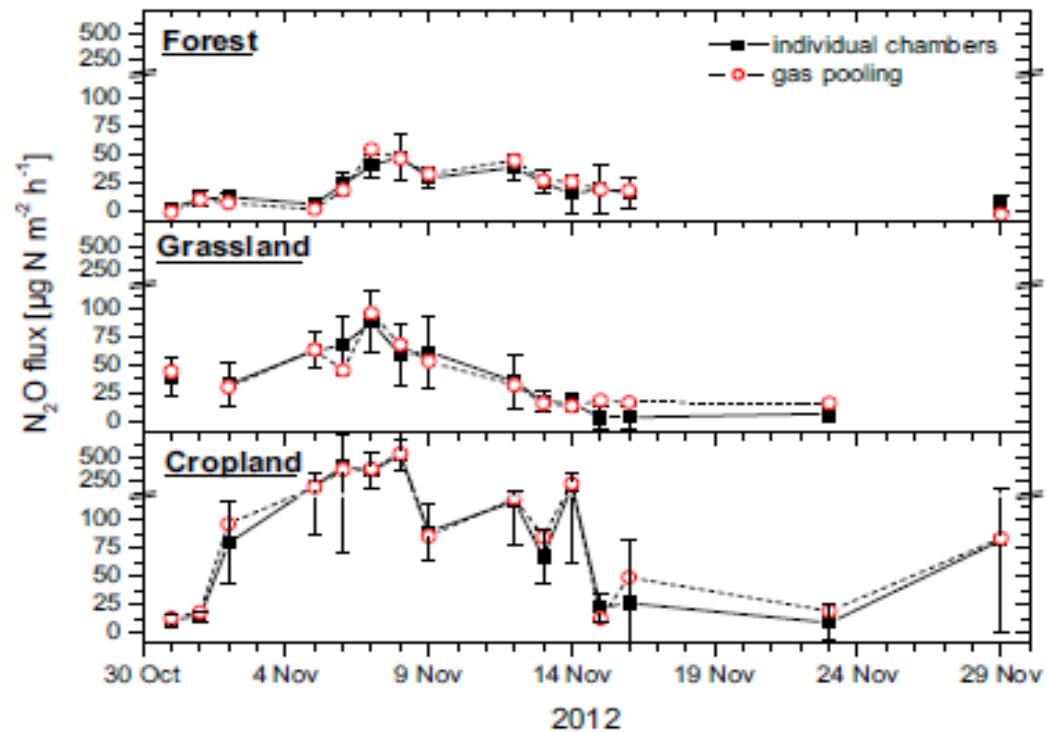
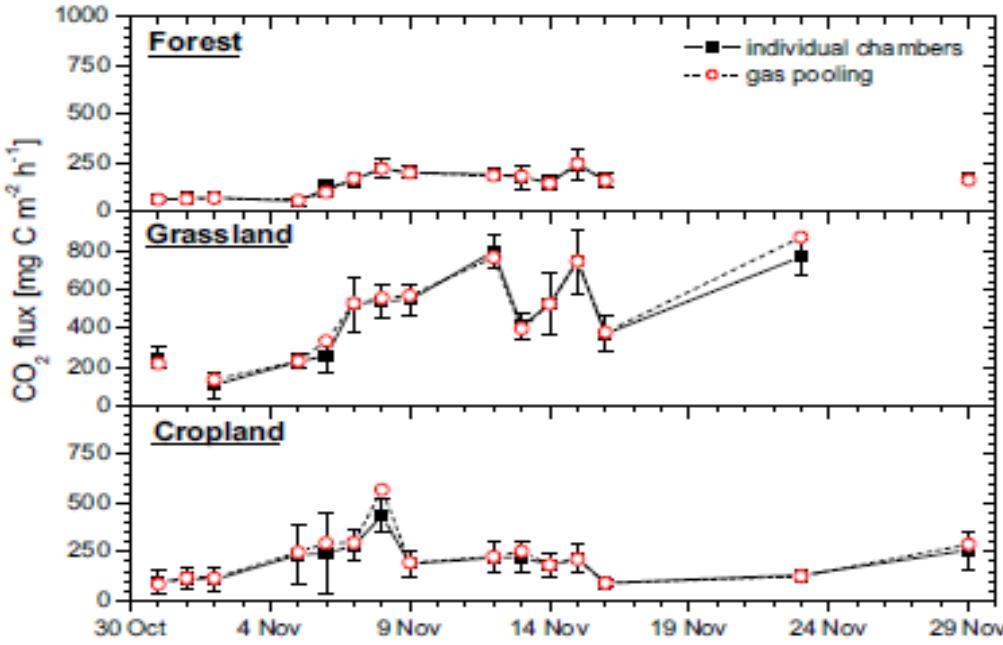
Gas Sample Pooling

