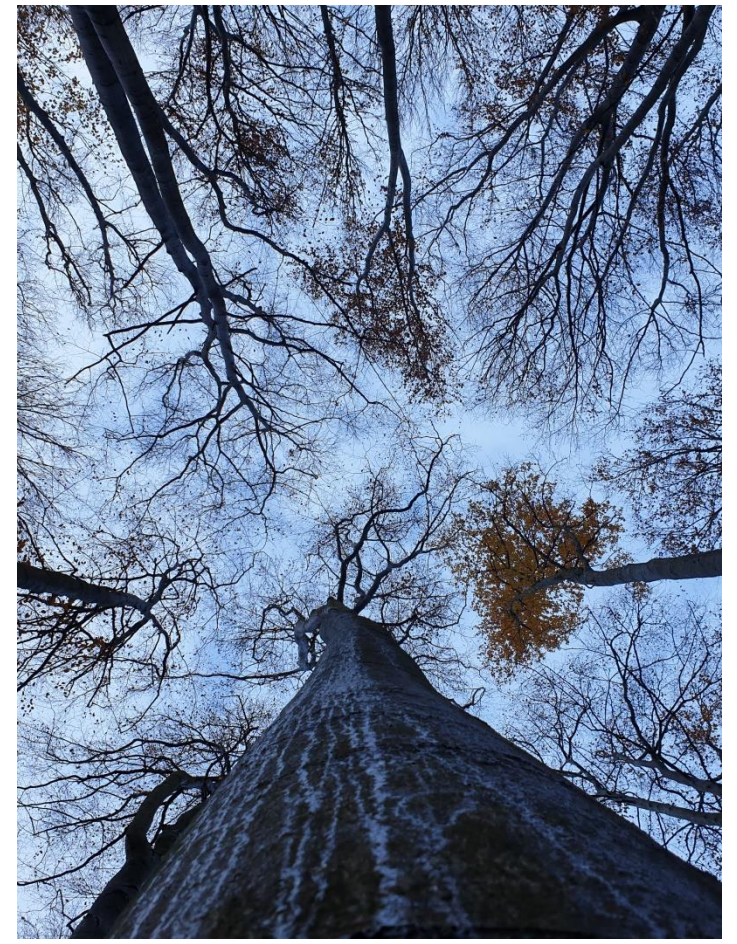


# Winter is coming – ecosystem-scale COS exchange during senescence of a deciduous forest



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# Introduction

- The gross uptake of  $\text{CO}_2$  on ecosystem level (GPP) can't be measured directly, but has to be inferred from models or proxies. One of the newly emerged constraints on GPP is the trace gas carbonyl sulfide (COS). COS enters the plant leaf through the stomata and diffuses through the intercellular space, the cell wall, the plasma membrane and the cytosol like  $\text{CO}_2$ . Within the cytosol, it is then catalyzed by the enzyme carbonic anhydrase (CA) in a one-way reaction to  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . Basically, this one way flux would make COS a very promising tracer for GPP on ecosystem level, but there is growing evidence that plants are also capable of emitting COS.

Mosses and even vascular plants that are under high stress like drought and fungal infection, have been reported to emit COS. Furthermore, a winter wheat field, that showed a good correlation between the  $\text{CO}_2$  and COS ecosystem fluxes during the peak growing phase turned into a source for COS after going into senescence. This indicates that yet unknown COS emission processes likely related to plant degradation, could complicate the use of COS as a tracer for GPP.

## Objective

- Since the majority of studies have focused on measuring COS ecosystem fluxes during peak growing times or on evergreen forests, we seek to quantify the relationship between the ecosystem-scale exchange of  $\text{CO}_2$  and COS of an ecosystem going into senescence.



# Methods

## Field site (see Braden-Behrens et al. 2019 & Anthoni et al. 2004)

- Managed beech forest (*Fagus sylvatica* L.) in Thuringia (central Germany)  
Location: 51°19'41, 58" N; 10°22'04, 08" E; 450 m a.s.l.
- Tower height 44 m
- Forest Age: 30-180 years; 125 years in the dominant wind direction
- Maximum effective leaf area 4 m<sup>2</sup>/m<sup>-2</sup>
- Average 20% largest trees were 37m

## Measurements & data analysis

- Sonic Anemometer: Gill R3
- Gas analyzer: Quantum Cascade Laser Mini Monitor  
(Aerodyne Research, Billerica MA, United States)
  - COS, CO<sub>2</sub>, H<sub>2</sub>O & CO
- Half hourly drift calibration
- Lag determination (see Hörtnagl et al. 2010)
- Spectral Correction (see Gerdel et al. 2017)

## Filter for fluxdata

- Integral turbulence test
- Stationarity
- +/- 100 (pmol m<sup>-2</sup>s<sup>-1</sup>)



# Methods

## Flux partitioning

- GPP was calculated using classic daytime flux partitioning (FP) (see Lasslop et al., 2010)

$$GPP = \frac{\alpha \beta R_{PAR}}{\alpha R_{PAR} + \beta}$$

$$RECO = r_b e^{E_0 \left( \frac{1}{T_{ref} - T_0} - \frac{1}{T_{air} - T_0} \right)}$$

$$NEE = GPP + RECO$$

- and using the FP+ algorithm, which includes COS within the daytime FP (see Spielmann et al. 2019)

$$LRU = \iota e^{\left( \frac{\kappa}{R_{PAR}} \right)}$$

$$F_{COSmodel} = \frac{GPP LRU \chi_{COS}}{\chi_{CO2}}$$

All parameters are determined by optimizing the modelled NEE as well as the modelled COS flux to their measured values

$\alpha$  ... canopy light utilization efficiency ( $\mu\text{mol CO}_2/\mu\text{mol photons}$ )

$\beta$  ... maximum CO<sub>2</sub> uptake rate of the canopy at light saturation ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )

$\iota$  ... LRU at infinite light intensity

$\kappa$  ... factor controlling the increase of LRU at low light

$\chi_{COS}$  ... mixing ratio of COS (ppt)

$\chi_{CO2}$  ... mixing ratio of CO<sub>2</sub> (ppm)

$r_b$  ... ecosystem base respiration at reference temperature ( $\mu\text{mol m}^{-2} \text{ s}^{-1}$ )

$E_0$  ... temperature sensitivity ( $^{\circ}\text{C}$ )

$T_{ref}$  ... reference temperature ( $15^{\circ}\text{C}$ )



# Preliminary Results

All of the following data need to undergo further analysis!

