Biogeosciences

Supplement of

Aquatic and soil CO$_2$ emissions from forested wetlands of Congo's Cuvette Centrale

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S1. Calculation of total dissolved concentrations based on Henrys law and the headspace equilibration method

The following tool explains step-by-step calculations for dissolved concentrations of CO_2 using the headspace equilibration technique based on the SOP by Bastviken et al. (2015). In the field, 6mL of bubble free water was injected into a N_2 flushed 12mL vial (Labco exetainer, UK) containing 50 μL of 50% (w/v) $ZnCl_2$ solution (Dong et al., 2006). The following protocol requires to convert the mole fraction of a gas x measured by a gas chromatograph [C_{ppm} typically in ppm, i.e. μmol mol^{-1}] to the partial pressure of that gas x in $atm \cdot mol \cdot mol^{-1}$:

$$P_x = \frac{C_{ppm}}{10^6} \cdot P_{headspace},$$

with $P_{headspace}$ as the total pressure of the gas mixture in the vial (Roper et al., 2013) (i.e. gas phase under equilibrium conditions) given in atm. This is equivalent to the headspace pressure, and can be calculated as follows:

$$P_{headspace} = P_{lab} \cdot \frac{V_{vial}}{(V_{vial} - V_{aq})}$$

, where V_{aq} denotes the total water volume injected into the exetainer [in L], V_{vial} the total vial volume [in L] and P_{lab} the laboratory pressure at time of flushing [in atm]. The total dissolved gas concentration (C_{total}) using the headspace equilibration technique is the sum of the partial gas pressure which partitioned into the gas phase (C_h) and the partial gas pressure remaining in the aqueous phase (C_{aq}):

$$C_{total} = \frac{C_h + C_{aq}}{V_{aq}}$$

C_h is derived via

$$C_h = \frac{P_x \cdot V_{hs}}{R \cdot T}$$

, where P_x is the partial gas pressure in the headspace measured using gas chromatography in $atm \cdot mol \cdot mol^{-1}$, V_{hs} the headspace volume in L, R the universal gas constant in L atm mol^{-1} K^{-1}, and T the laboratory temperature in K (where equilibration took place). The gas concentration still dissolved in the aqueous phase C_{aq} is derived via

$$C_{aq} = P_x \cdot V_{aq} \cdot K_H$$

, where K_H denotes Henry's constant for the respective trace gas.

The **Henry's law constant** is either defining the volatility of a gas species from solution to the atmosphere, or the solubility of a given gas from atmosphere to solution. In the latter definition, the constants' value is increasing with increasing solubility and is species specific. Henry's law solubility constant is defined as:

$$K_H = \frac{C_{aq}}{P_x}$$

, with K_H in units of $\frac{M}{atm}$ which equals $\frac{mol}{kg \cdot bar}$ or $\frac{mol}{L \cdot atm}$ [3]. The K_H coefficient used in this SOP is taken from the NIST Standard Reference Database:

$$K_{H|CO_2} = 0.035$$

at 298.15 K. Note, when working with groundwater samples or marine samples, it is advised to implement a salinity correction for K_H.

#1. Example R code to determine dissolved gas concentrations of CO2. Note, for other gases like methane or nitrous oxide the respective Henrys constants as well as molecular weight need to be changed accordingly.

```r
# ######################
# global parameters ####
# ######################
elevation       = 300           # in m.a.s.l.
K               = 0.035         # HENRY's law constant for CO2 in mol L-
1 atm-1

V.vial          = 0.012         # volume vial in L
V.aq            = 0.006         # volume of water in L
V.hs            = V.vial - V.aq  # volume gas in headspace in L

R               = 0.08206       # universal gas constant in L atm mol-1
K-1,
T               = 273.15 + 24   # laboratory temperature in K; ETHZ GC L
ab 24 degree targeted

P.lab           = 1                             # laboratory pressure
in atm
P.headspace     = P.lab * V.vial/(V.vial-V.aq)   # headspace pressure i
n atm

P.x             = 2000 / 10^6  * P.headspace    # 2000 is example CO2 co
ncentration in ppm (micromol/mol); P.x in atm mol mol-1

# ######################

C.h     = (P.x  * V.hs)/(R * T)           # moles CO2 in headspace

C.aq    =  P.x  * V.aq * K                # moles CO2 in solution

C.total = C.h + C.aq                      # total moles CO2 of sample


co2.aq.mol = C.total/V.aq                       # total moles of CO2 mol
es per unit water (unit water equals amount water injected to vial) # mole
s CO2 / L

co2.aq.mg  = C.total/V.aq * 44 * 1000            # convert moles CO2 / L
to mg CO2 / L using molecular weight of CO2 (44 g/mol)

co2.ppm    = 581.68 * co2.aq.mg - 5.2707; co2.ppm # FINAL dissolved CO2 co
ncentration in ppm.

## [1] 7776.334
```