to overcome spatial heterogeneity of soil GHG emissions



Arias-Navaro et al., 2013

Gas Sample Pooling



Arias-Navaro et al., 2013

ICON GHG emissions from diversifying rice cropping systems

DFG

KIT-Campus Alpin
IMK-IFU: Atmosphärische Umweltforschung

KIT
Karlsruhe Institute of Technology

Sampling system



Maize chamber



Aerobic rice chamber



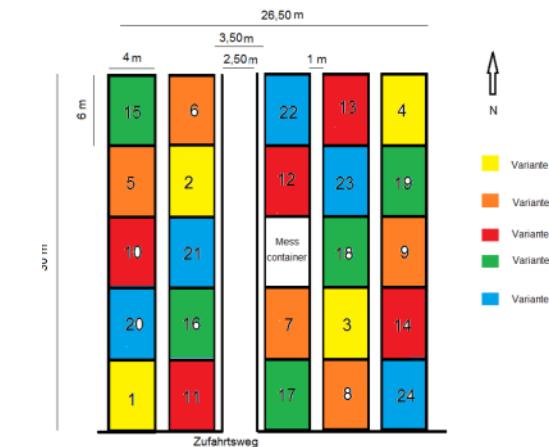
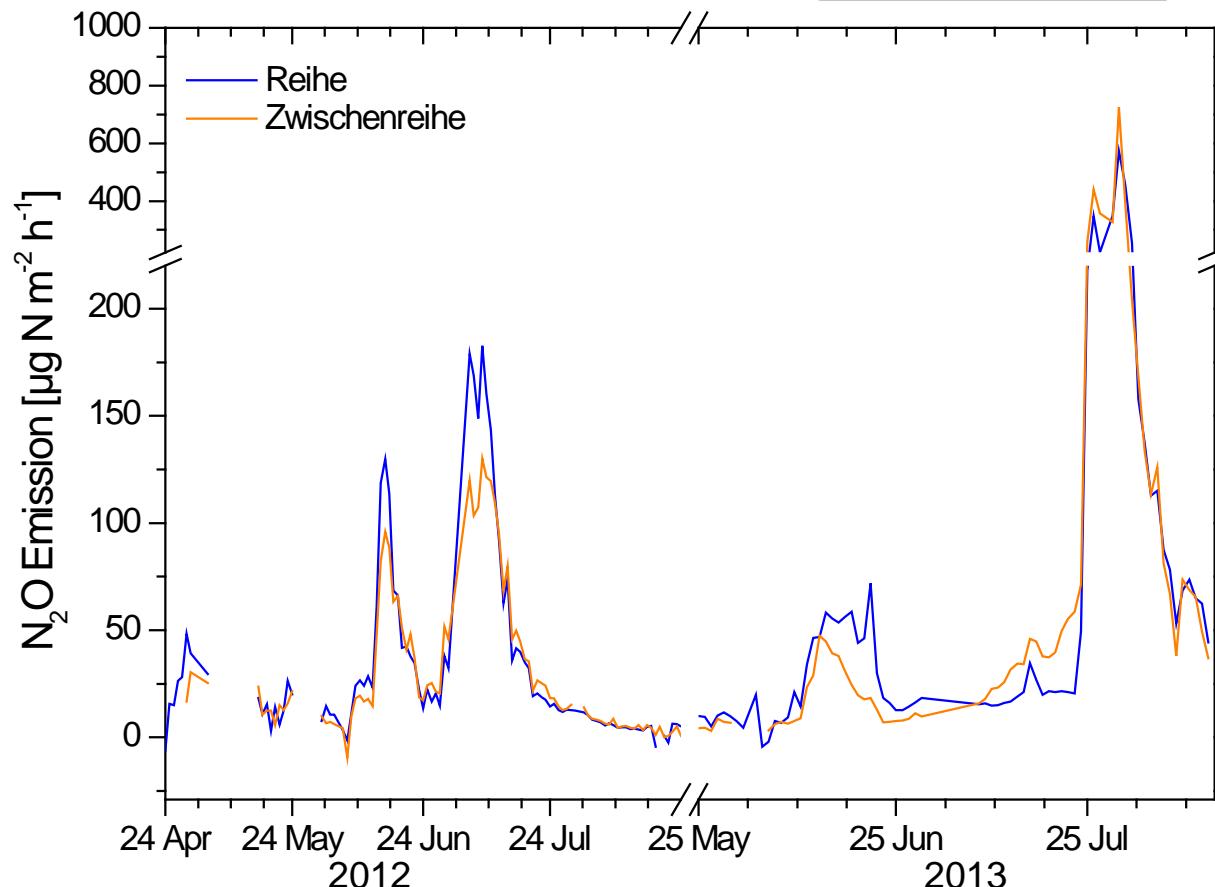
Flooded rice chamber