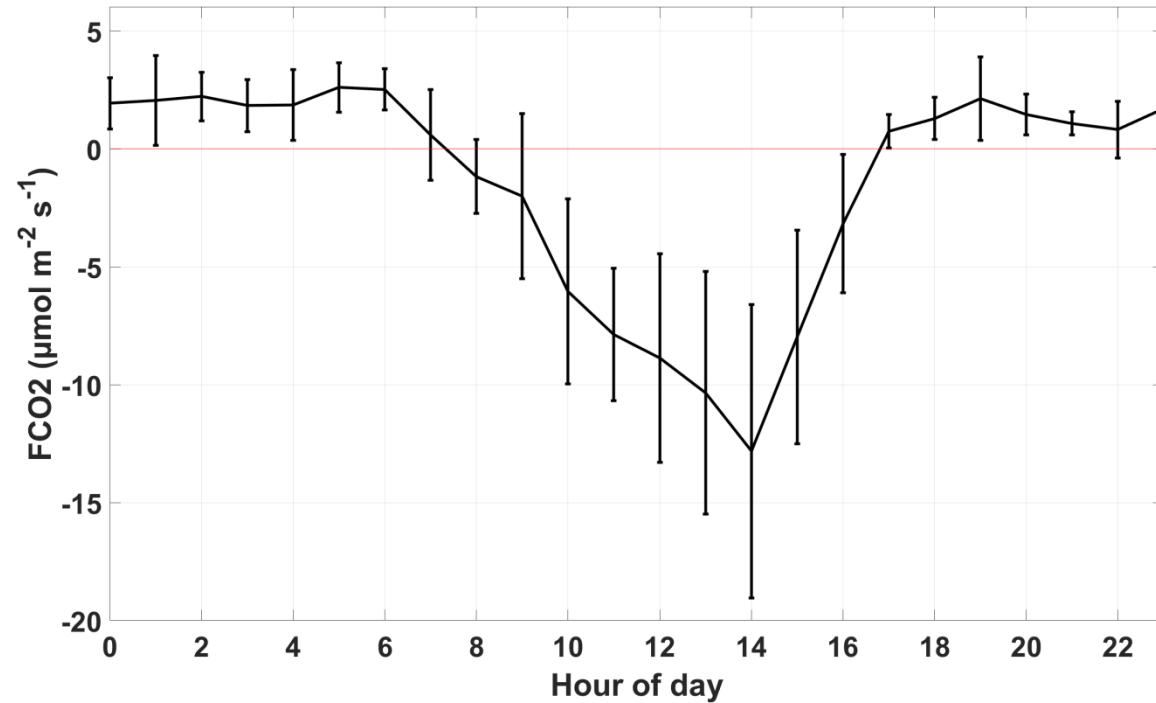




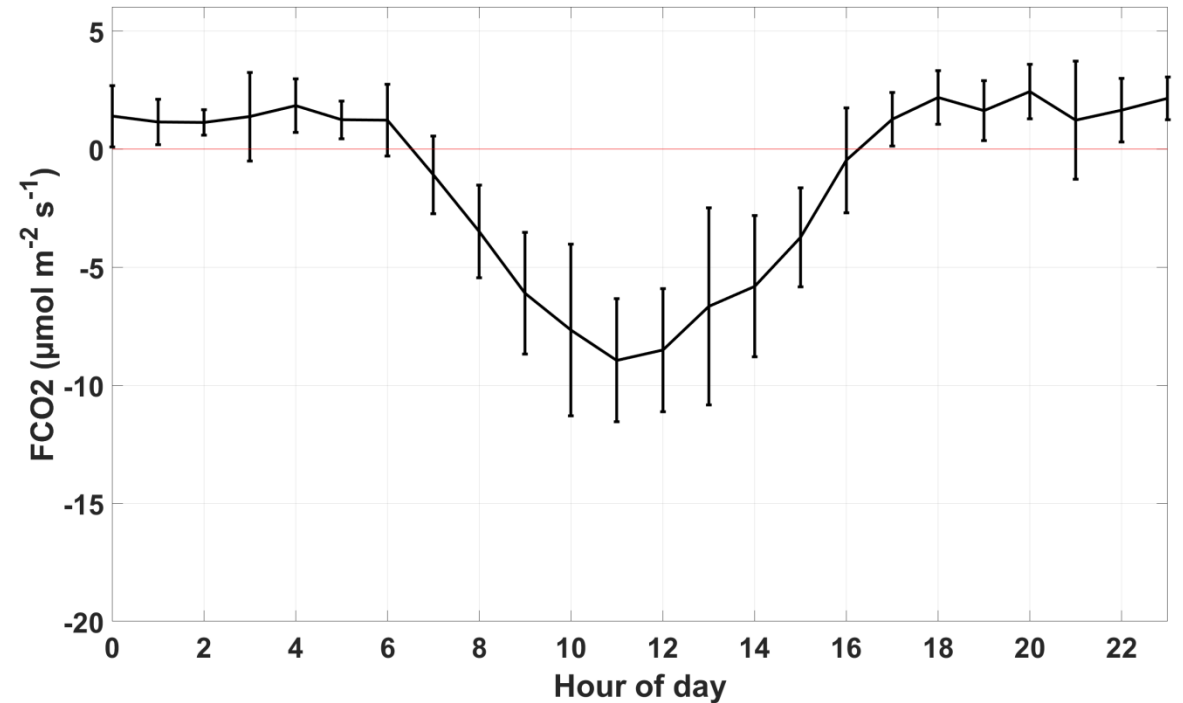
# Week of the year 40-41

Mean Diurnal variation

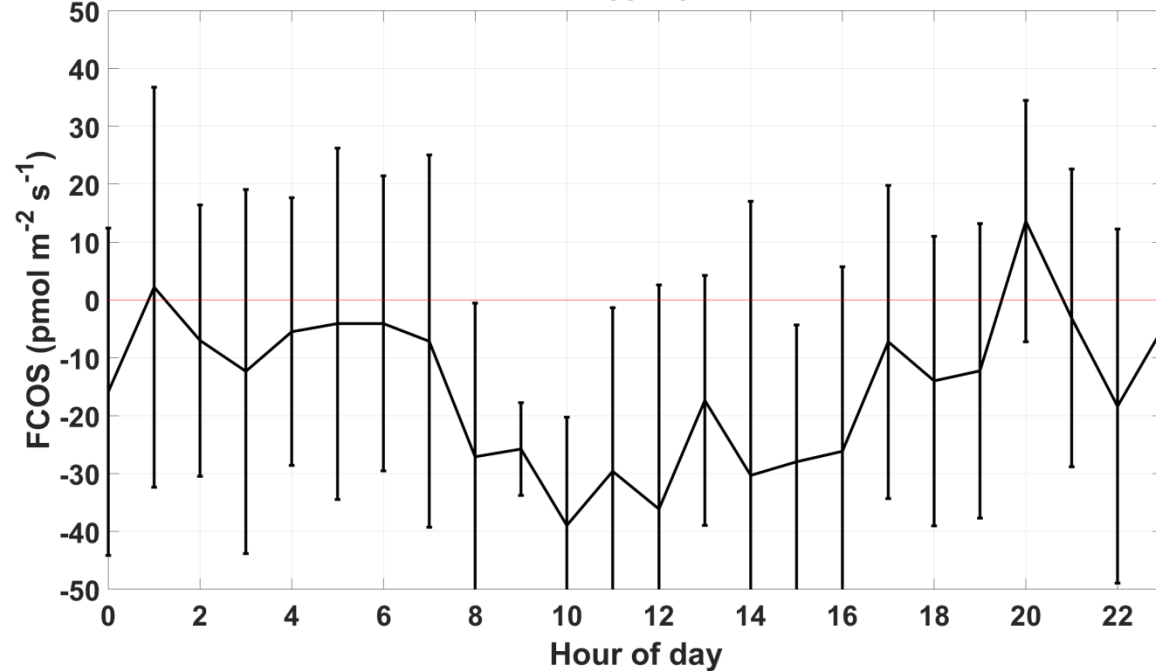
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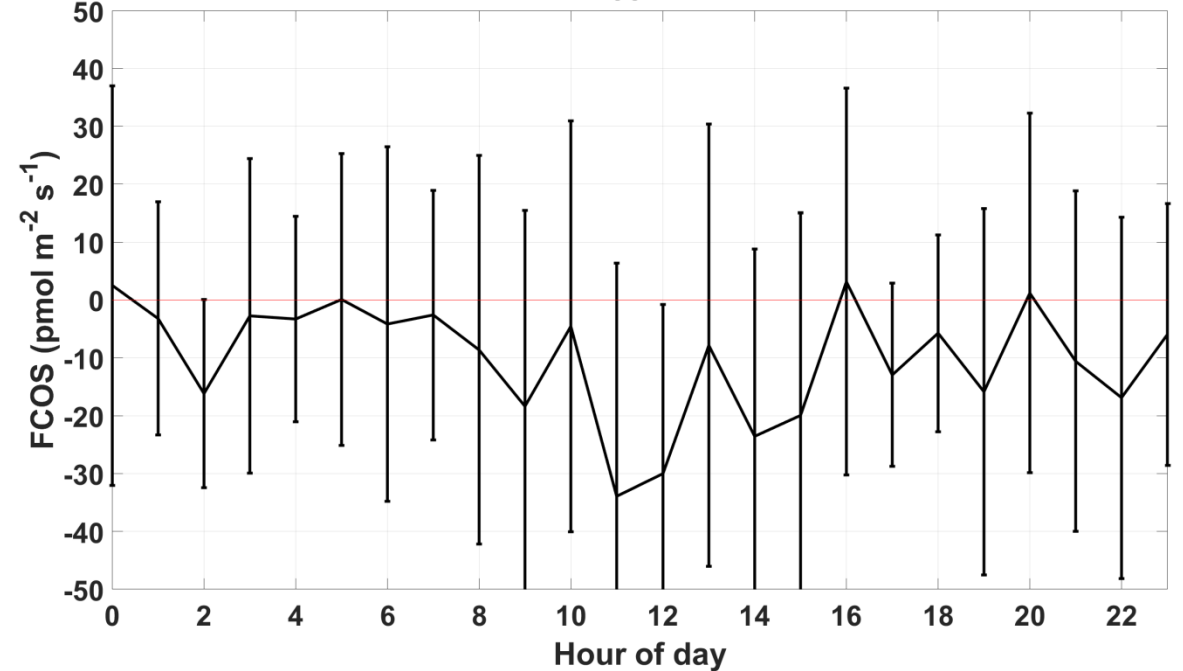
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week40



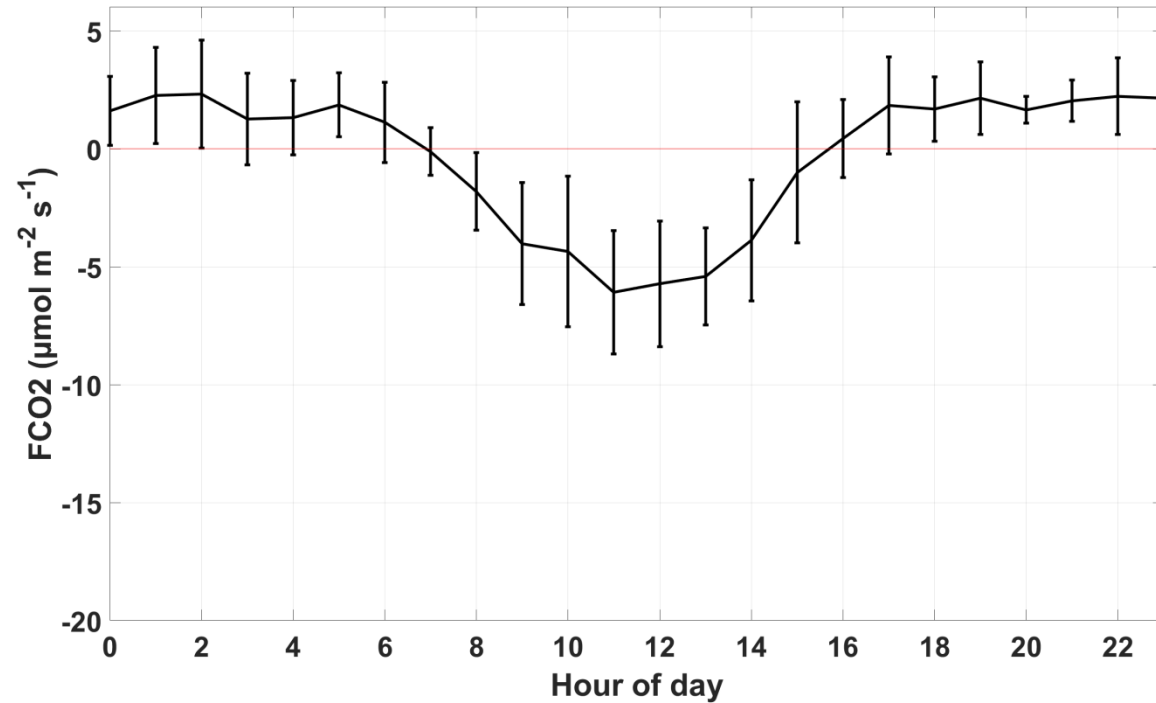
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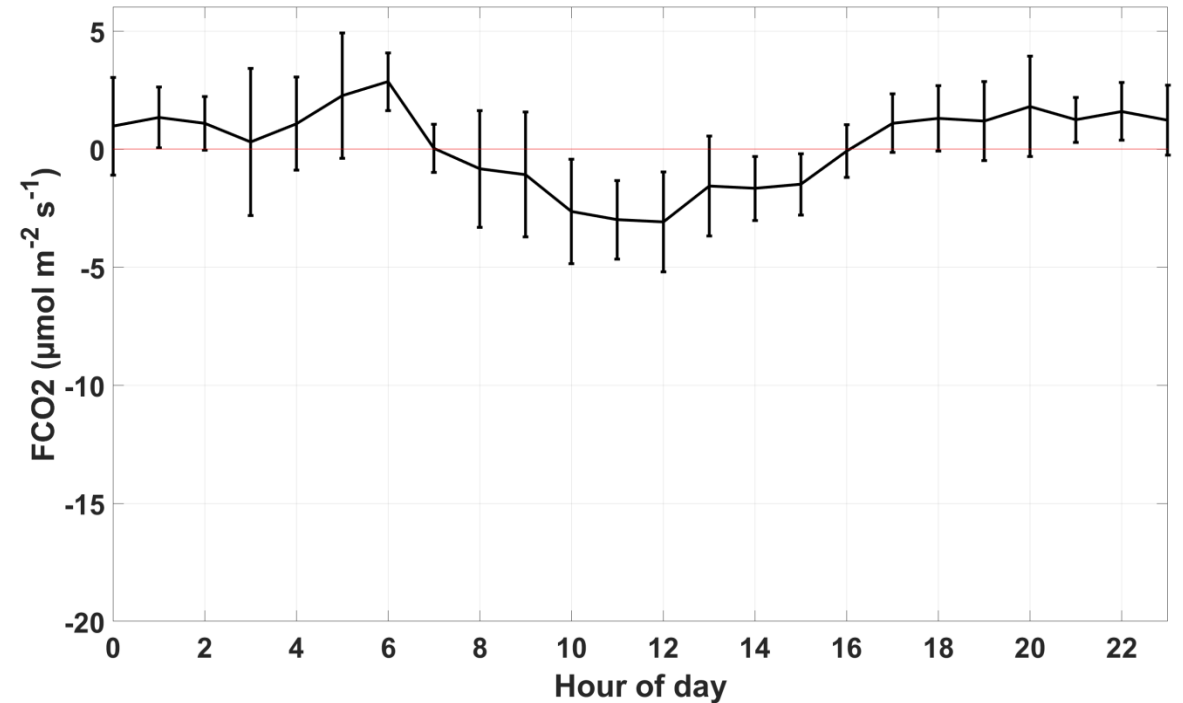
# Week of the year 42-43

