What can ecosystem-scale oxygen measurements tell us about the terrestrial carbon cycle?

Alexander Knohl[1], Andrew C. Manning[2], Anne Klosterhalfen[1], Christian Markwitz[1], Jan Muhr[1], Penelope A. Pickers[2], Yuan Yan[1], Emanuel Blei[1], and Jelka Bradens-Behrens[1]

[1] Bioclimatology, University of Göttingen, Göttingen, Germany
[2] Centre for Ocean and Atmospheric Sciences, School of Environmental Scienes, University of East Anglia, Norwich, UK

Corresponding author: Alexander Knohl (aknohl@uni-goettingen.de)
Presenting author: Andrew Manning (a.manning@uea.ac.uk)

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UEA University of East Anglia

Talk outline

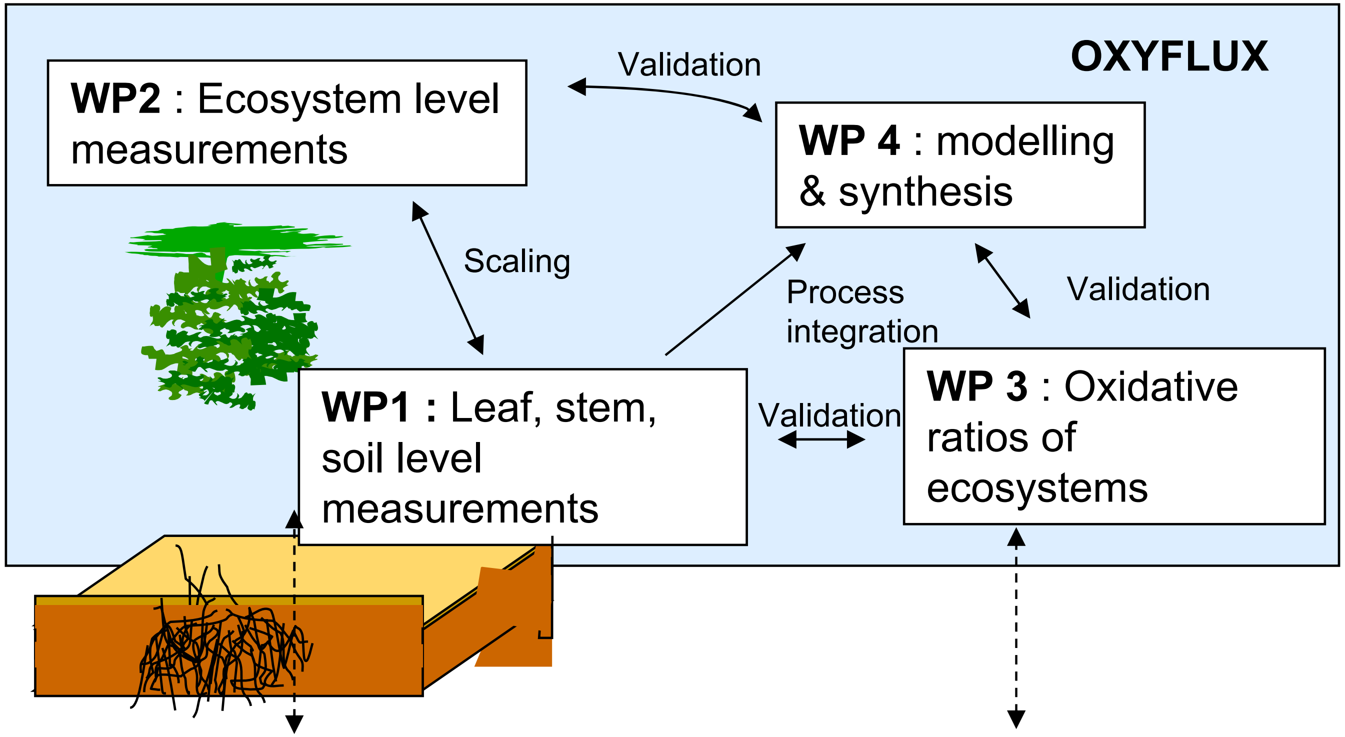
- Introduction to OXYFLUX project
- Stem chamber O_2 measurements
- Branch chamber O_2 measurements
- Vertical gradient O_2 measurements
- Terrestrial ecosystem modelling with O_2

OXYFLUX: ERC project from 2016-2023

- Some project aims:
  - Examine ER/OR (exchange ratios/oxidative ratios) of different ecosystems components
    - Leaf photosynthesis
    - Soil and stem respiration
    - Direct from organic matter
    - Canopy-scale
  - O_2 eddy covariance?
  - Incorporate O_2 into ecosystem modelling
  - A holy grail of terrestrial ecologists: partition photosynthesis and respiration fluxes
    - $F_{CO2} = F_P + F_R$
    - $F_{O2} = ER_P \times F_P + ER_R \times F_R$

European Research Council
Established by the European Commission

OXYFLUX: 2016-2023



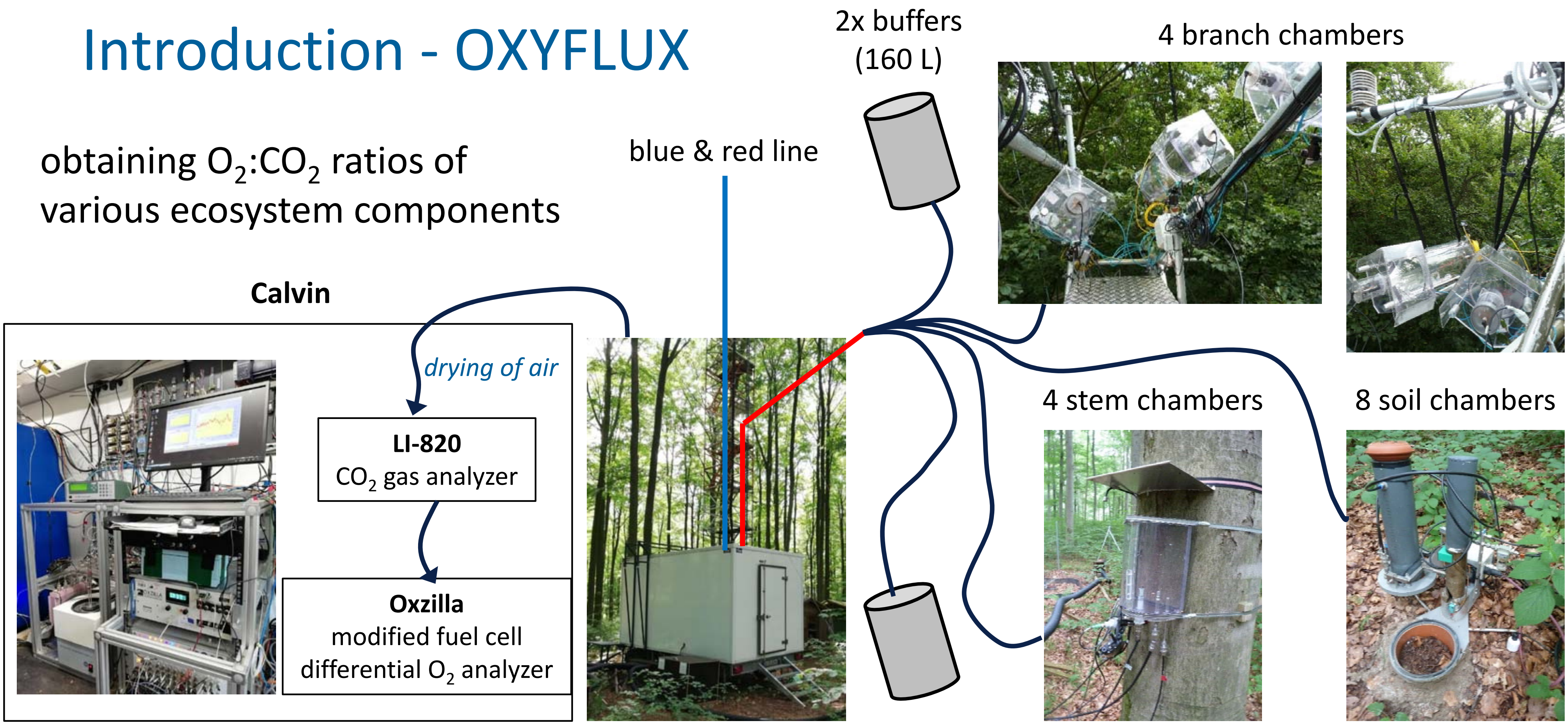
Agricultural and forest field sites (WP1 & 2)

Environmental gradients and global FLUXNET sites (WP3)

European Research Council
Established by the European Commission

Introduction - OXYFLUX

obtaining O_2:CO_2 ratios of various ecosystem components



Apparent respiratory quotient (ARQ) of soil

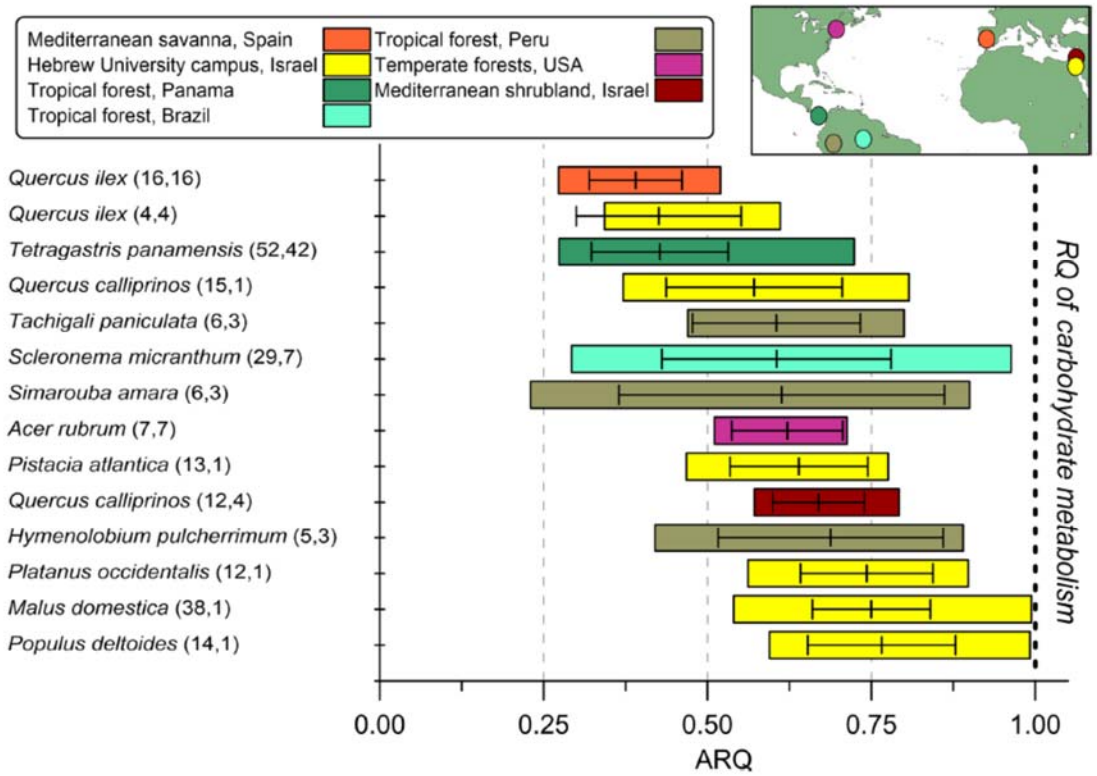
Table 1. The $[CO_2]$, $[O_2]$, and ARQ (average values of replicates) for in situ measurements in acidic and neutral soils in temperate and alpine forest sites (sites 4, 5, 6). Apparent respiratory quotient (ARQ) values different from the 0.9 ± 0.1 expected for respiration (based on plant composition) were observed in these soils.