#2. Deriving ppm (µatm) from mg CO_2 L^{-1}

Location specific conversion of dissolved mg CO_2 L^{-1} back to partial CO_2 pressure in water (pCO_{2w}) [µatm] requires information on local elevation to derive local pressure in atm via:

$$P_{local} = \frac{101325e^{-elevation/8434.7}}{101325}$$

with elevation in meter above sea level. 101325 is standard atmospheric pressure in Pa (1 atm). The final partial pressure of pCO_{2w} in ppm [µatm] dissolved in the sampled water body is calculated according to:

$$pCO_{2w} = \frac{C_{total}[mol/L]}{K_H} \cdot 10^6 \cdot P_{local}$$

#3. R example for conversion to ppm [or µatm]

```
P.local  = (101325 * exp(-elevation/8434.7))/101325  # in atm

pCO2w   = (co2.aq.mol/K) * 10^6 * P.local;pCO2w # in µatm

## [1] 8238.51
```

#4. Calculation of flux from water body to atmosphere

The flux from water to the atmosphere (F_{CO_2}, µmol m^{-2} s^{-1}) is calculated using a simple gas transfer model:

$$F_{CO_2} = k_x \cdot K_H \cdot (pCO_{2w} - pCO_{2a})$$

, where k_x is the temperature normalized freshwater gas transfer velocity [m s^{-1}], K_H is the Henry's constant for CO_2 [mol m^{-3} atm^{-1}], $pCO_{2w,a}$ the partial pressure of CO_2 in water and atmosphere, respectively [µatm]. For pCO_{2a} the tropospheric mean value of 2020 (400 µatm) was used. Since the magnitude of k_{600} is governed by numerous factors (wind speed, water current velocity, slope, etc.) changing microscale turbulence, published transfer velocities for the respective type of water body may be used.

```
# Simple gas transfer model

K     = 35 # solubility of CO2 in mol m-3 atm-1
k.x = 3.5 # gas transfer velocity in cm h-1 in freshwater (wetlands), calc
ulated from in situ measurements.
pCO2a = 400 # mean tropospheric CO2 concentration in µatm as of 2020

F.CO2 = (k.x/3600/100) * K  * 10^-6 * (pCO2w - pCO2a) * 1000000  # µmol m-
2 s-1
        # m s-1           # mol m-3 atm-1  # µatm  to atm          # mol
to µmol

paste(round(F.CO2,2),"µmol m-2 s-1")

## [1] "1.83 µmol m-2 s-1"
```
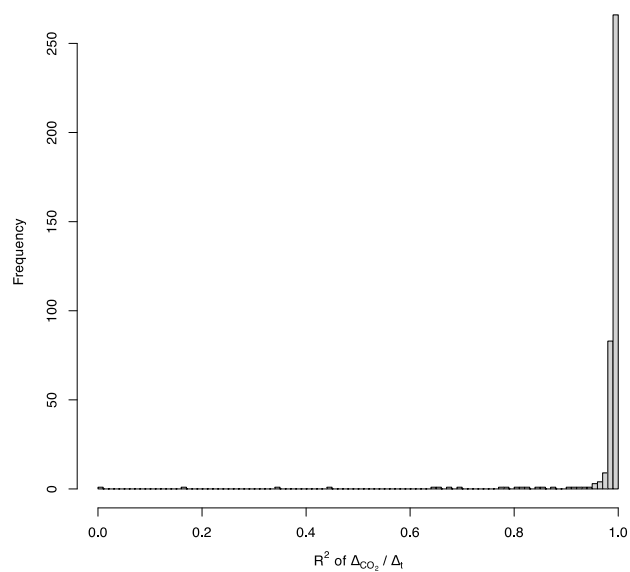
S2. Supplementary figures