Mean Diurnal variation

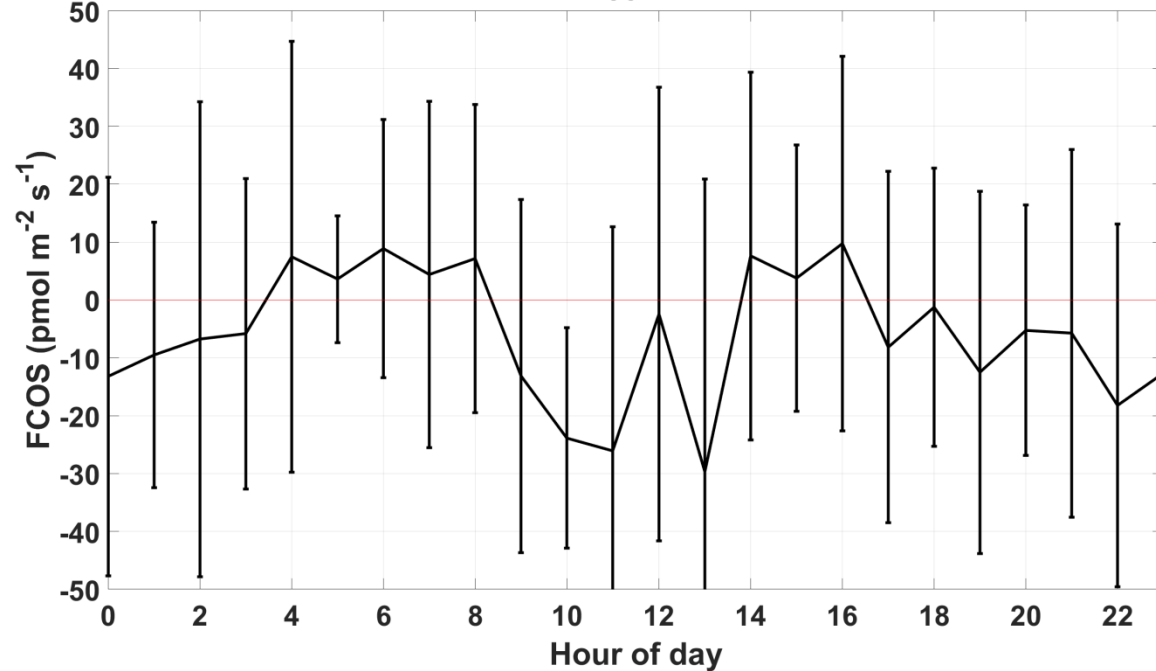
week42



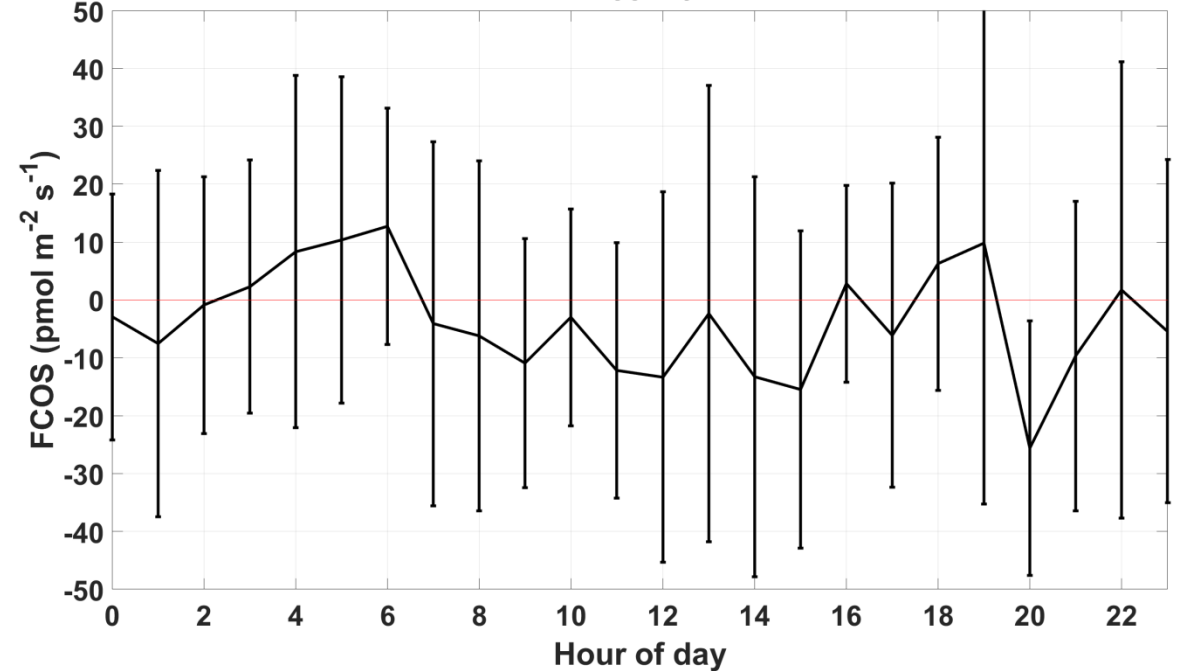
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week42