Date	Site	Description	Soil pH	Depth (cm)	CO_2 %	O_2 %	ARQ
30/05/2001	4	Temperate forest	4.5	85	0.46	20.40	0.58 ± 0.05
31/07/2001	4	Temperate forest	4.5	85	0.73	20.20	0.70 ± 0.05
07/06/2011	5	Alpine forest	7.3	40	0.62	19.06	0.23 ± 0.04
09/09/2013	5	Alpine forest	7.3	30	0.28	20.67	0.64 ± 0.06
09/09/2013	6	Alpine forest	4.9	30	0.26	20.77	0.96 ± 0.24

"Our results demonstrate that, in contrast to the common assumption, soil ARQ (and RQ) values are rarely 1.0 and often deviate from this value considerably. …"

Angert et al. 2015

ARQ of stems



- Considerable variation in ARQ (CO_2/O_2)
- ARQ of stems much lower than expected

Hilman et al. 2019

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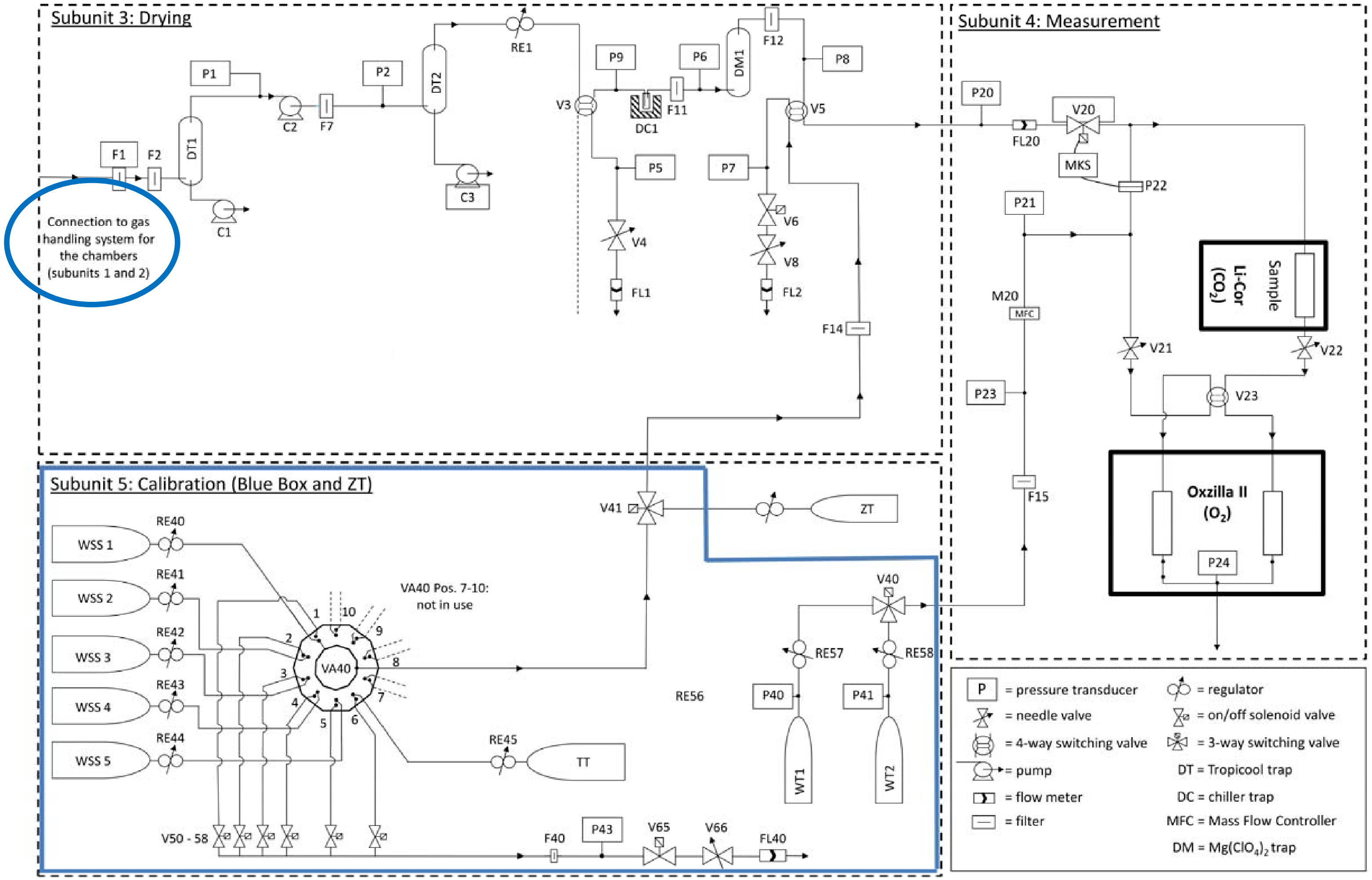
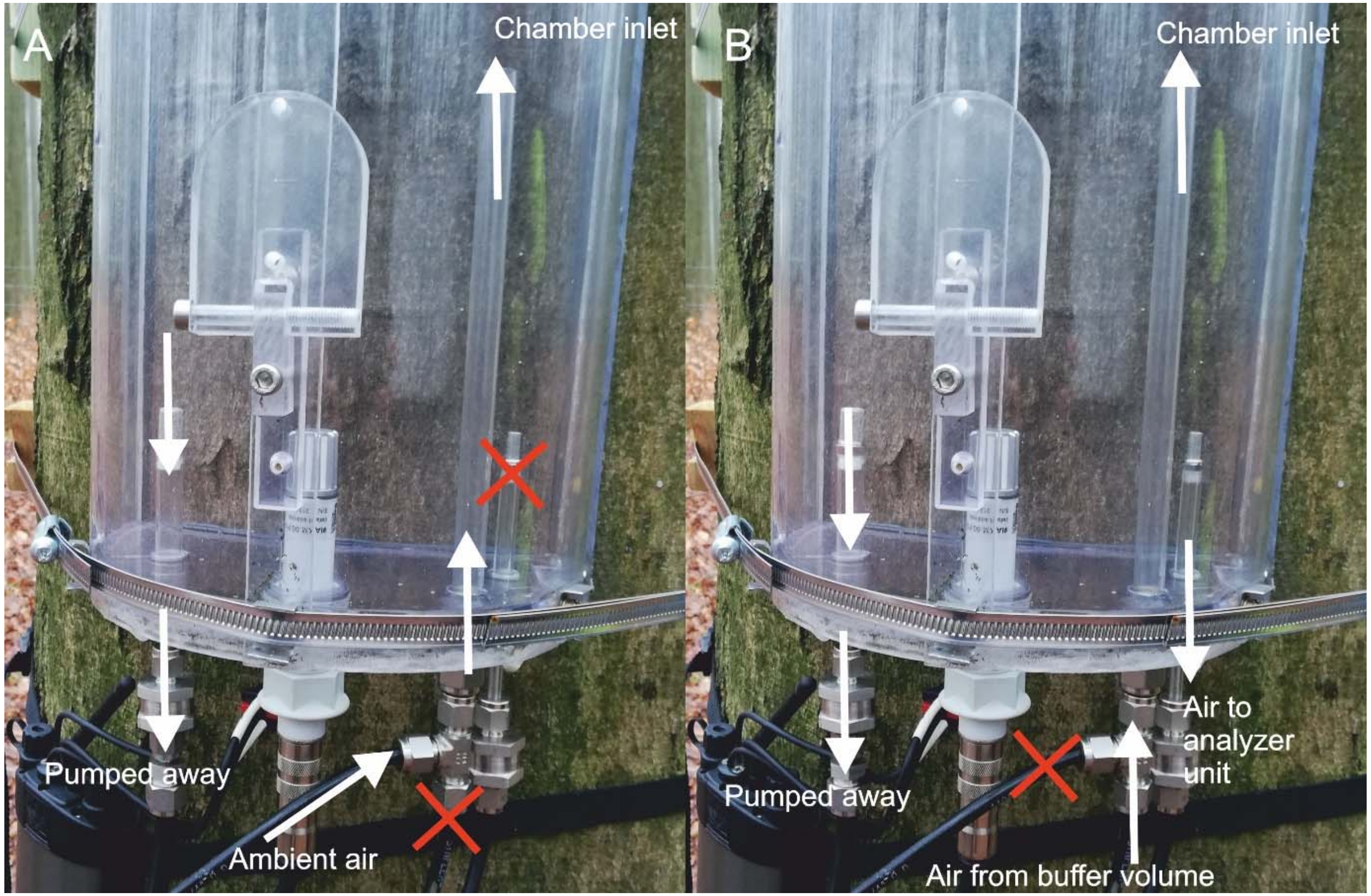
"Typical" Oxzilla system, with heavily-modified front-end