Field setup



Chamber positions Row and Interrow



GHG exchange of grassland ecosystems along a climate sequence in the TERENO pre-Alps Observatory



Graswang (860m)



Rottenbuch (750m)

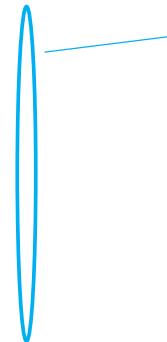


Fendt (600m)



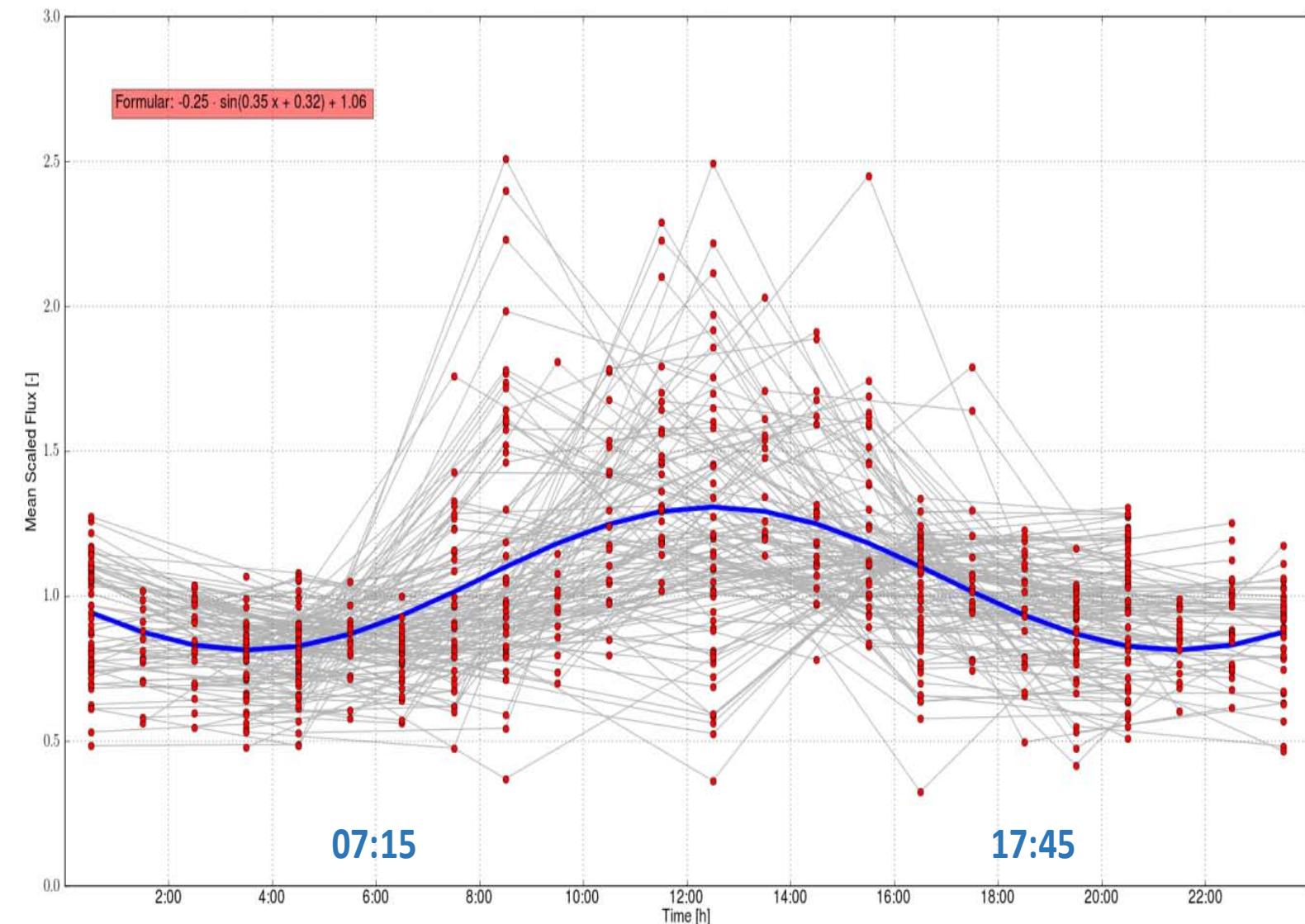
Automated GHG measuring system

diurnal flux patterns



Diurnal patterns of CH₄ emissions

Sampling system



Sampling time / frequency matters

Annual flux deviation sampling time