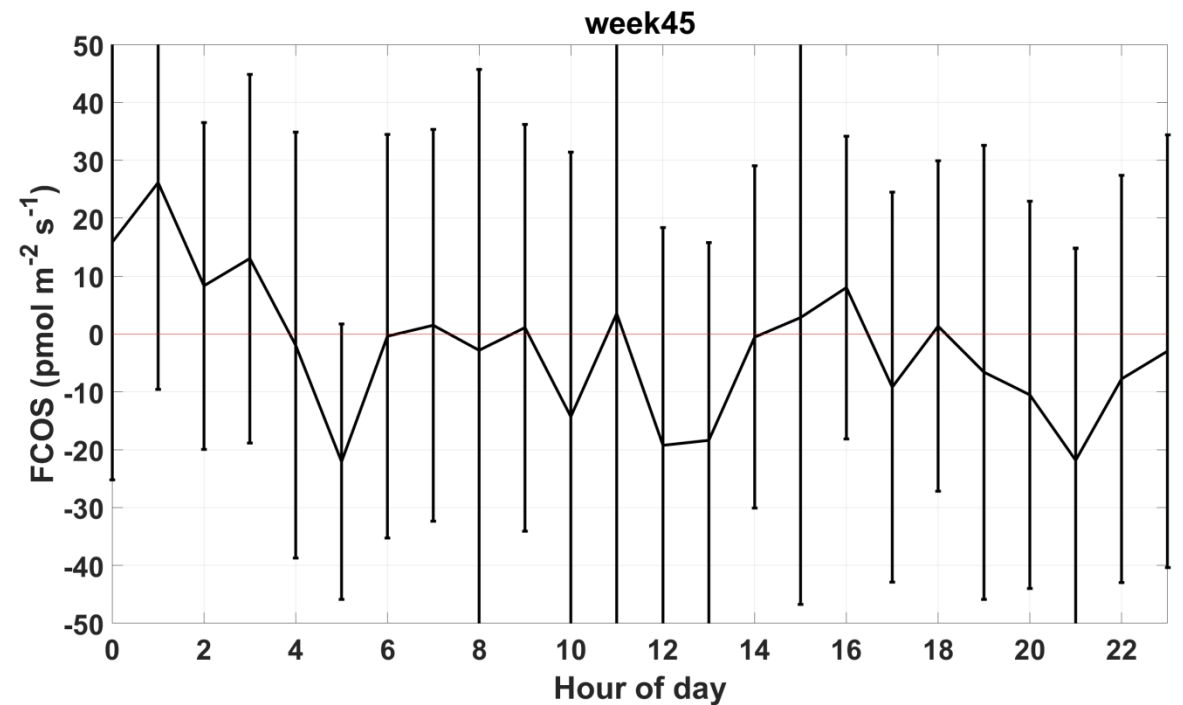
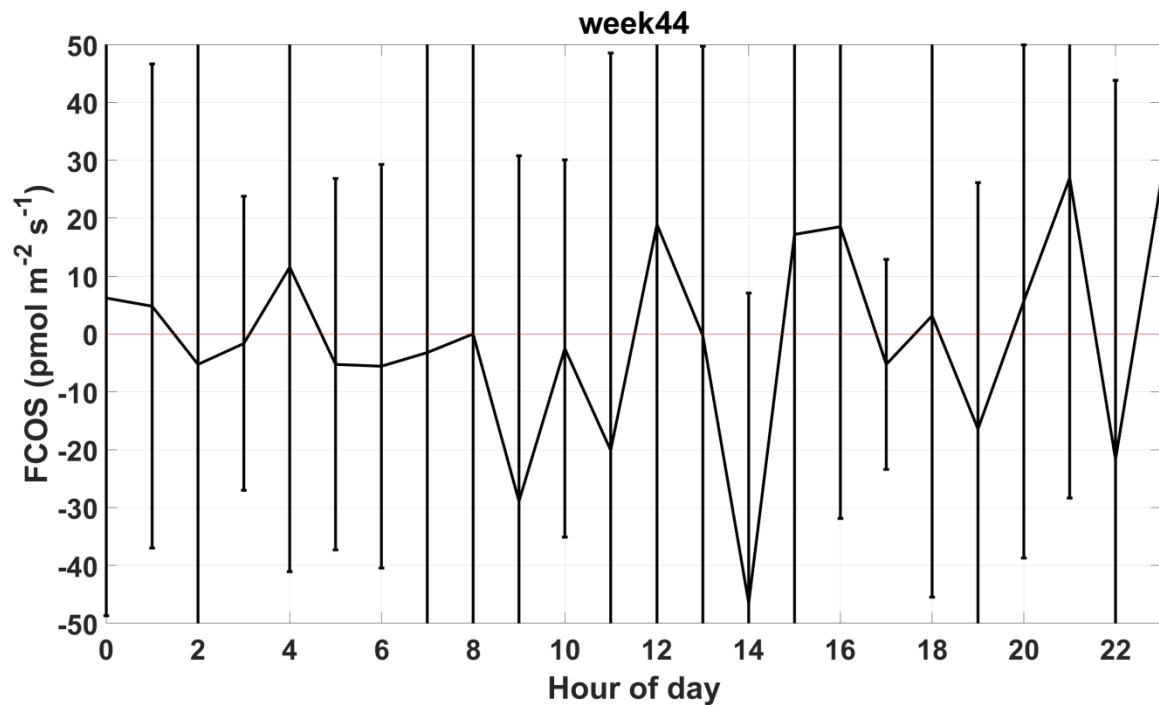
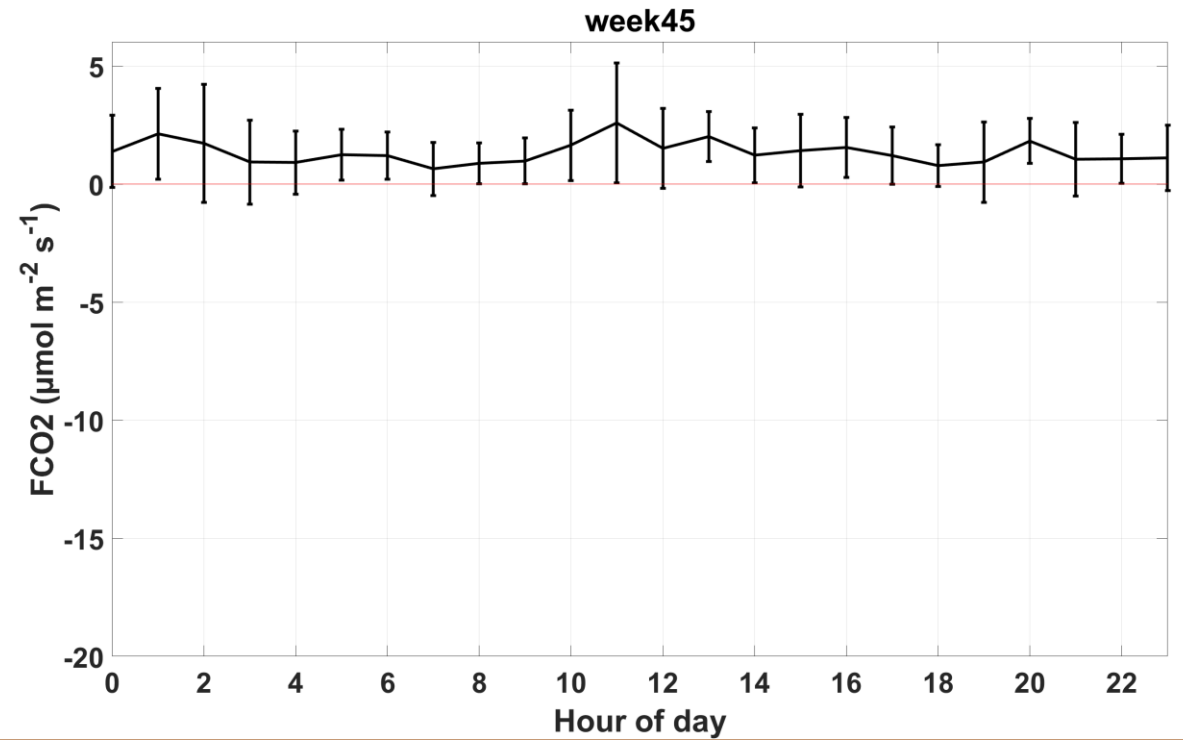
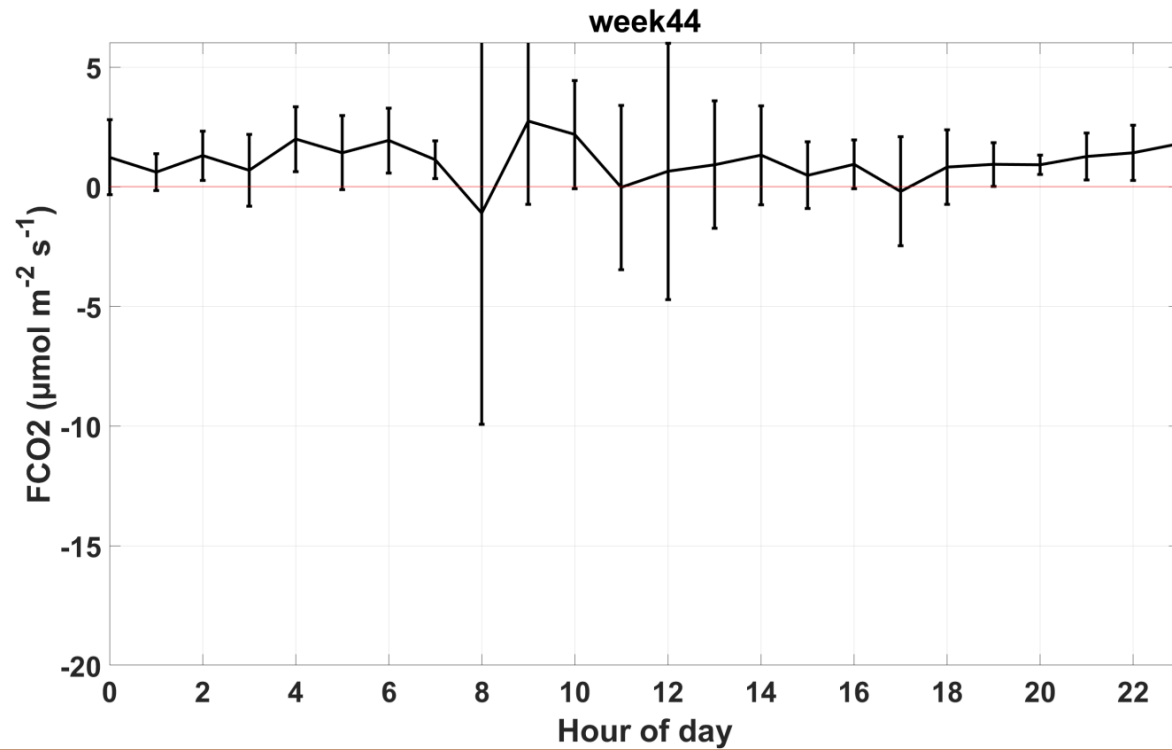