Fig S 1. Histogram showing the frequency of the coefficient determination (r^2) for the linear regression of CO2 concentration increase over time.
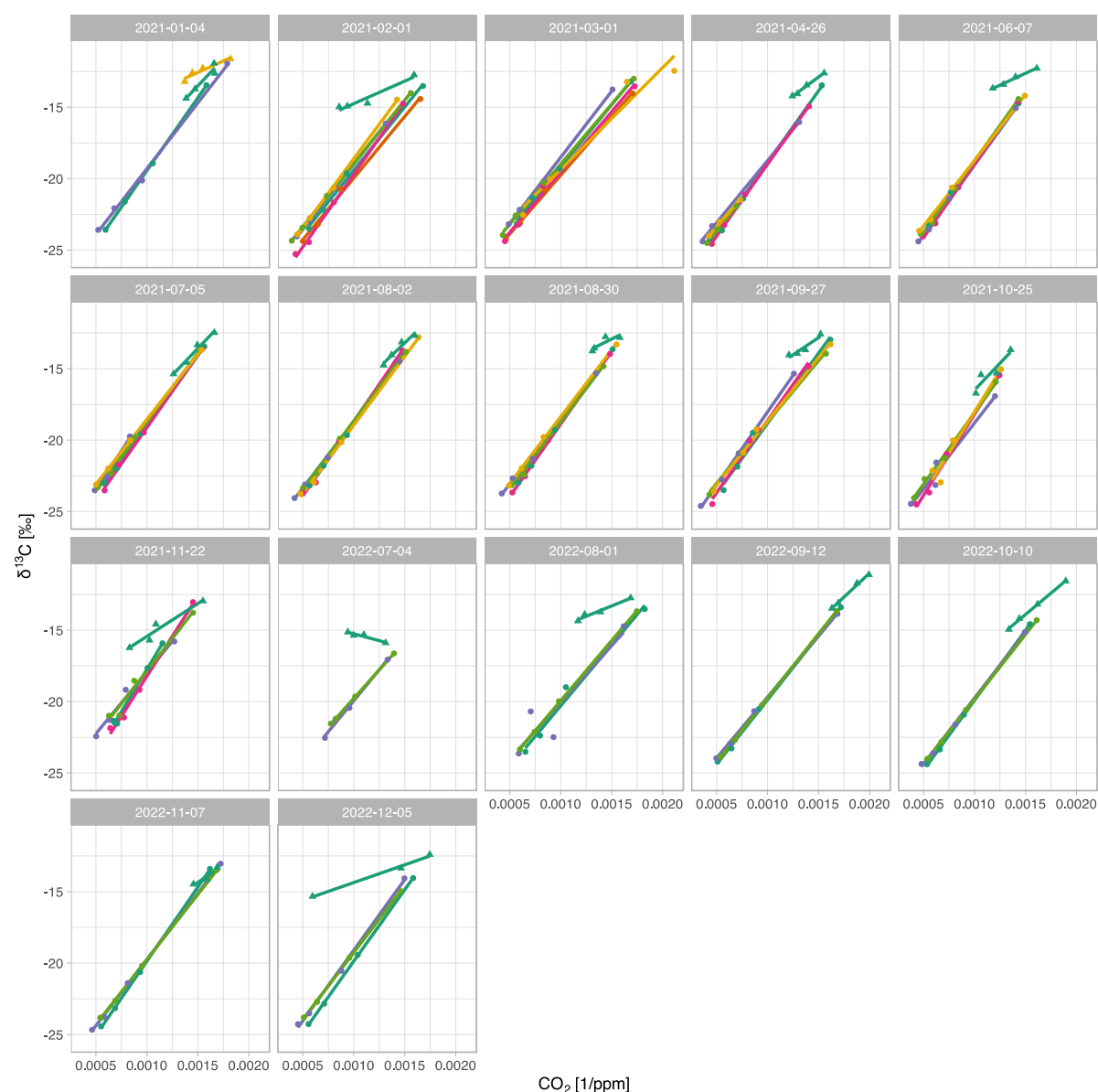
Fig S 2. Individual Keeling plots for each date separated by the 6 different chambers (colors) and inundation status (triangle = floating chambers; circle = soil chambers).
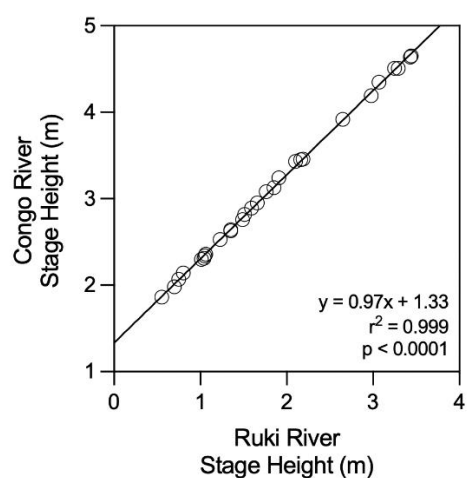