Chamber	Annual emission (continuous measurements) (\pm s.e., kg Nha $^{-1}$ yr $^{-1}$)	Sampling time (LST)	Percent deviation (%)
1	3.2 \pm 0.2	08:00	7.5
		12:00	22.2
		16:00	11.9
2	2.0 \pm 0.1	09:00	5.3
		13:00	18.7
		17:00	13.2
3	2.4 \pm 0.2	06:00	-8.1
		10:00	8.6
		14:00	27.8
4	2.7 \pm 0.2	07:00	-12.2
		11:00	22.2
		15:00	34.3

LST: Local standard time

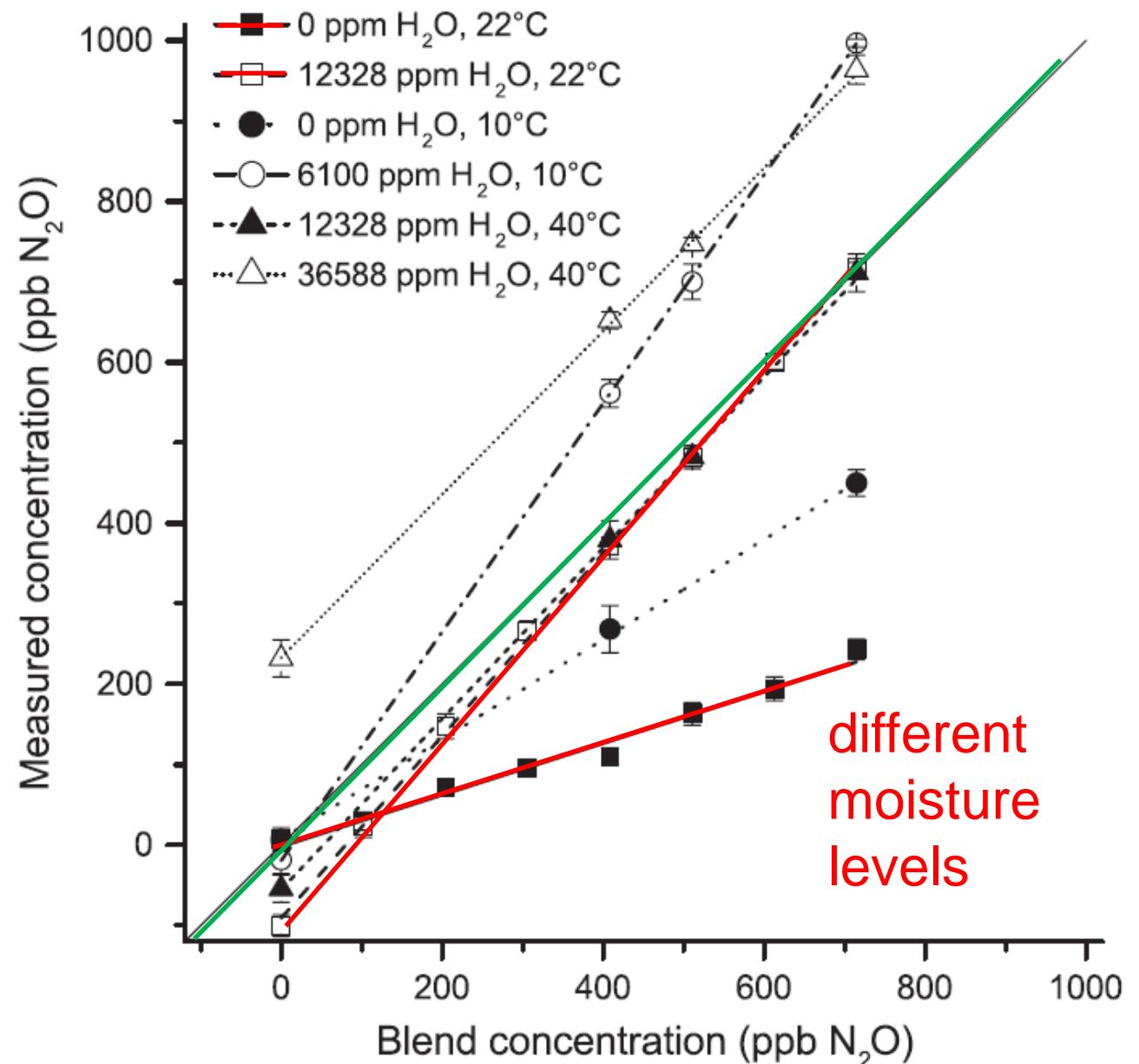
Annual flux deviation sampling frequency