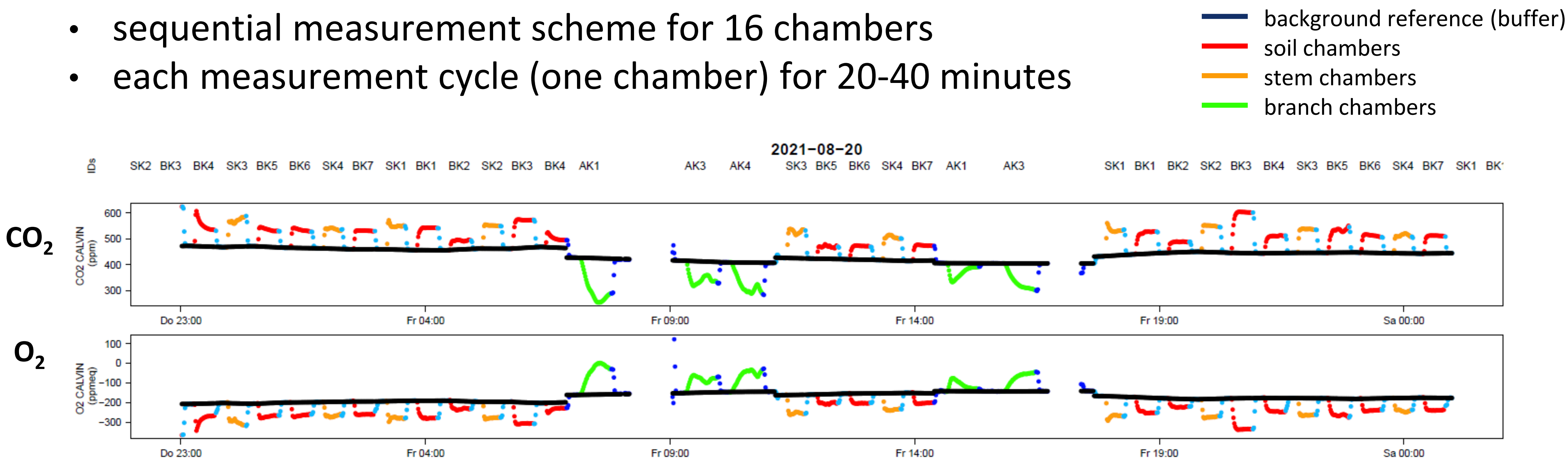


Stem chambers – on beech trees: Leinefelde, Germany field station



Introduction - Instrumental set-up

- sequential measurement scheme for 16 chambers
- each measurement cycle (one chamber) for 20-40 minutes



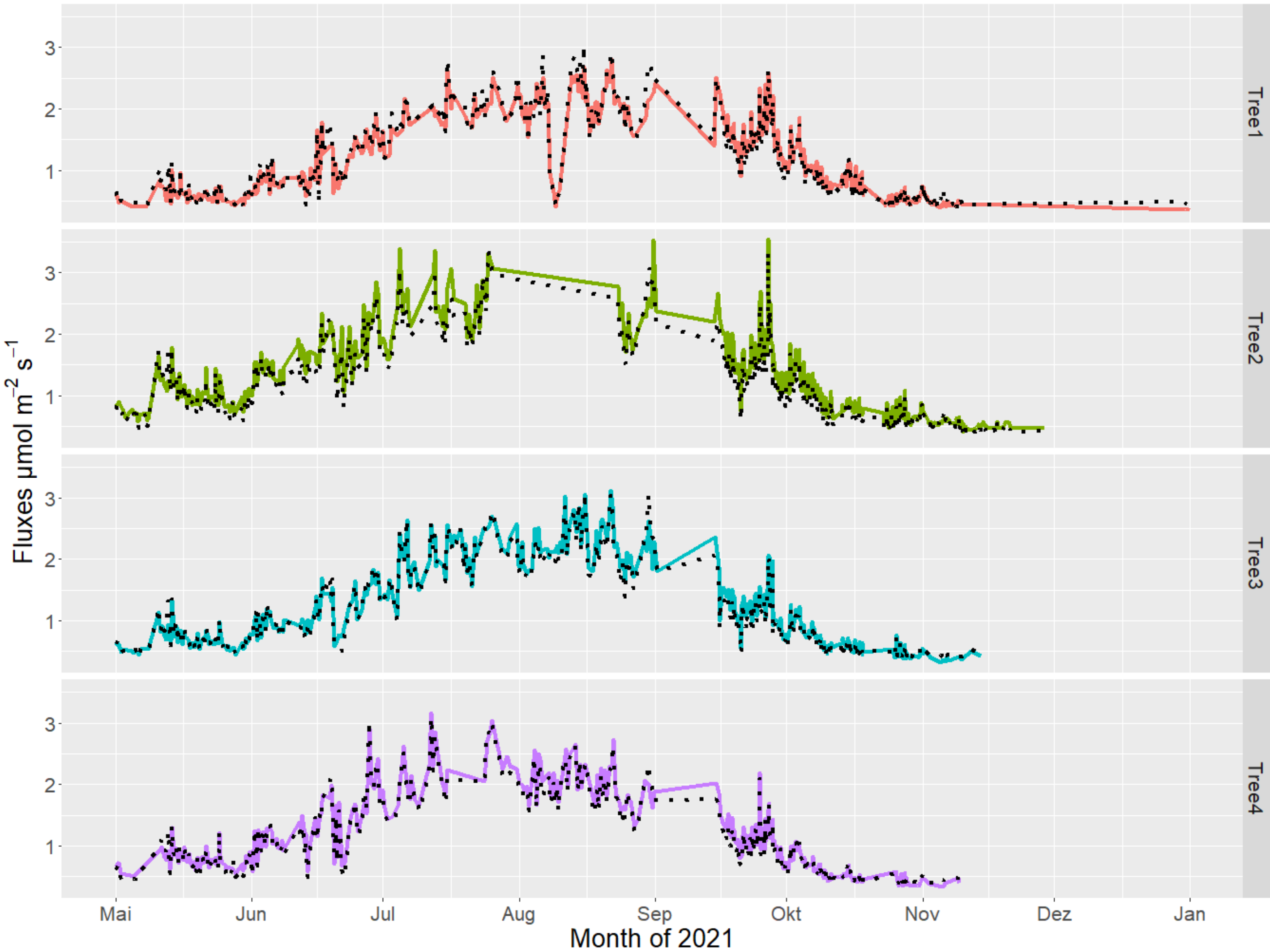
→ 4 steady-state, open-throughflow branch chambers