Fig S 3. Relationship between the Congo river stage height (m) and the Ruki river stage height (m). This relationship was calculated based on data collected fortnightly from 11/2019 to 11/2020.
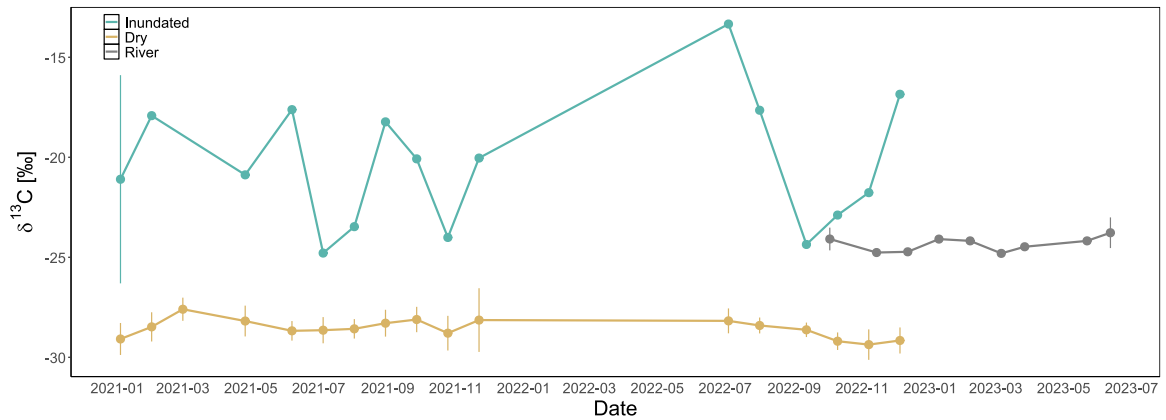
Fig S 4. Mean δ¹³C values of the soil CO₂ flux over the observation period separated into dry and inundated based on chamber type (floating chamber, soil chamber). Mean δ¹³C values of the riverine dissolved CO₂ (Ruki river) are displayed in grey. All values displayed with standard deviations.
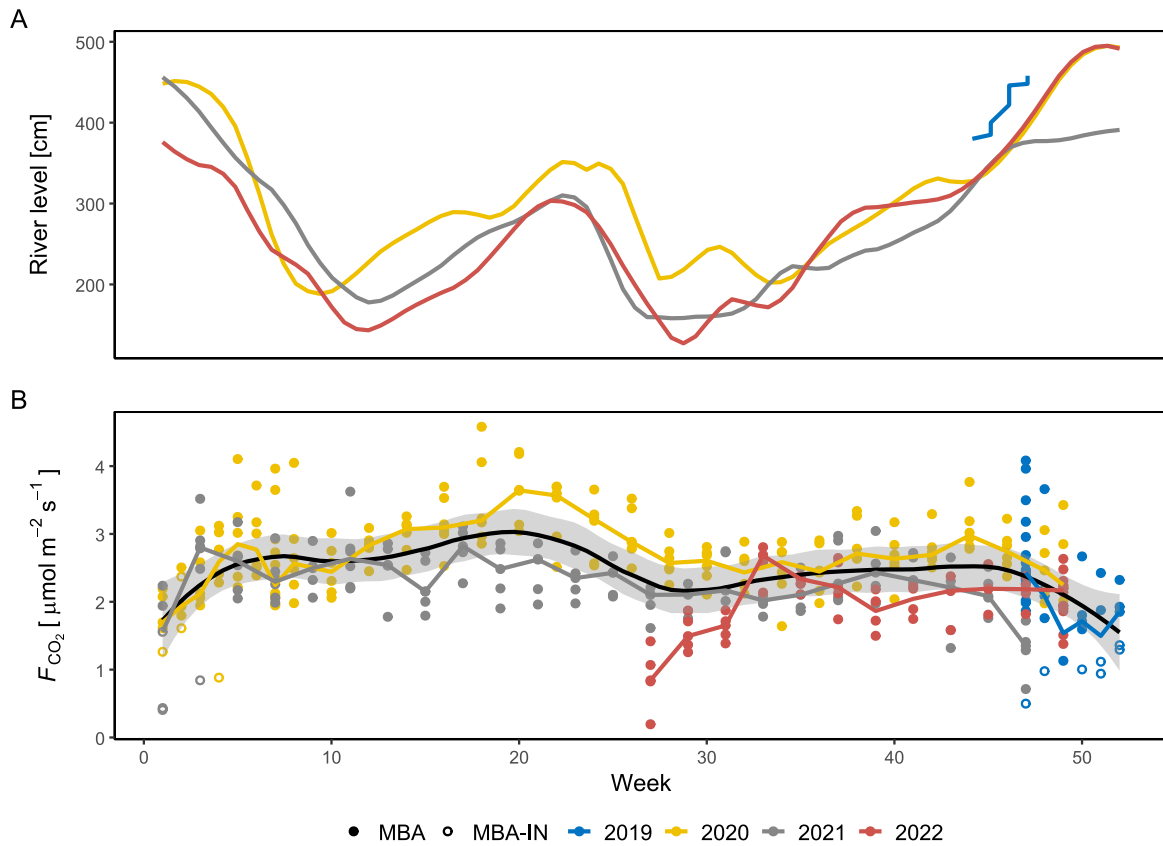