Sampling interval (days)	Deviation range (%)
1	3.3–7.3
2	3.8–6.6
3	-1.8–16.9
4	-3.3–16.4
5	1.2–11.7
6	-4.9–20.0
7	-10.7–21.3
8	-5.3–12.9
9	-9.3–17.8
10	-9.5–25.3
20	-15.5–44.2
30	-31.1–70.5

Liu et al., 2010

Analytical Instruments

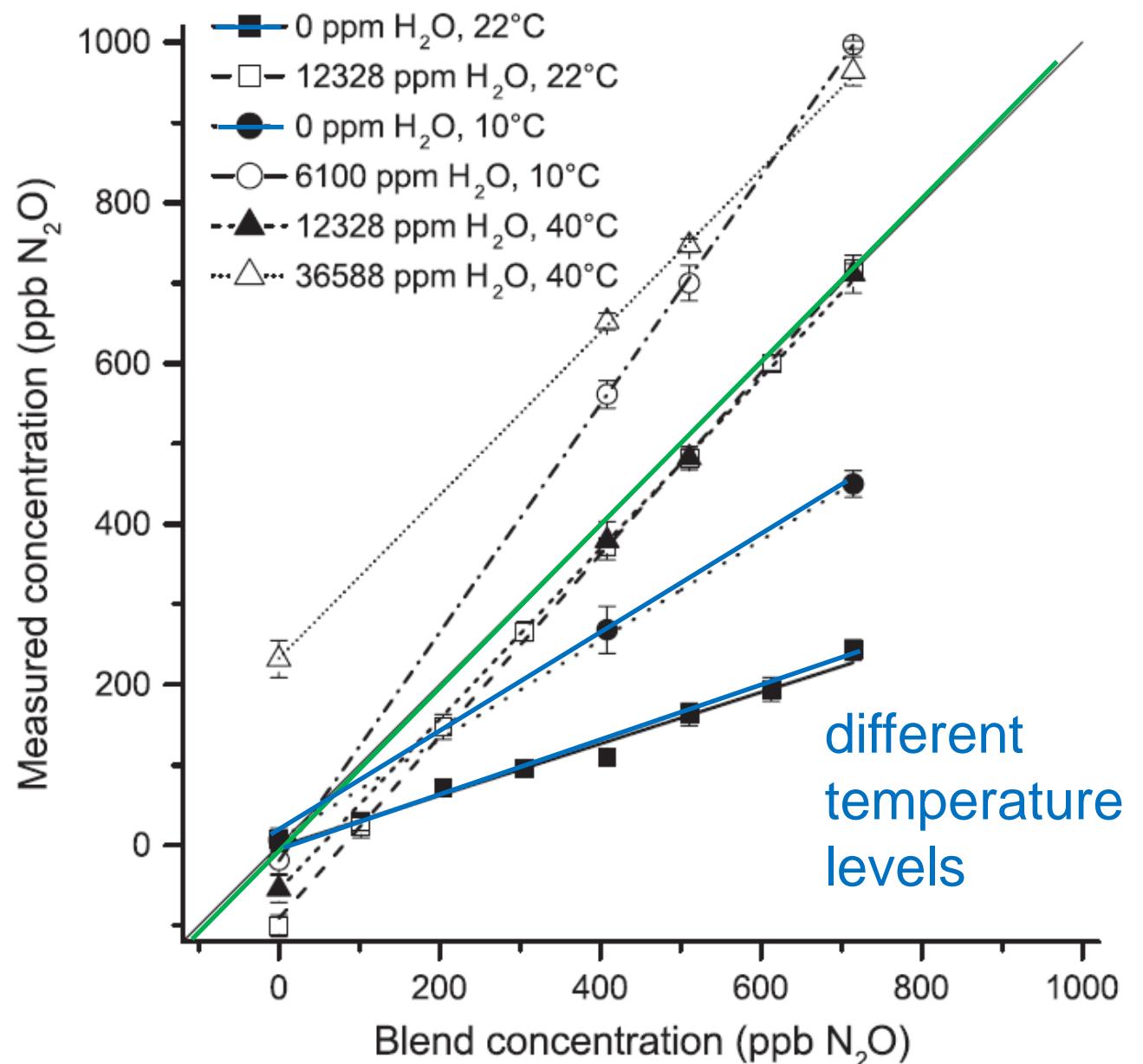
- Gas Chromatography
- Infrared-Spectroscopy
- Photoacoustic Spectroscopy