week43



# Week of the year 44-45

Mean Diurnal variation

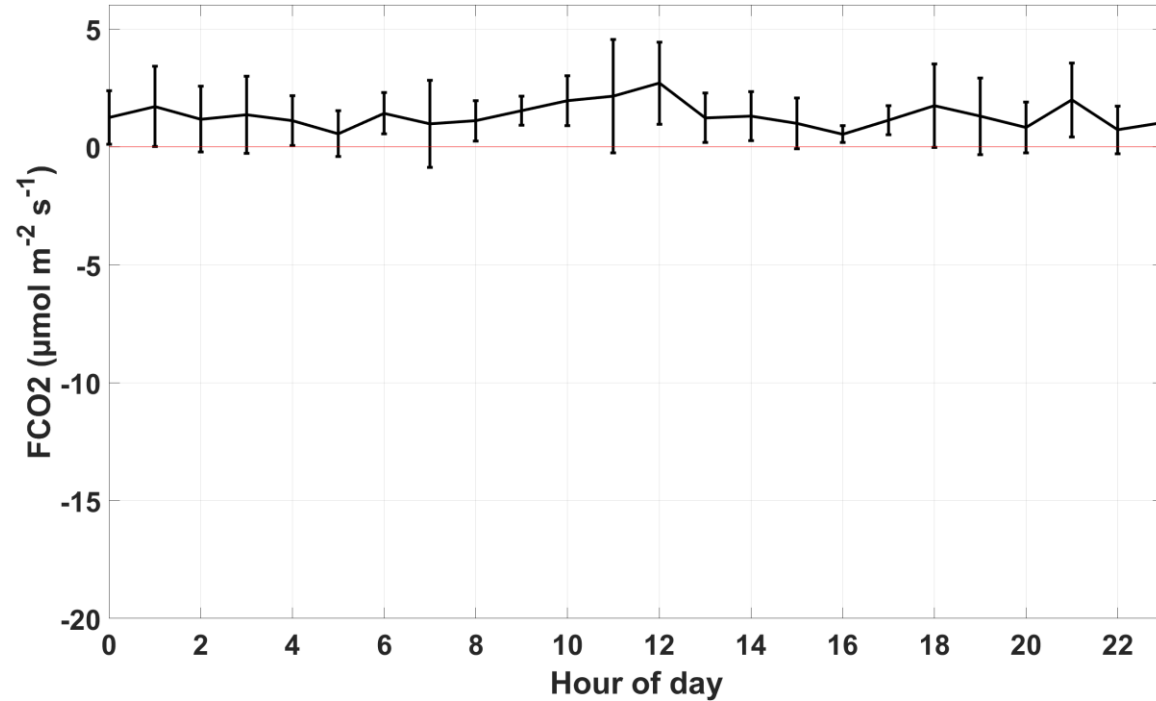




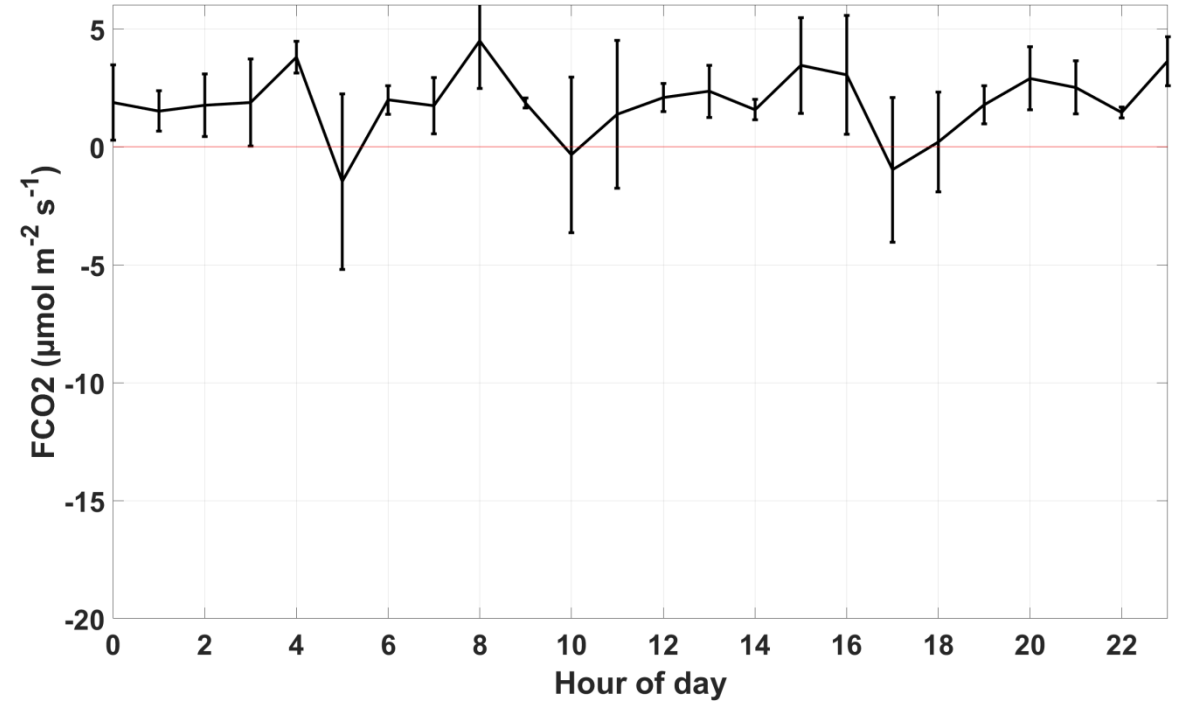
# Week of the year 46-47

Mean Diurnal variation

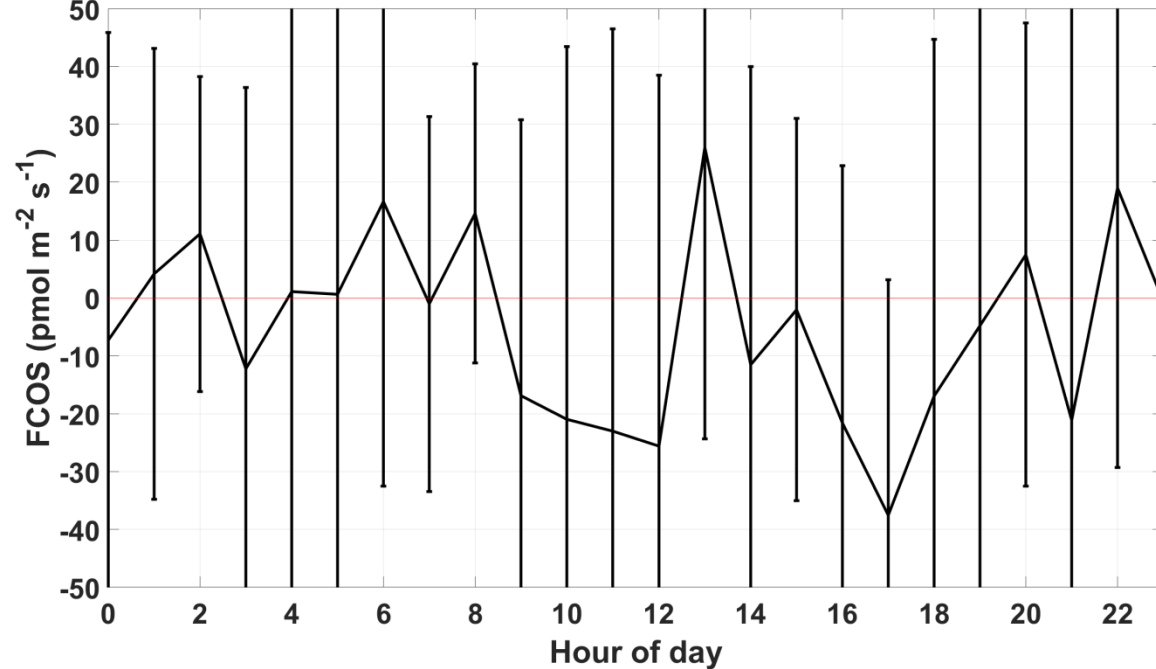
week46



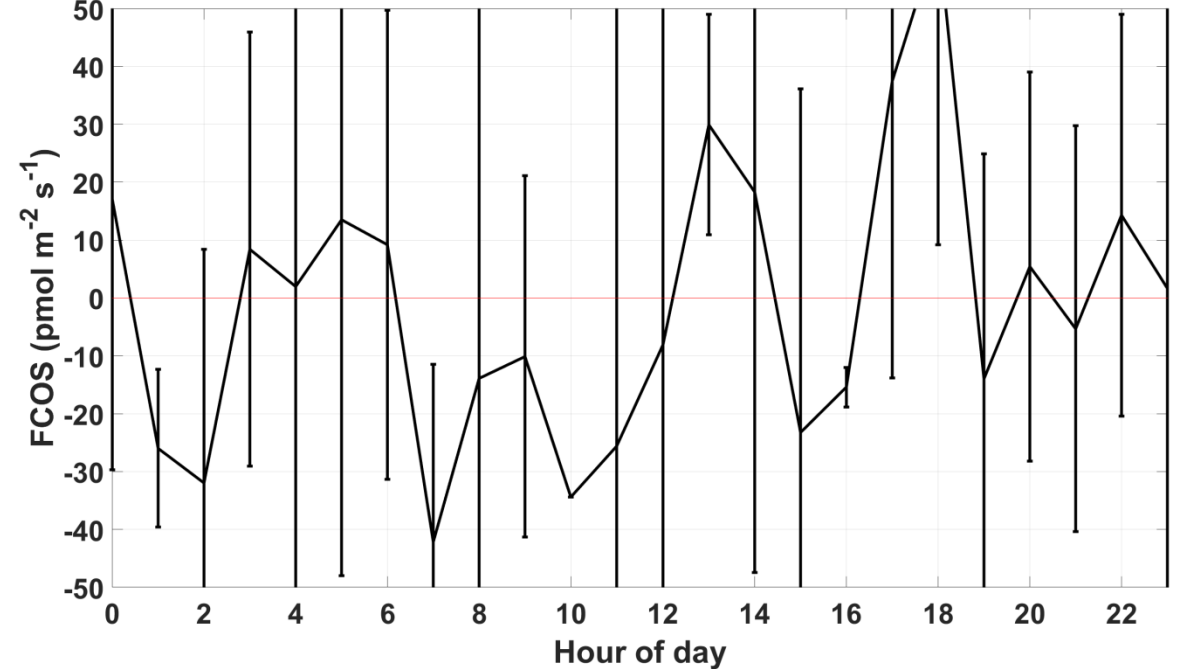
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week46