Stem O_2 and CO_2 time series fluxes

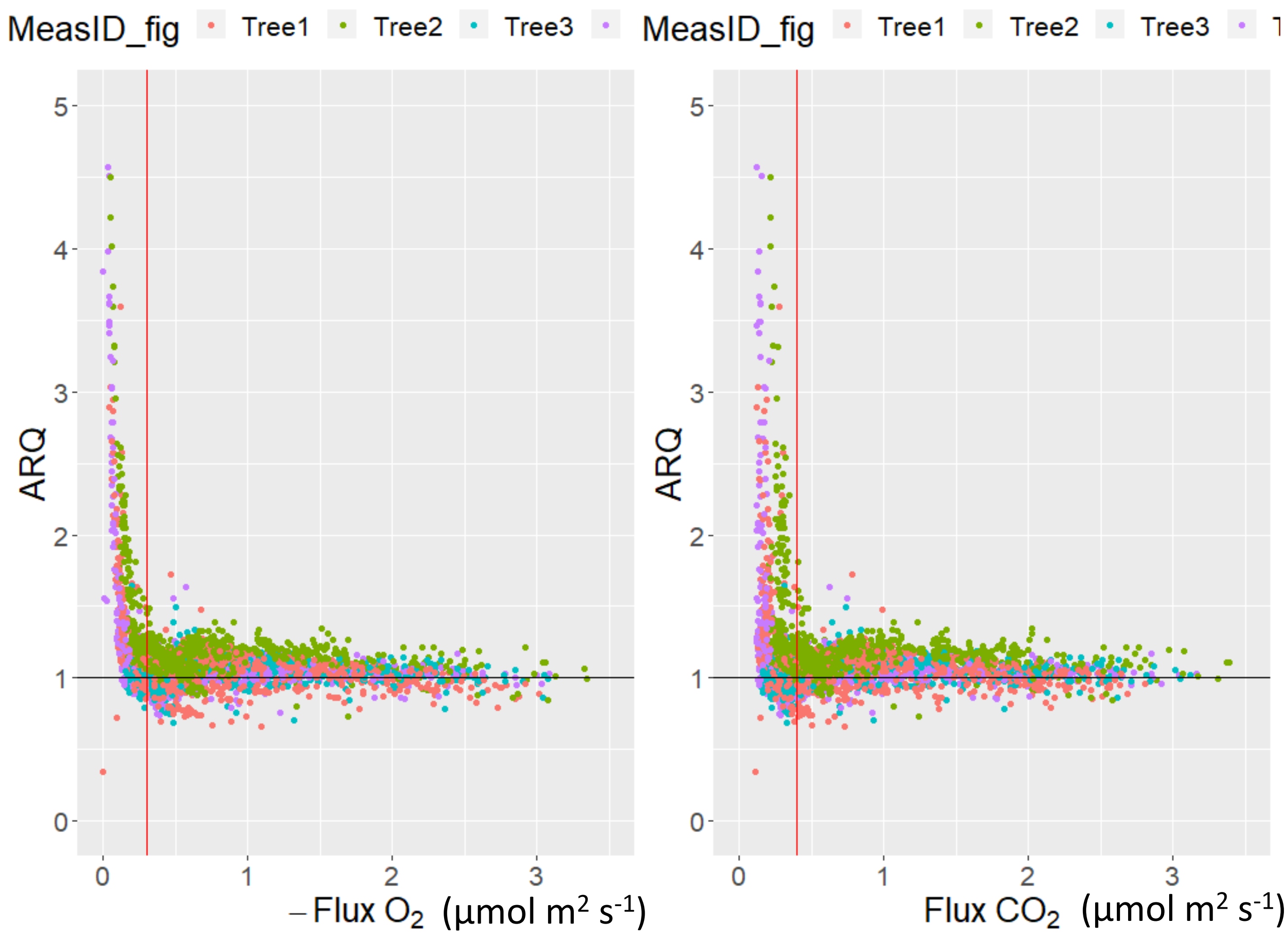
CO_2 in colour

O_2 as black dots

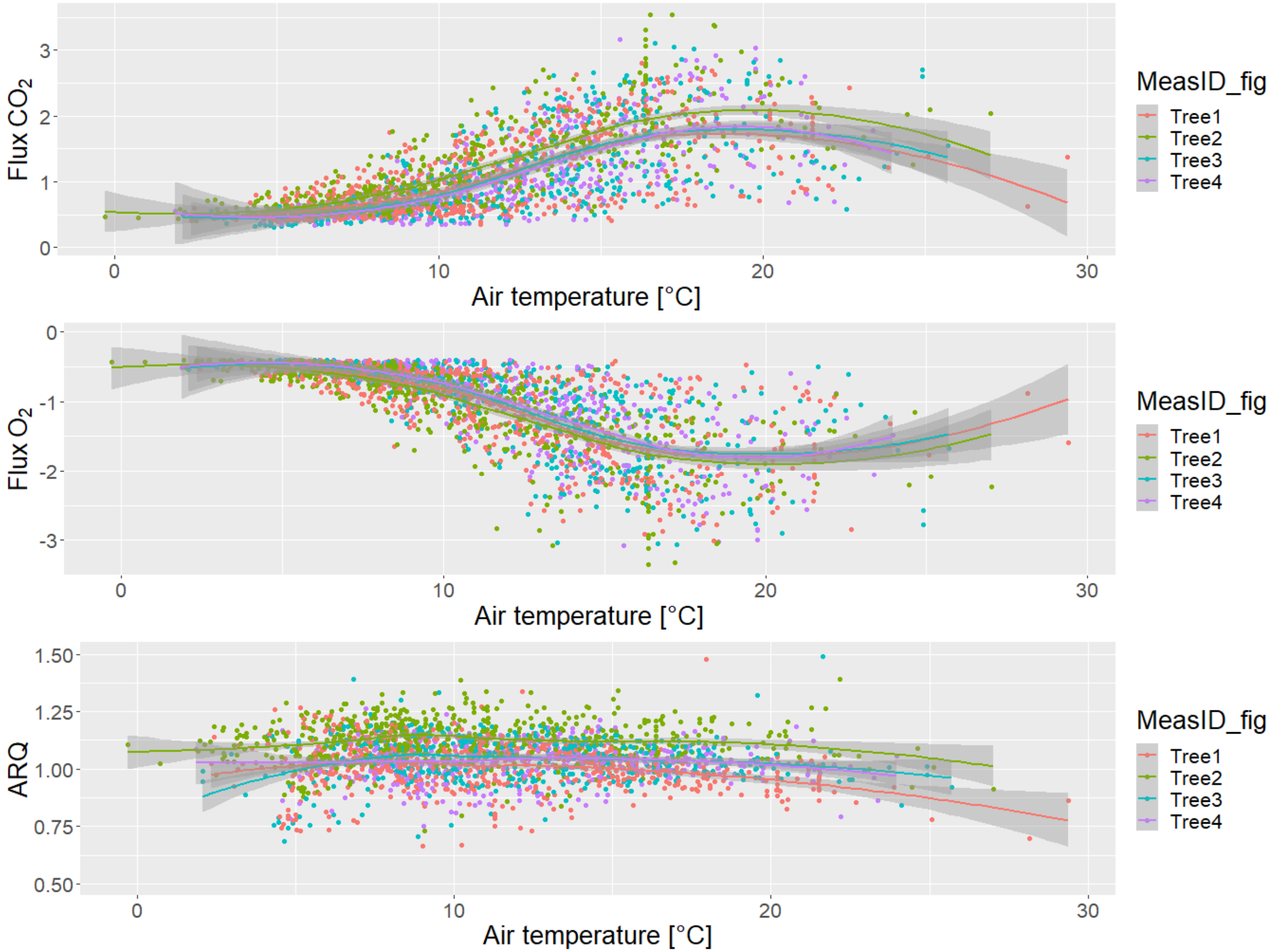
4 different beech trees



Stem chambers: ARQ results



Seemingly little or no ARQ correlation with temperature or season



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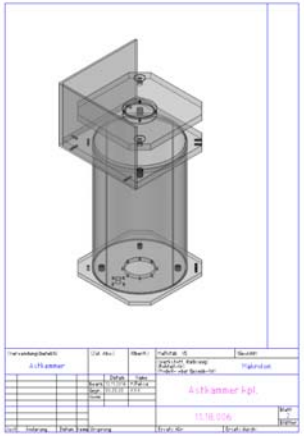
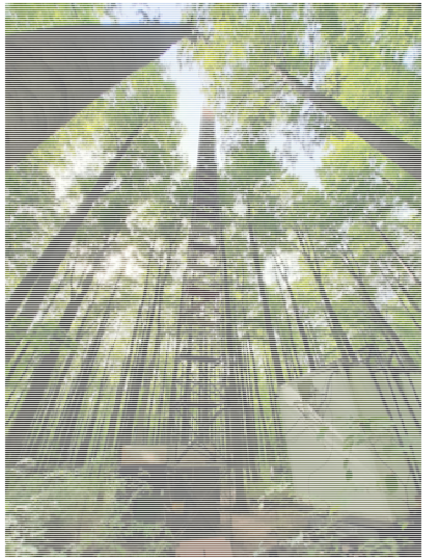
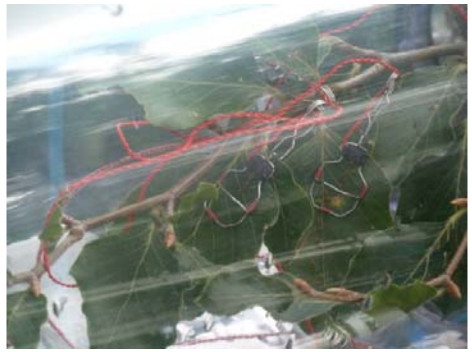
Introduction - Instrumental set-up

- Leinefelde site in Central Germany:
  - 51°20 N, 10°22’ E
  - pure beech forest, managed
  - even-aged, about 140 years old
- study period:
  - 17 June - 08 October 2021
- available data:
  - *1 min* — CO_2, O_2 and H_2O mole fractions for chambers and buffer
  - *1 min* — chamber meteorology: PAR, T, T_{leaf}, RH
  - *10 min* — tower meteorology: SW_IN, T_{air}, RH, P, …
  - *30 min* — eddy-covariance flux data: NEE, GPP, LE



Marek Peksa





Methods - Data processing

- flux calculation (F_{CO_2}, F_{O_2}) for steady and unsteady state conditions:

$$F_{CO_2} = \frac{\Delta CO_2 \cdot flow - V\rho \frac{dCO_2}{dt}}{S} \qquad F_{O_2} = \frac{\Delta O_2 \cdot flow - V\rho \frac{dO_2}{dt}}{S}$$

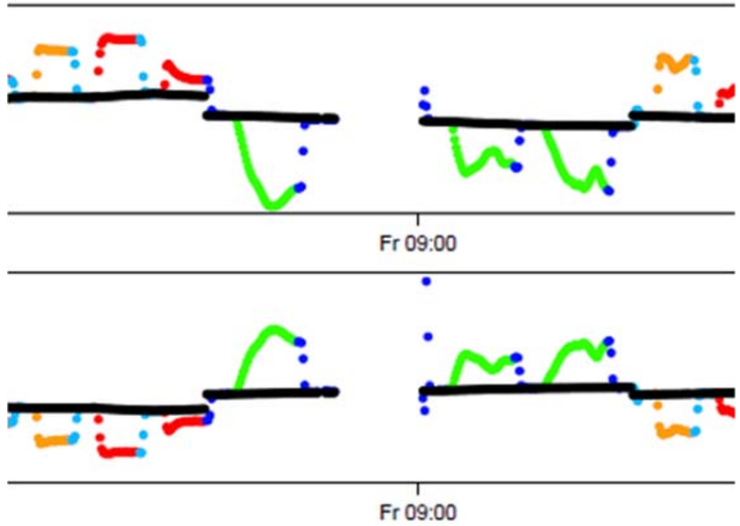
with

ΔCO_2, ΔO_2	**difference between incoming and outgoing CO_2 or O_2 mole fractions** (µmol mol^{-1})
$flow$	flow rate (mol s^{-1})
S	**leaf area** (m^2)
V	chamber volume (m^3)
ρ	air density (mol m^{-3})
$\frac{dCO_2}{dt}$, $\frac{dO_2}{dt}$	**rate of change of CO_2 or O_2 mole fractions** (µmol mol^{-1} s^{-1})

after Saathoff and Welles et al. (2021), doi: 10.1111/pce.14178.

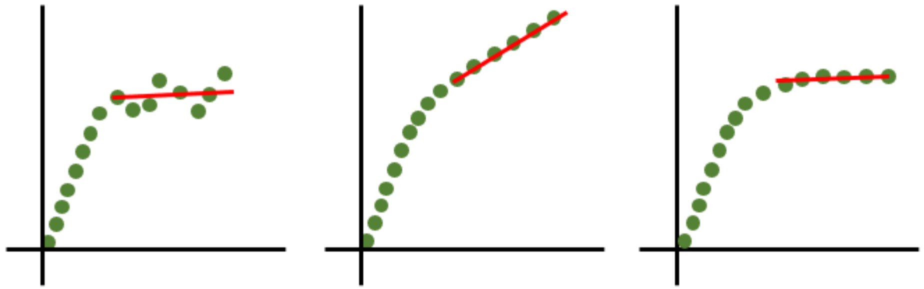
Methods - Data processing

- finding measurement cycles of high quality (steady state)



change of mole fraction with time
(— last 6 min of each cycle)

detection with:



Methods - Data processing

- finding measurement cycles of high quality (steady state):

change of mole fraction with time
(— last 6 min of each cycle)

detection with R^2 | slope | R^2 and slope

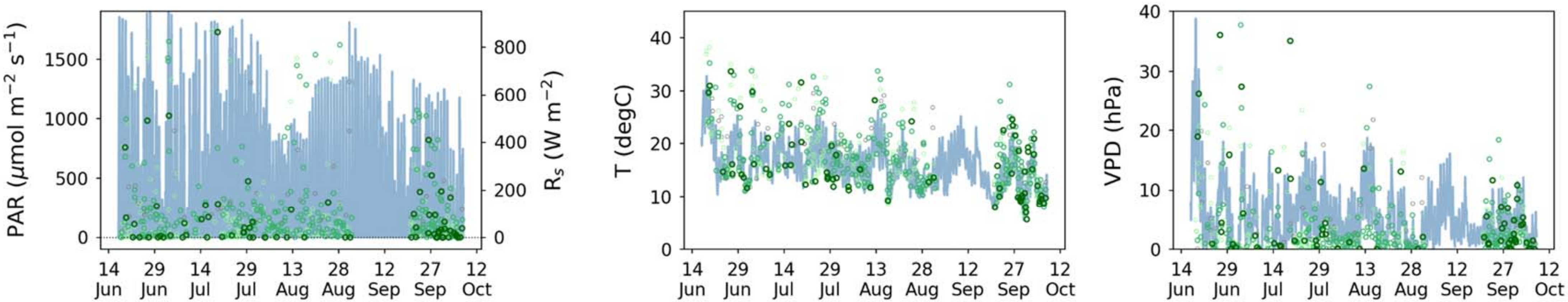
all → high R^2 for CO_2 → high R^2 for O_2 → high R^2 and small |slope|