Rosenstock et al., 2013

Analytical Instruments

- Gas Chromatography
- Infrared-Spectroscopy
- Photoacoustic Spectroscopy



Rosenstock et al., 2013

Major issues with chamber methodologies

Effects on soil environmental conditions

Soil temperature

- ▶ can be minimized (<2 °C) using insulated chambers with reflective covers and short deployments

Soil moisture

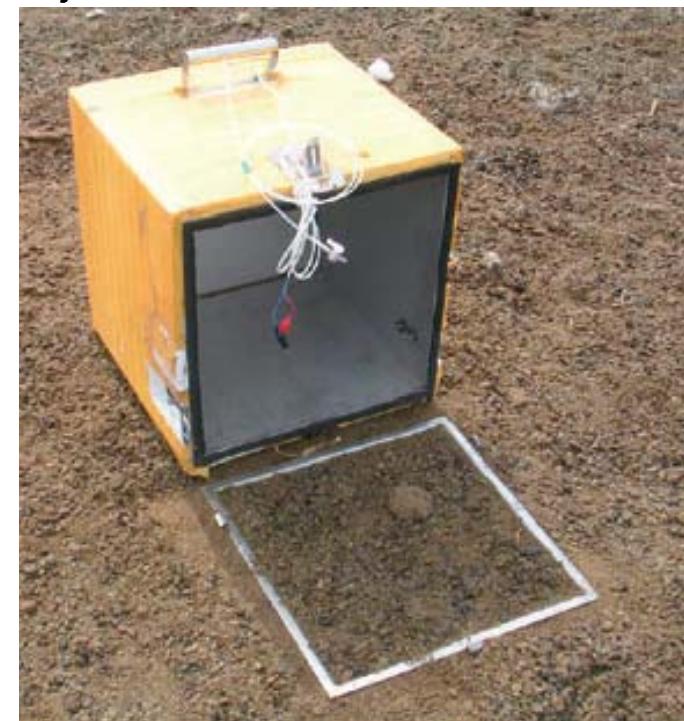
- ▶ low profile collars nearly flushing with the soil surface can minimize micro-climate issues
- ▶ collars should be relocated if soil moisture differs from that in adjacent soil

Root activity

- ▶ delay between collar insertion and start of measurements
- ▶ hours to weeks/ months depending on insertion depth

Soil disturbance

- ▶ use of collars instead of push-in chambers
- ▶ insertion depth ≥ 0.4 cm/min of deployment



Rochette, 2011; De Klein 2012; Butterbach-Bahl et al., 2011

Major issues with chamber methodologies

Effects on soil-chamber gas transfer

Pressure fluctuations

- ▶ properly designed venting tube transmitting changes in barometric pressure to the chamber headspace while minimizing leakage and contamination