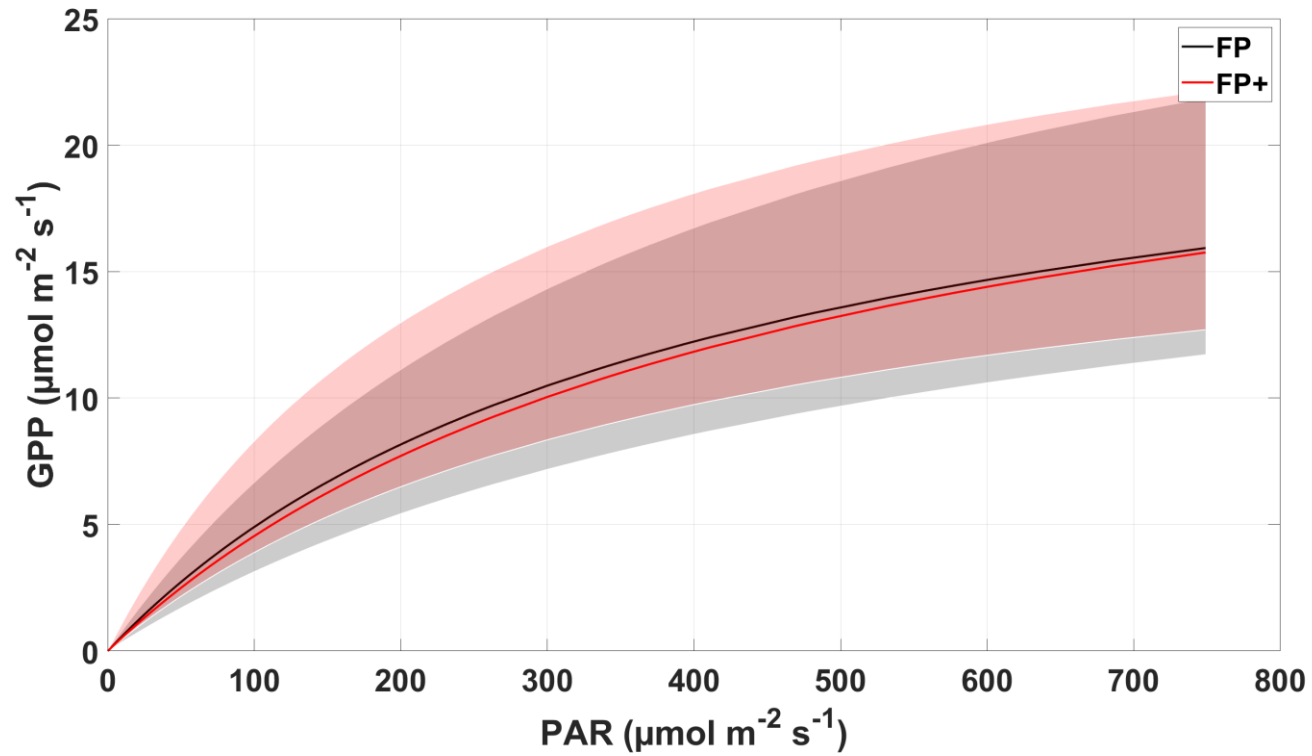


week47

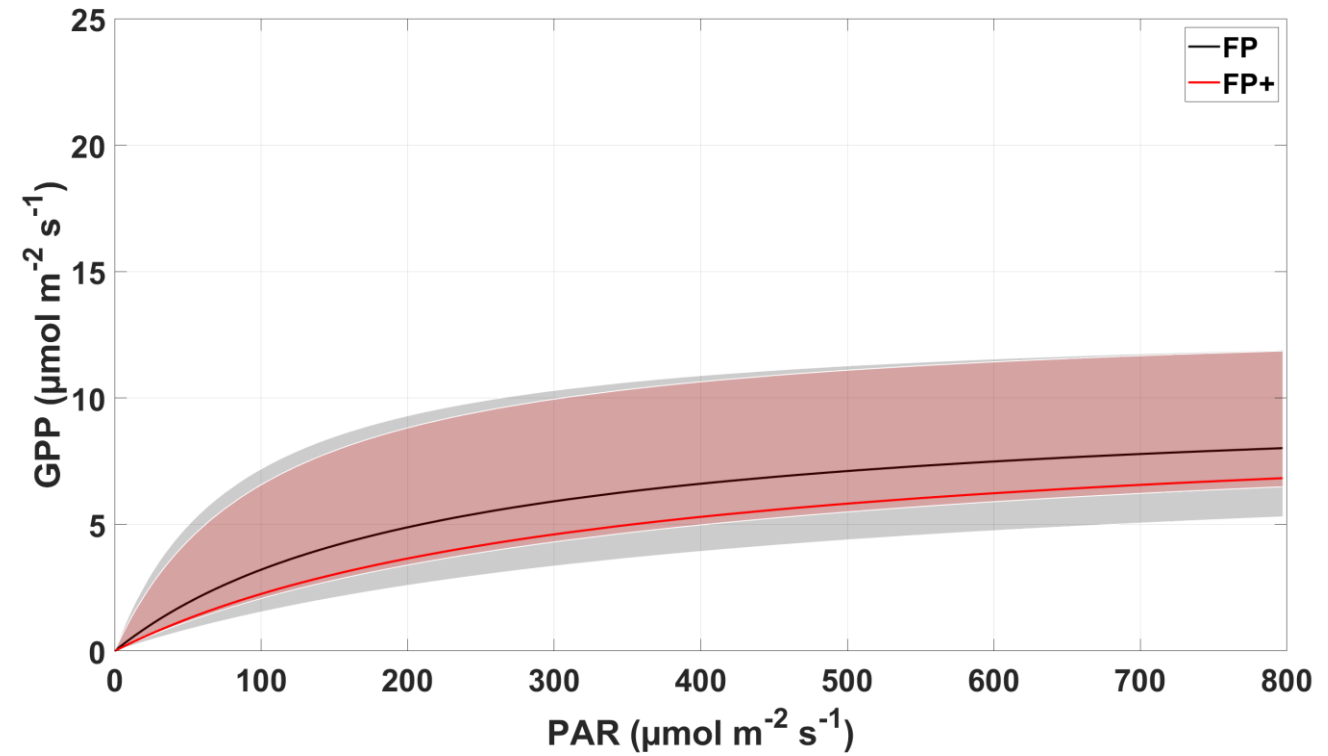


# GPP

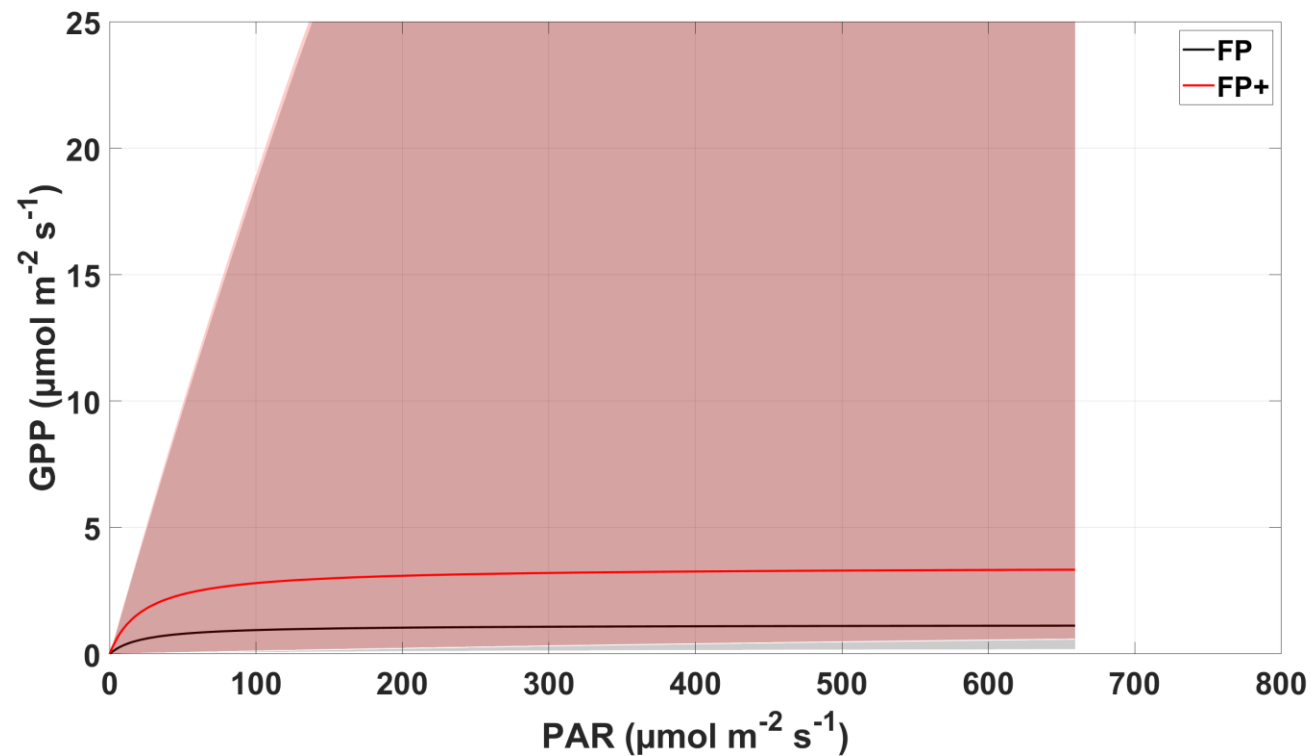
Week 40-41



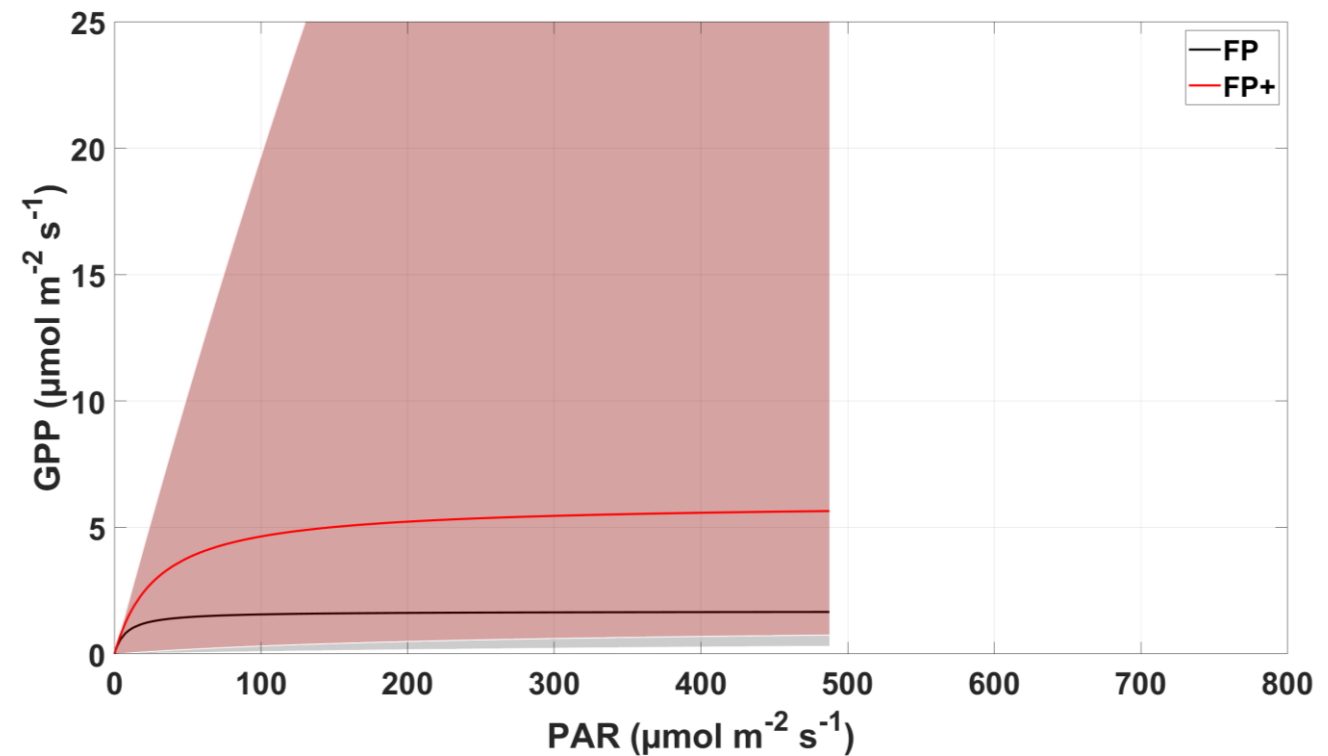
Week 42-43



Week 44-45



Week 46-47

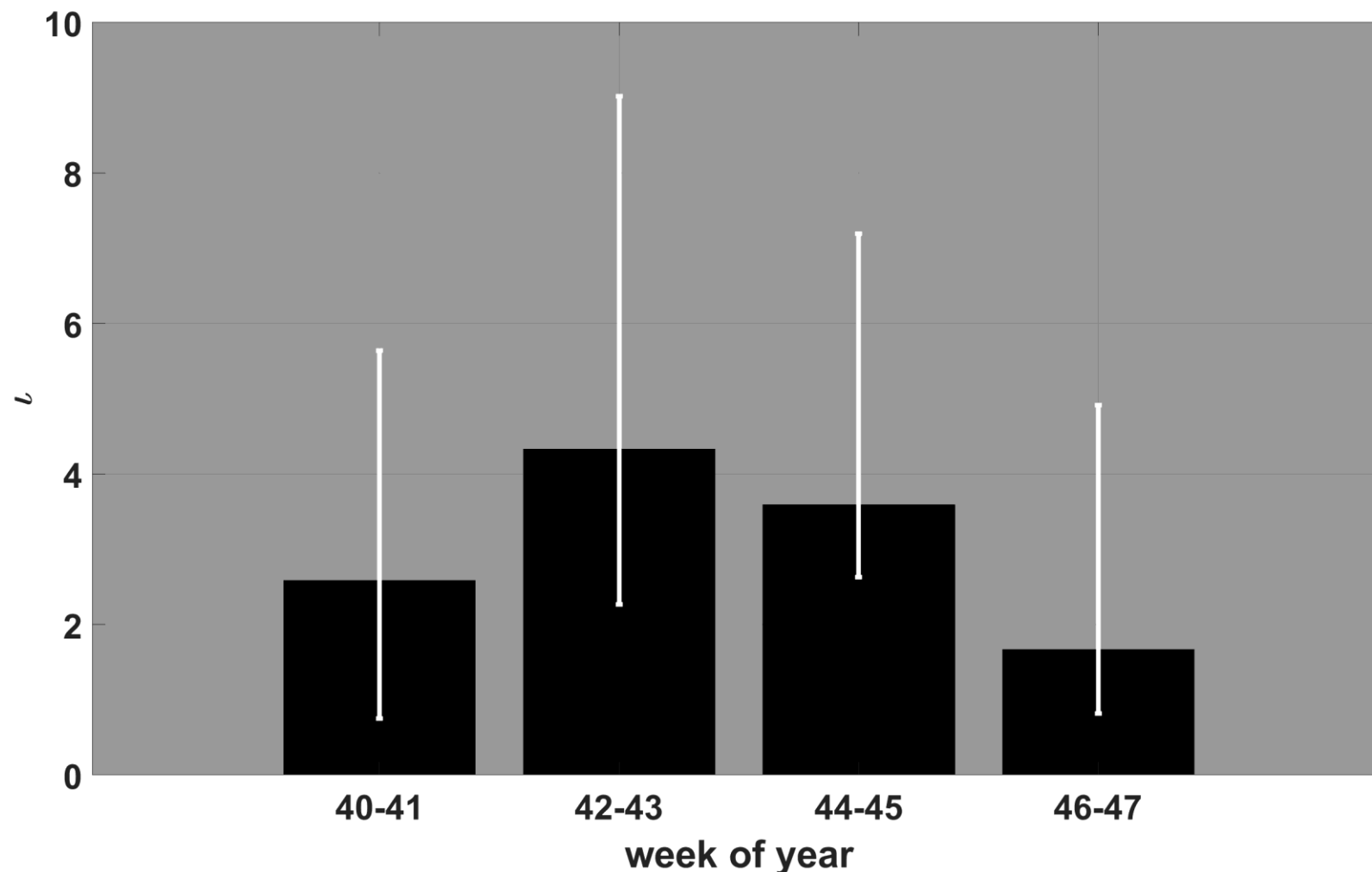




# COS and CO<sub>2</sub> fluxes

- The COS and CO<sub>2</sub> uptake on ecosystem level decreased concurrently over the course of the measurement campaign
- The forest turned into a net source for CO<sub>2</sub>, whereas the COS fluxes got more erratic.
  - We observed uptake as well as COS emissions towards the end of the campaign.
- Classic FP yielded higher GPPs as FP+ within the first 4 weeks
- In the last 4 weeks of the campaign the highly variable COS fluxes seem to interfere with the calculation of the low GPP