Results - Meteorological conditions

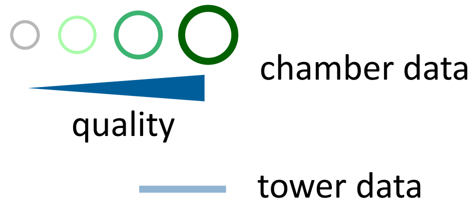
chamber data

quality

tower data



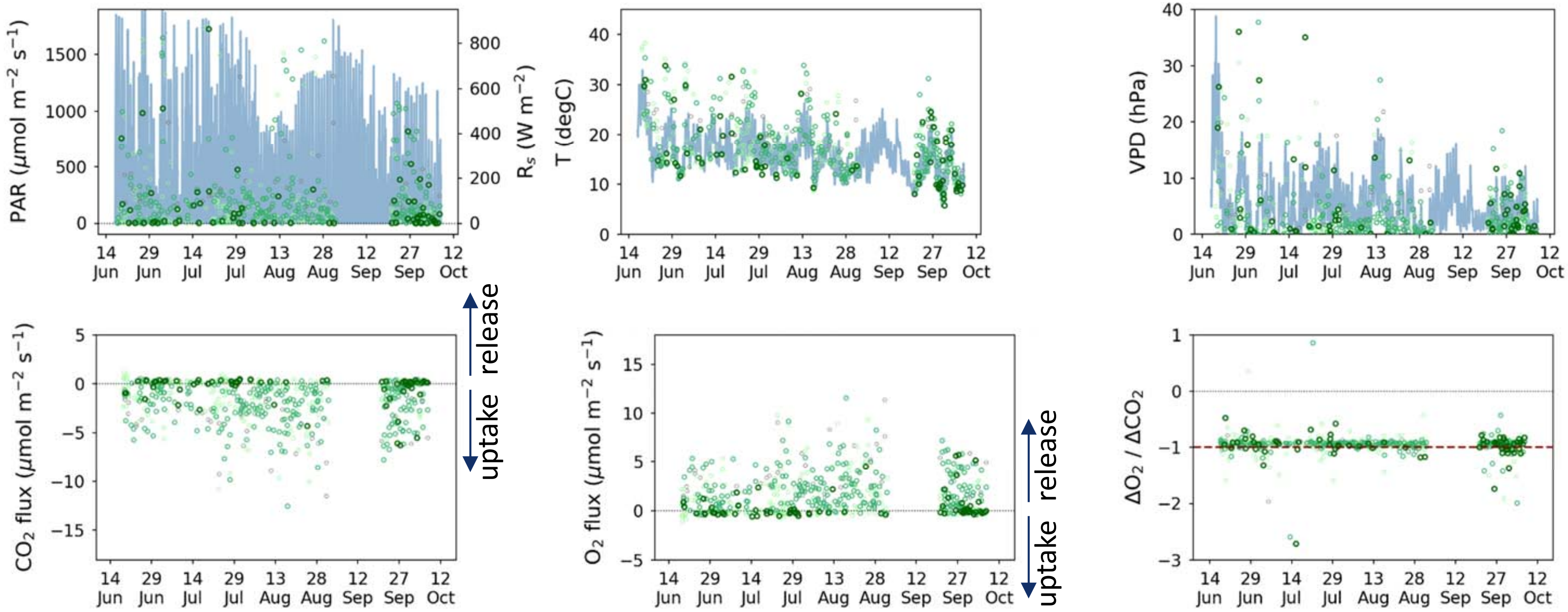
Results - Seasonal dynamics



- 632 measurement cycles (425 daytime, 207 nighttime)

meteorology

fluxes

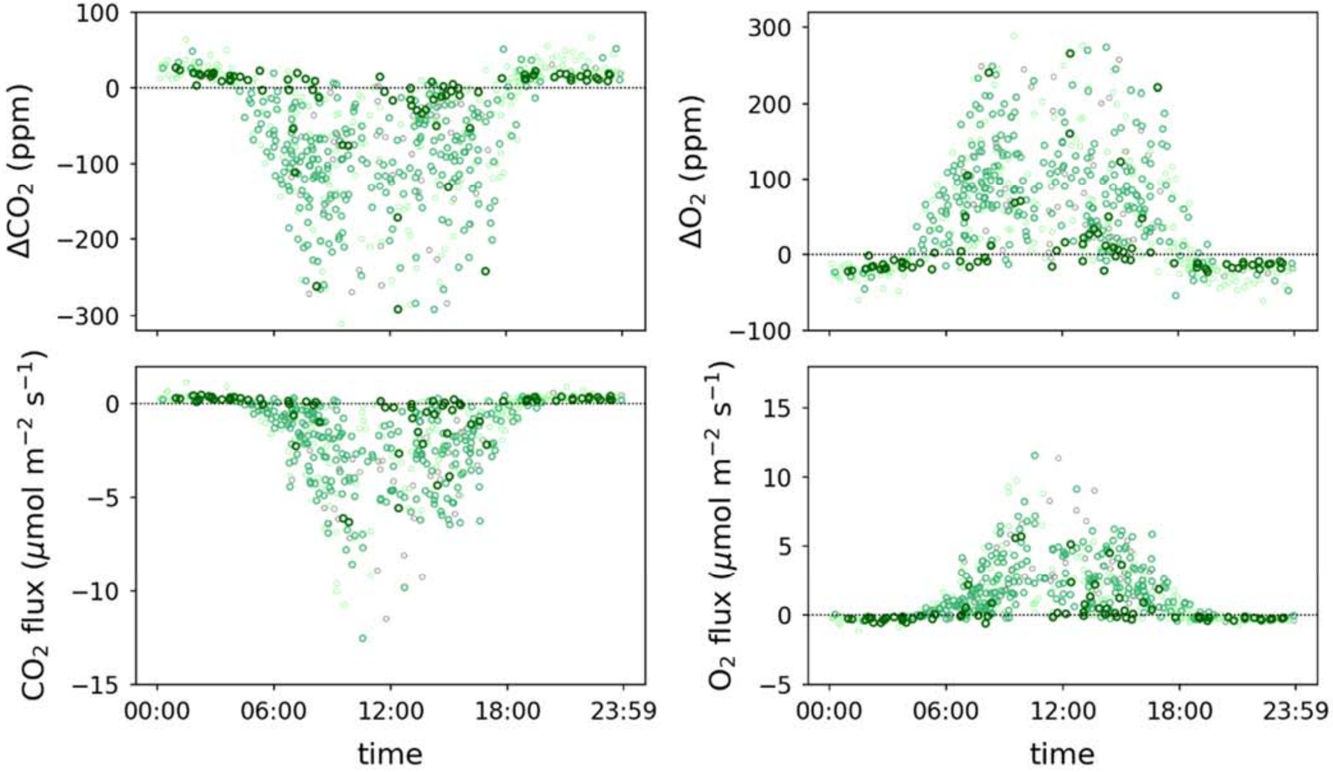


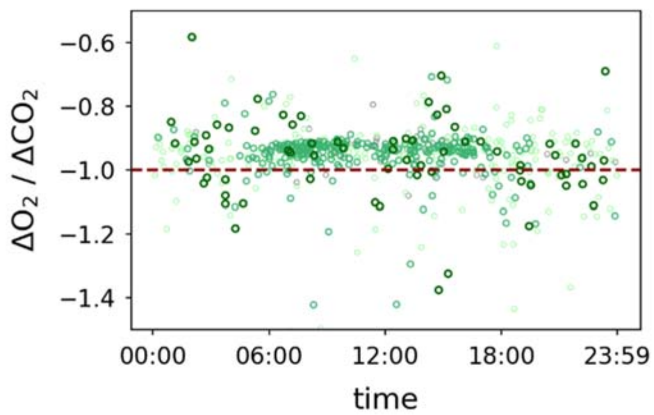
Results - Diel variations

- 632 measurement cycles (425 daytime, 207 nighttime)

mole fractions

fluxes



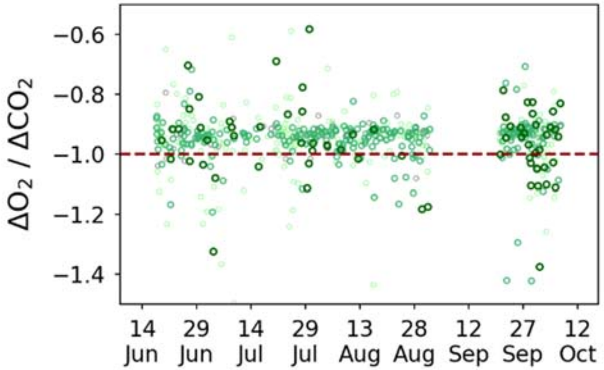


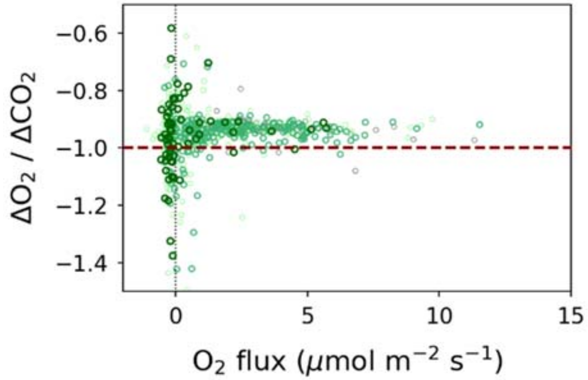
No diel cycle in ER

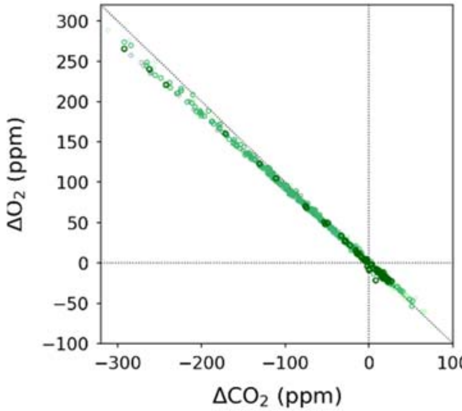
chamber data

quality

Results - O_2:CO_2 exchange ratio







- exchange ratio between -0.9 and -1.0 mol mol^{-1}
- high variation for low flux magnitudes