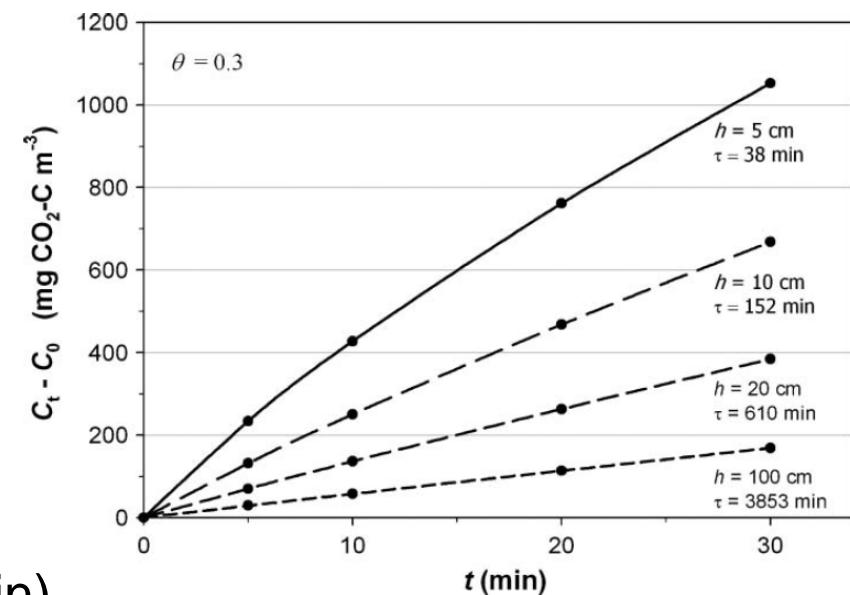
Turbulence regime

- ▶ use of fans seems to be of advantage at least in large chambers



Soil-chamber-atmosphere vertical gas concentration gradient

- ▶ use of non-linear models, often less biased than linear models, but may display higher sensitivity to measurement error
- ▶ several calculation methods are proposed (LR, HMR, Q) which differ in degree of complexity, all aim to estimate pre-deployment emissions by calculating $\partial C / \partial t$ at deployment time = 0
- ▶ bias can be minimized by adjustment of chamber height (>10 cm, better 20 - 40 cm) and deployment time (<30 min) in relation to expected fluxes



Rochette, 2011; De Klein 2012; Butterbach-Bahl et al., 2011

Major issues with chamber methodologies

Leakage and contamination

Gas tight chamber collar connection

Flux calculation

- ▶ temperature and pressure corrected (take measurements)
- ▶ based on ≥ 4 measurements (including t_0 sample)



Air sample handling and storage

- ▶ pressurizing samples into pre-evacuated vials (10-20 ml)
- ▶ minimize duration of sample storage (<5 days)



Measurements

- ▶ use sufficient samples with calibration standards
- ▶ test linearity of ECD at high concentrations
- ▶ avoid bias with CO₂ e.g. by bypass, ascarite columns, CO₂ in carrier gas

Rochette, 2011; De Klein 2012; Butterbach-Bahl et al., 2011

Protocol/ Guidelines

Nitrous Oxide Chamber Methodology Guidelines



December 2012
Edited by Cecile de Klein
and Mike Harvey
Version 1



GLOBAL
RESEARCH
ALLIANCE
ON AGRICULTURAL GREENHOUSE GASES

Nitrous Oxide Chamber Methodology Guidelines

Version 1

Editors

C. A. M. de Klein

AgResearch, Invermay Research Centre, Private Bag 50034, Mosgiel,
New Zealand

cecile.deklein@agresearch.co.nz

M. J. Harvey

NIWA, Private Bag 14-901, Kilbirnie, Wellington, New Zealand
mike.harvey@niwa.co.nz

Nitrous Oxide Chamber Methodology Guidelines
Cecile de Klein & Mike Harvey (Eds)

1. Introduction— Cecile de Klein & Mike Harvey (New Zealand)
2. Chamber design— Tim Clough (New Zealand) et. al.
3. Deployment protocol— Philippe Rochette (Canada) et. al.
4. Air sample collection, storage and analysis— Frank Kelliher (New Zealand) et. al.
5. Automated GHG measurement in the field— Peter Grace (Australia) et. al.
6. Data analysis considerations— Rod Venterea (US) et. al.
7. How to report your experimental data— Marta Alfaro (Chile) et. al.
8. Health and safety considerations— David Chadwick (UK) et. al.



Tereno Fendt site