  - The erratic nature of COS fluxes leads to an extremely high uncertainty in GPP (FP+)

# LRU



- $\iota$  increased between the weeks 40-41 and 42-43.
- The lower  $\iota$  for the weeks 44-47 result from the extreme variability of the COS fluxes turning from COS uptake to emission. As COS emission can't be used for the calculation of GPP, they were excluded, leading to the lower LRUs plotted here (weeks 44-47).

Reminder:  $\iota$  ... LRU at high incoming PAR.

LRU ... relative uptake of COS to CO2 flux used to calculate GPP



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# References and Acknowledgements

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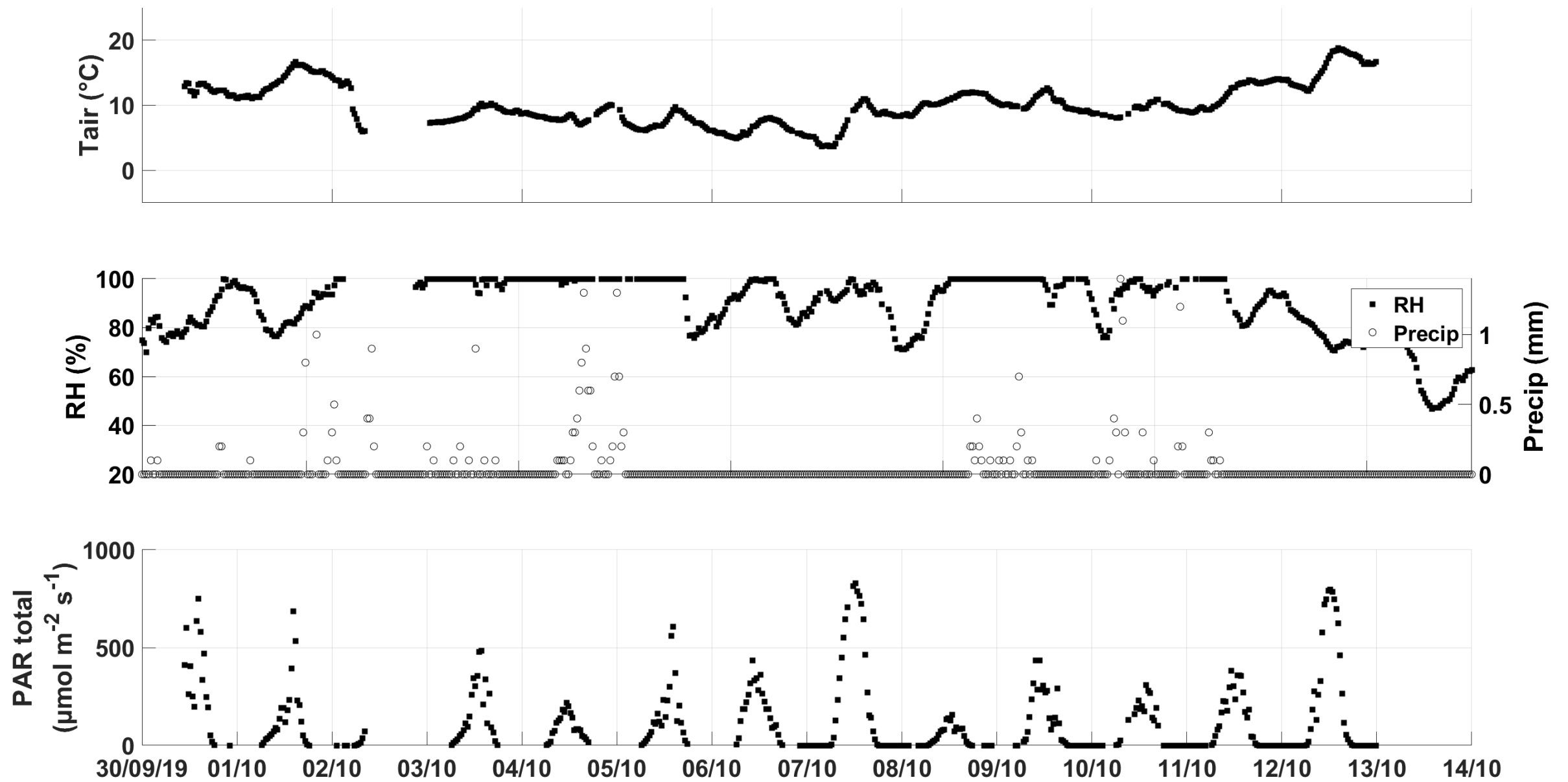
# Additional Material