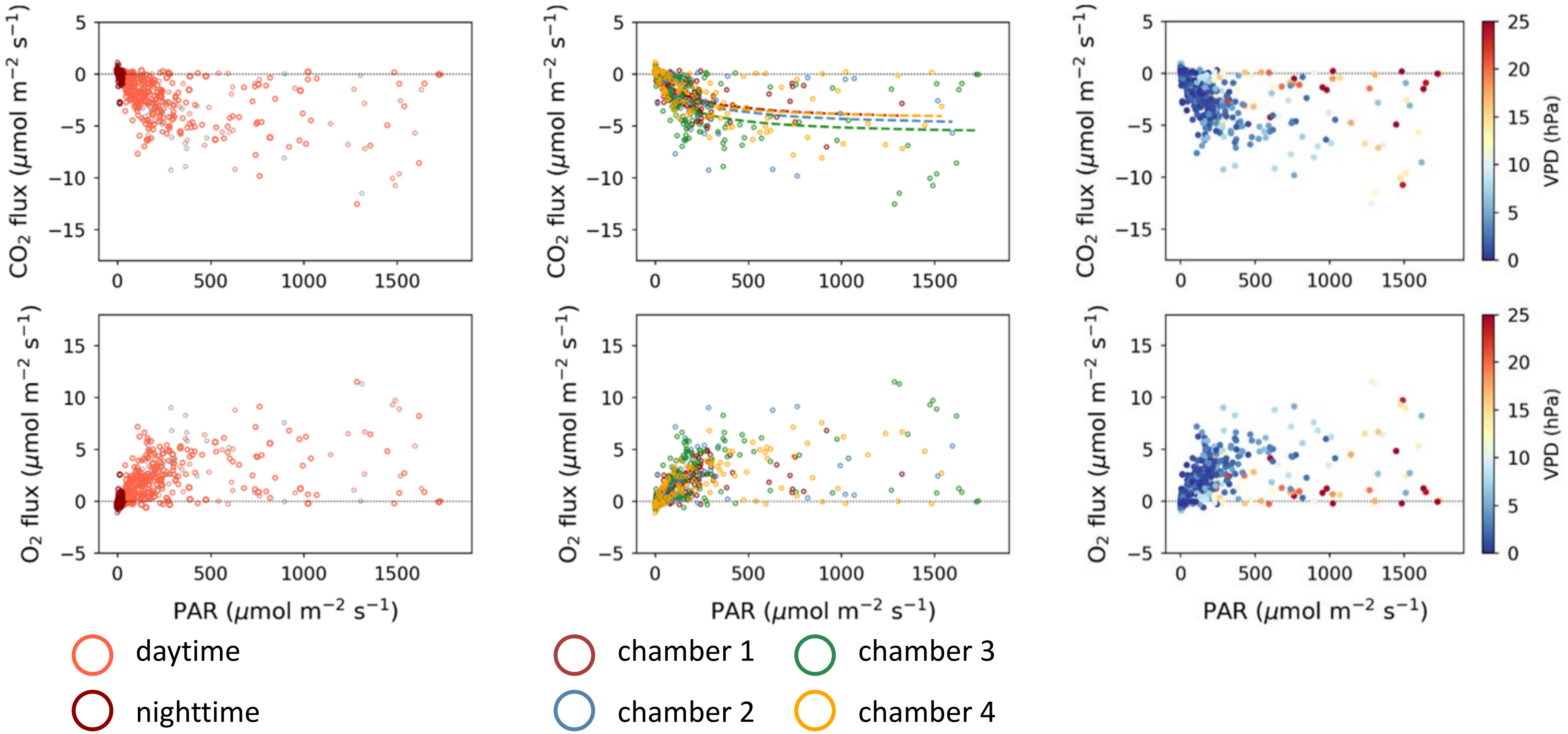
→ but most 'high quality' conditions

→ extra filtering necessary

Results - correlations with meteorological conditions

CO_2 flux

O_2 flux



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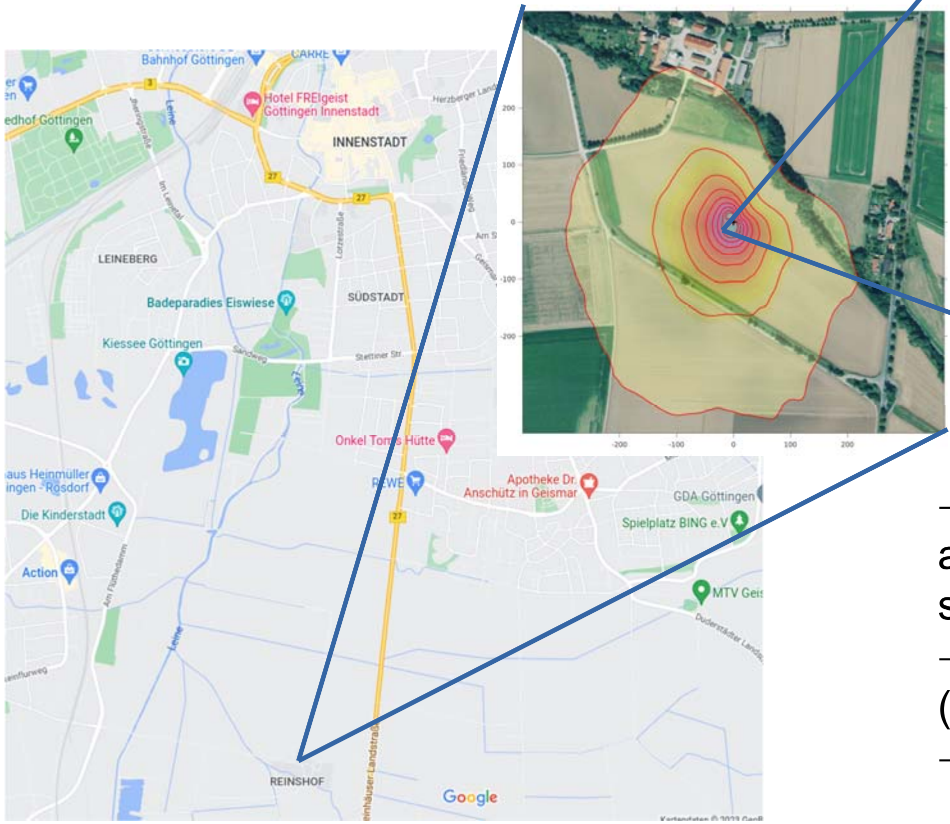
Methods – site description – Agricultural site



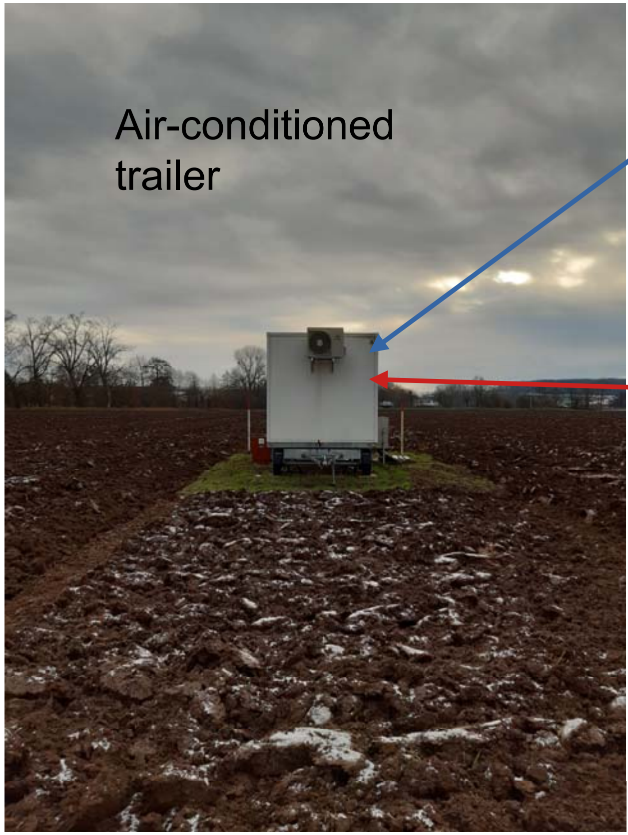
Picture from Ana Meijide

→ **monocropping** agric. system with annually varying crop rotation (2023 sugar beat)

→ **conventional soil cultivation** (deep tillage, fertilisation)

→ 80% clay, clayey loams

Methods – measurements: Measure at 0.5, 1 and 3 m agl

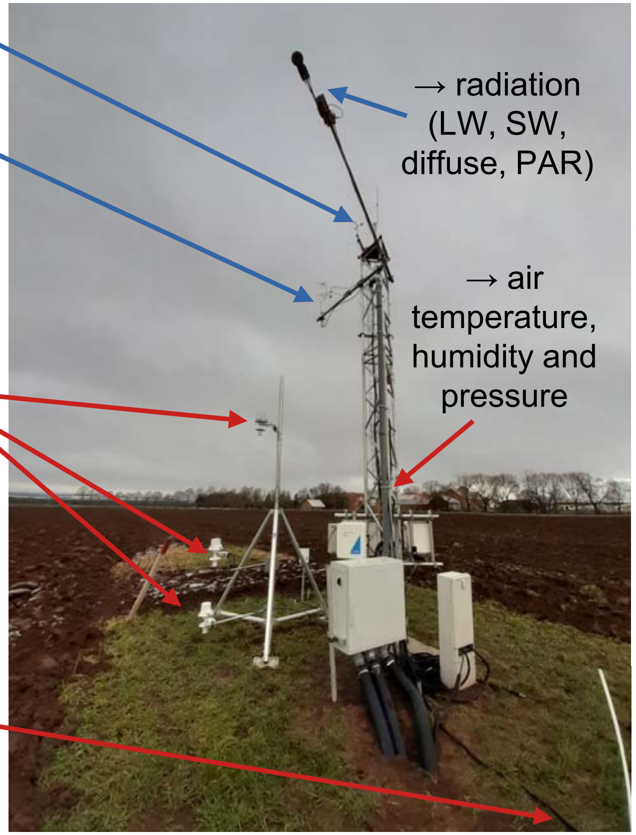


→ wind speed and -direction

→ EC N_2O, CO_2, H_2O fluxes

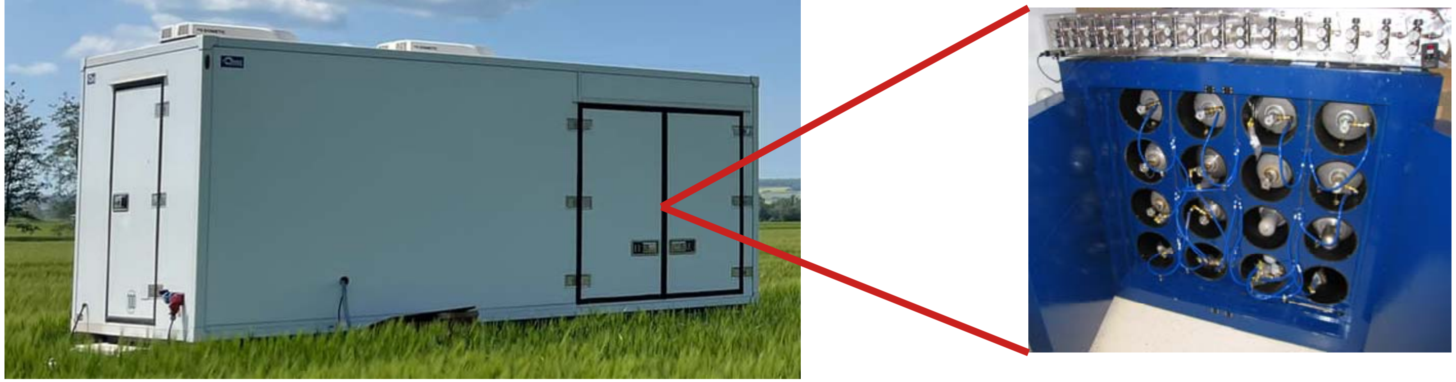
→ O_2, H_2O and CO_2 Concentration at 0.5, 1 and 3 m