## Abbreviations

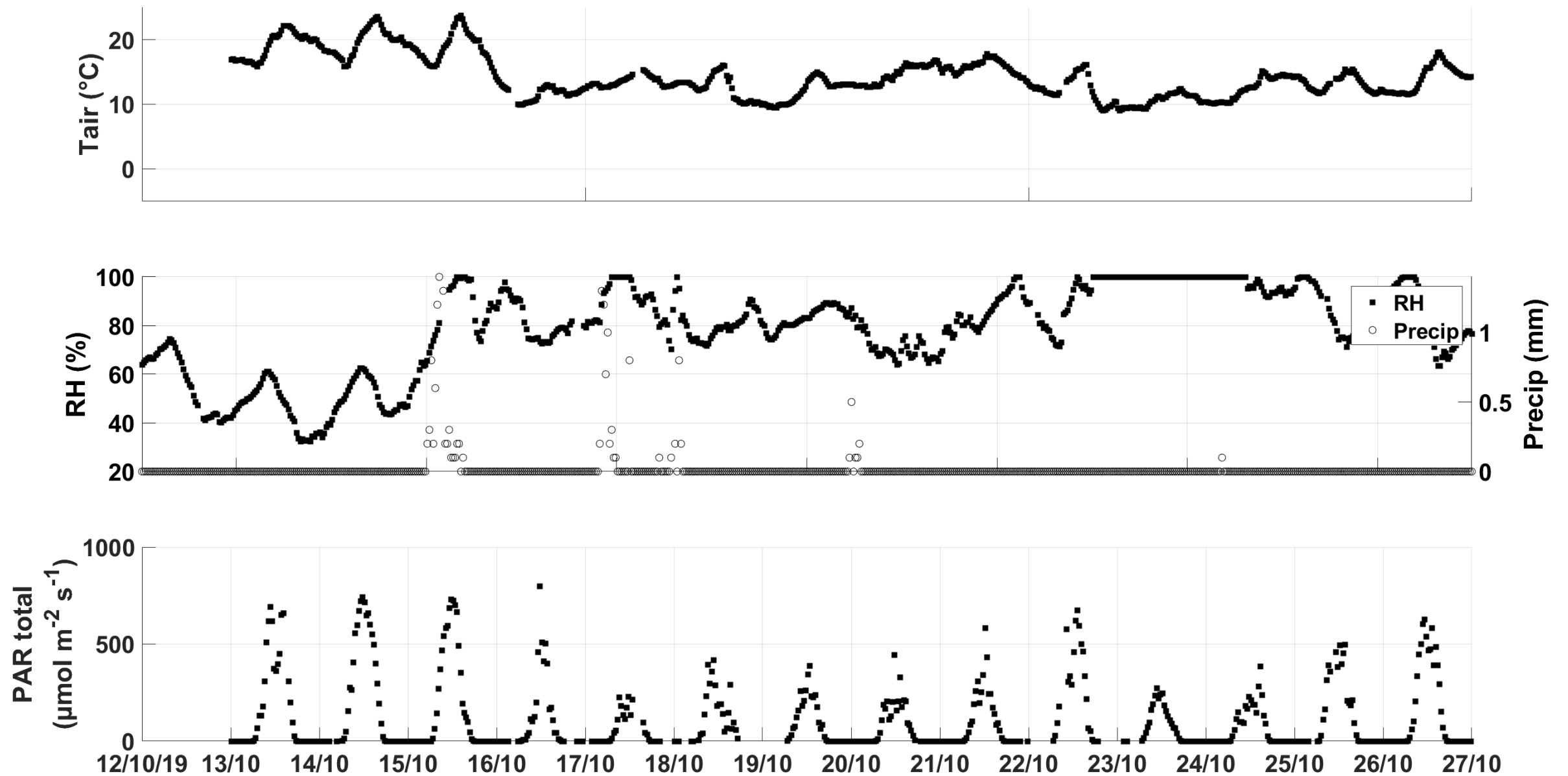
- GPP... Gross primary production
- COS ... Carbonyl sulfide
- ERU ... Ecosystem relative uptake
- LRU ... Leaf relative uptake
- PAR ... Photosynthetic active radiation
- RH ... Relative humidity (air)
- Precip ... Precipitation
- FP & FP+ ... flux partitioning & FP including COS

## Meteorological data

# Week of the year 40-41

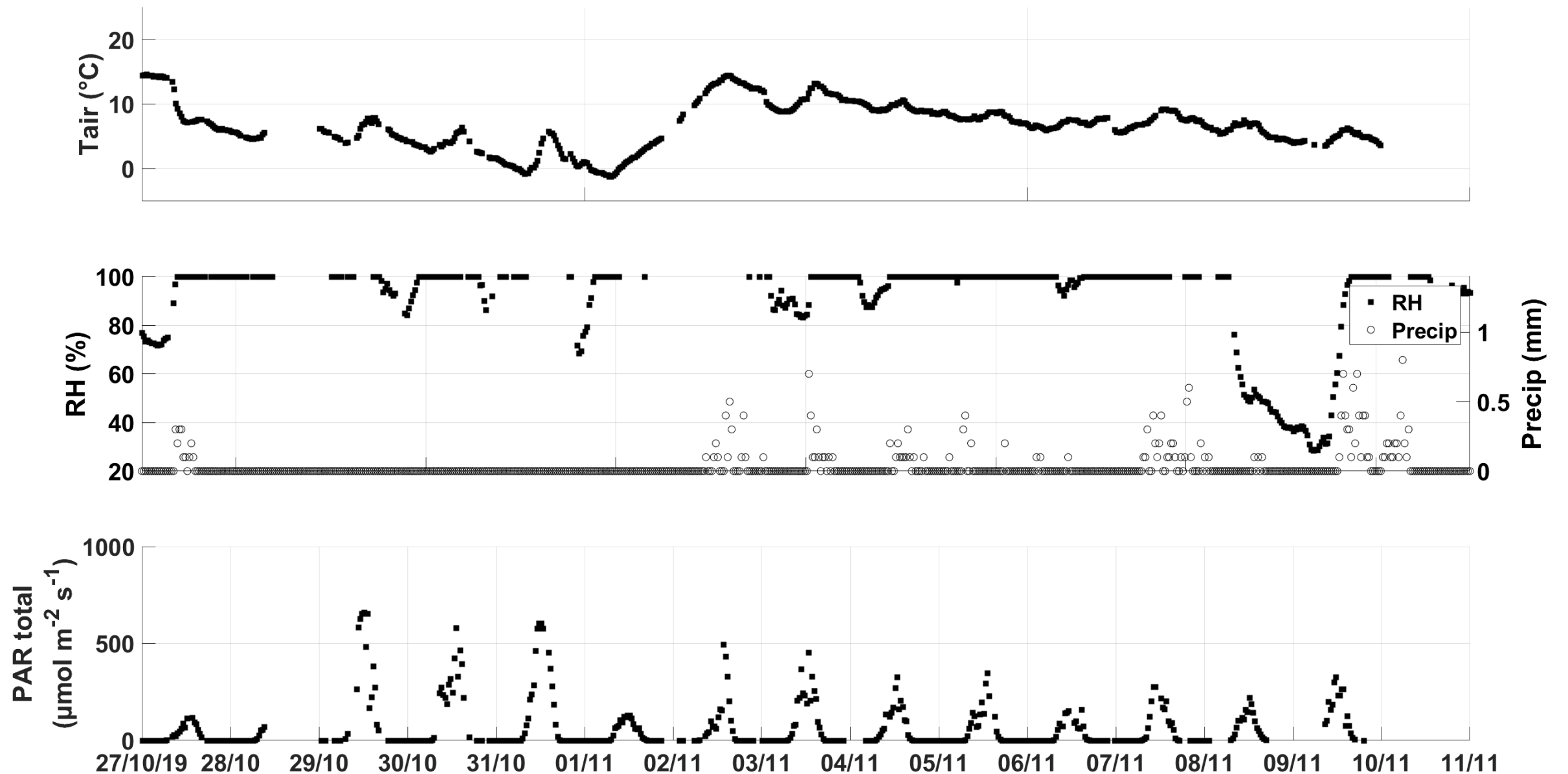


# Week of the year 42-43





# Week of the year 44-45



# Week of the year 46-47