→ soil temperature, -humidity and -heat flux



Methods – O_2 and CO_2 measurements

‘Blue-box’ with calibration cylinders

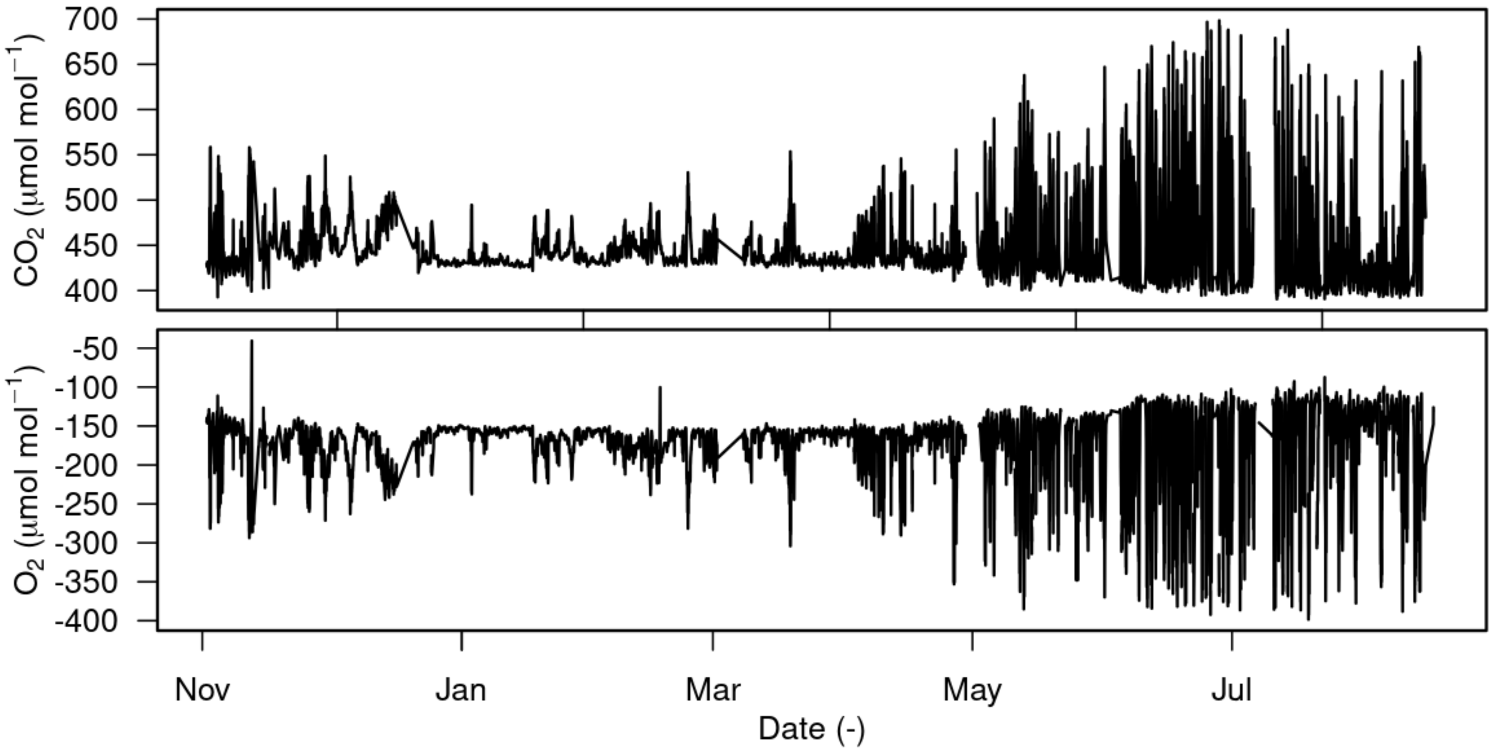


FC-2 Differential Oxygen Analyzer (Oxzilla)

- air dried to < 1 ppm H_2O_v
- flow rate of 0.1 Lpm
- 3 heights are sequentially switched with 8-port Valco valve for 5 minutes each
- 1 minute averages
- 1 minute removed

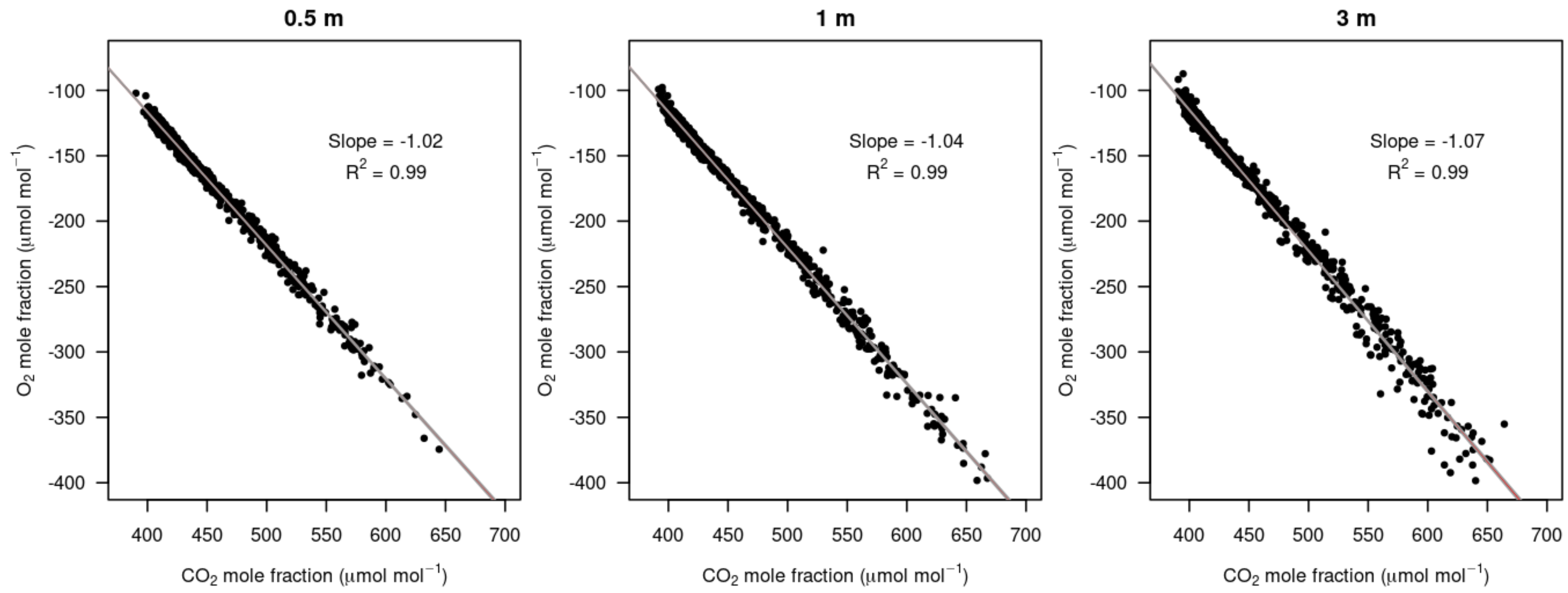
LI-820 CO_2 gas analyser (LI-COR)

Results – O_2 and CO_2 mole fraction Nov 2022 – Aug 2023



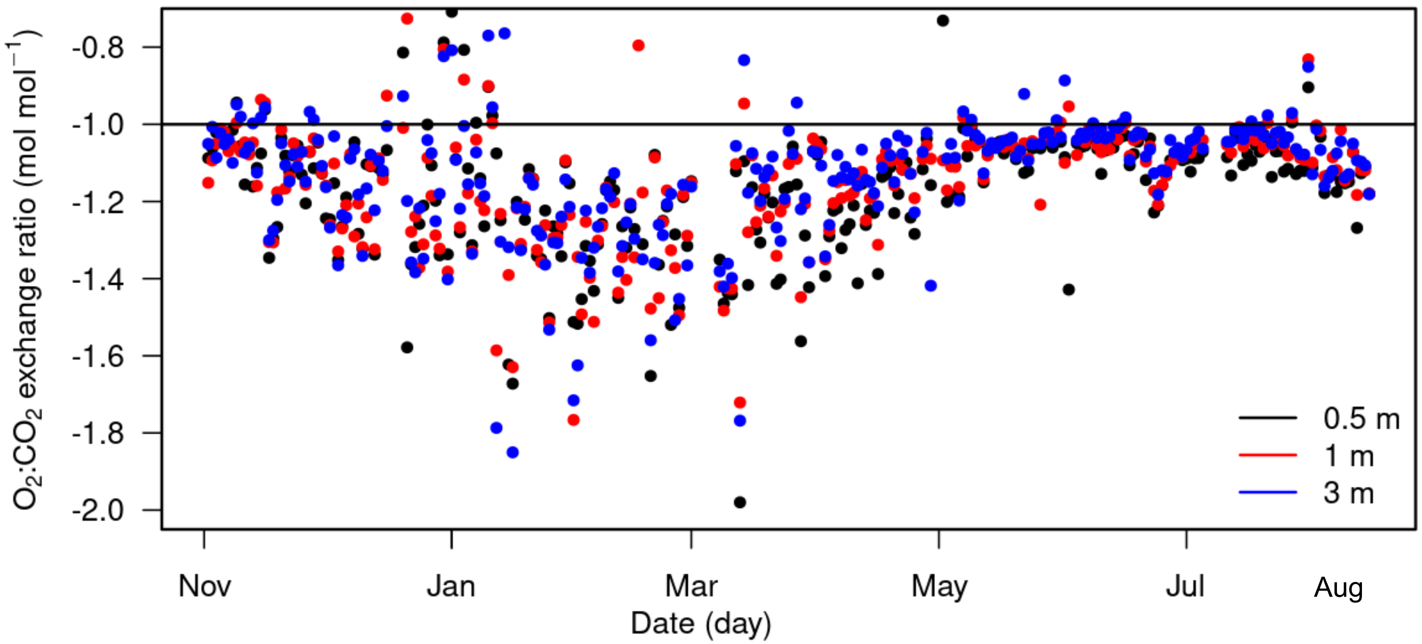
→ O_2 and CO_2 mole fraction are anticorrelated

Results – O_2:CO_2 exchange ratio July 2023 from mole fractions at three heights (day and night)

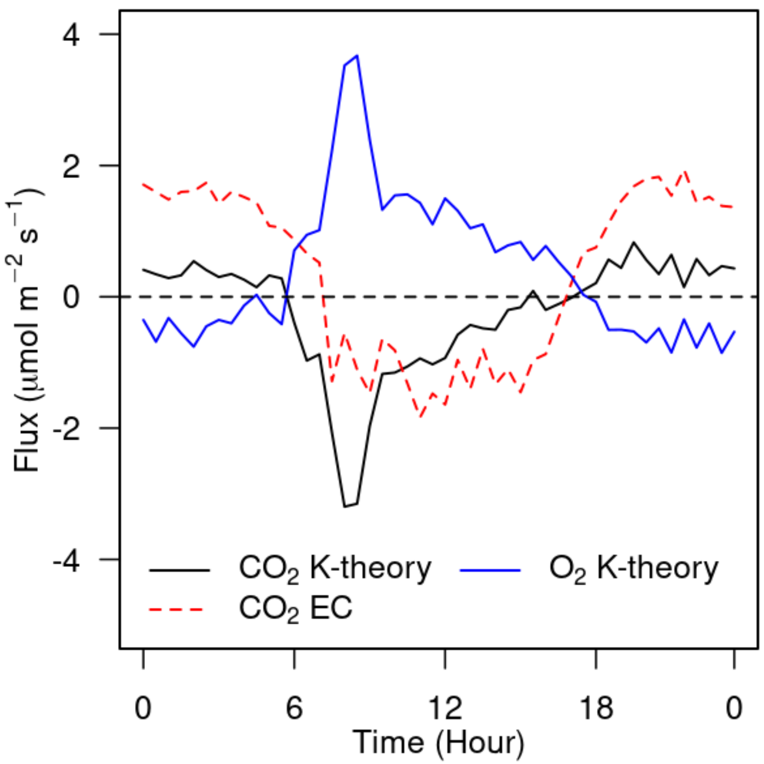


→ O_2:CO_2 exchange ratio closer to -1.1 with increasing height

Results – O_2:CO_2 exchange ratio Nov 2022 – Aug 2023

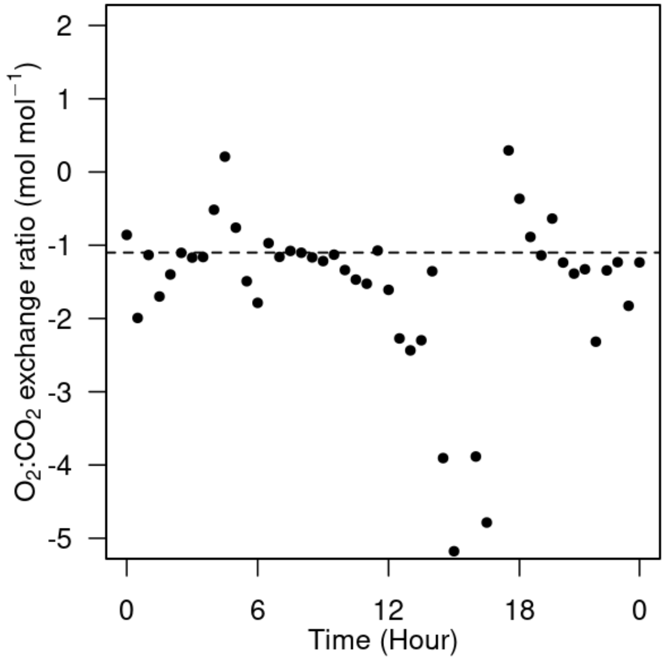


Results – O_2 and CO_2 net fluxes from K-theory and EC (median diel cycle)



→ O_2 and CO_2 fluxes from same method (K-theory) are anticorrelated and follow same variability

→ CO_2 fluxes from EC show higher resiration than from K-theory, photosynthesis rates similar



Something strange happens at sunrise and sunset…
Otherwise, ER ~1.1

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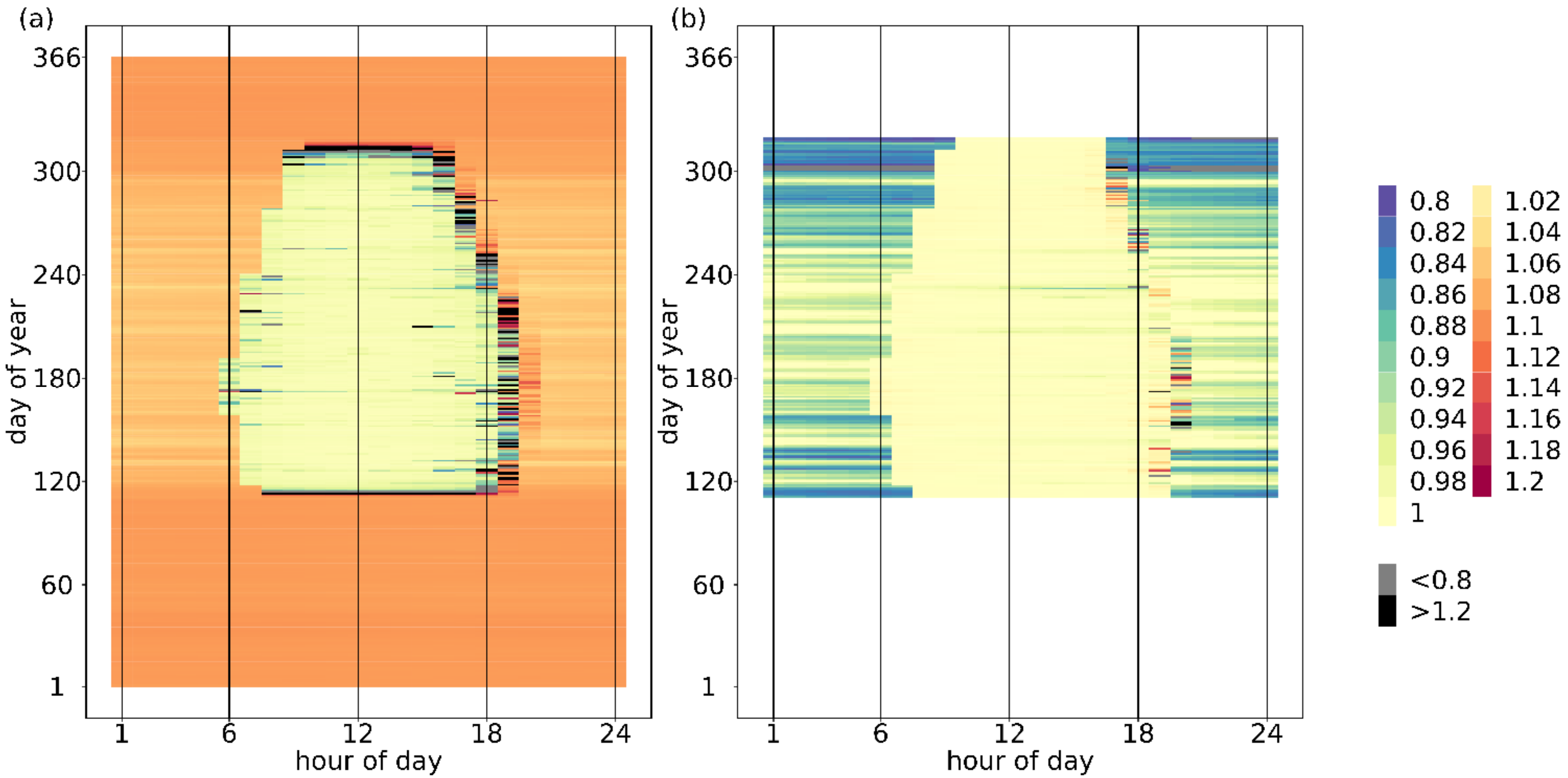
“CANVEG”

- 1-dimensional, multi-layer atmosphere-biosphere gas exchange model
  - Baldocchi, 1997: doi:10.1046/j.1365-3040.1997.d01-147.x
  - We added O_2 fluxes to the model, to study ER
  - ER_{eco} = ER of entire ecosystem
    = 1.06 to 1.12 mol mol^{-1}
  - ER_{conc} = ER above and within the canopy
    = 1.12 to 1.15 mol mol^{-1}
- Re-examined the holy grail goal, with this model:
  - Concluded that it *is* possible to partition CO_2 fluxes into photosynthesis and respiration, if we measure O_2 fluxes and we know ER_{eco}.
    - But some further improvements in O_2 instrument precision needed for results to be meaningful.

CANVEG ER results: seasonal and diel variations



ER_{eco} $ER_{assimilation}$

Conclusions

- Terrestrial ecosystem O_2 measurements are even harder than "traditional" atmospheric O_2 measurements!
- There are some very strange results in previous literature, which we believe are likely large measurement artefacts because of researchers being unaware of the many challenges of high-precision O_2 measurement.
- Our provisional results suggest:
  - ARQ from **stem respiration** ~1.0 mol mol^{-1} (much greater than previous literature; in line with theory)
  - **Leaf-level** ER ~0.9-1.0 mol mol^{-1} (complicated analysis owing to non-steady state)
  - **Soils**? TBD. Complicated further by diffusion, pressure gradients, calcareous soil
  - **Vertical flux gradient** measurements promising as eddy covariance alternative
    - ER ~1.18 mol mol^{-1}, seasonally varying with crop development (probably fossil influence which needs to be removed…)