Fig S 5. Evolution of the level (cm) of the Congo River over the study period at the water gauge station in Mbandaka. (B) Soil CO₂ fluxes and respective median value line for available data of each year (2019, 2020, 2021 and 2022). The black line represents the global average. For visualization purposes, the line was smoothened with a k-nearest-neighbor regression (LOESS) method, shaded area is the confidence interval. Measures taken while the chamber was partially flooded are represented with open circles (MBA – IN).
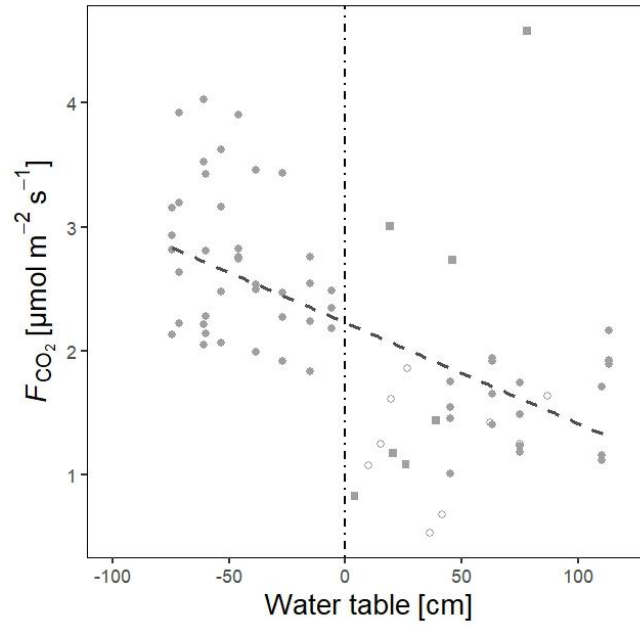
Fig S 6. Soil fluxes against the water table based on a separate field campaign from November 2023 to March 2024. Linear regression line is displayed (brown). Most measurements (n = 59) were made at the SFF site (●). However, additional measurements (n = 27) were made at two neighboring locations at lower elevation in the Jardin d'Eala: a perennially flooded location (■) and a location near to the river (○). Results of a linear mixed effect model (water table as fixed effect, chamber id as random effect; Fco2 ~ Water table + (1 | ch.ID)) explained 47.6/63.4% (R2adj, m / R2adj, c) of the variability with a significant negative effect of the water table (-0.53 with p-value < 0.001)
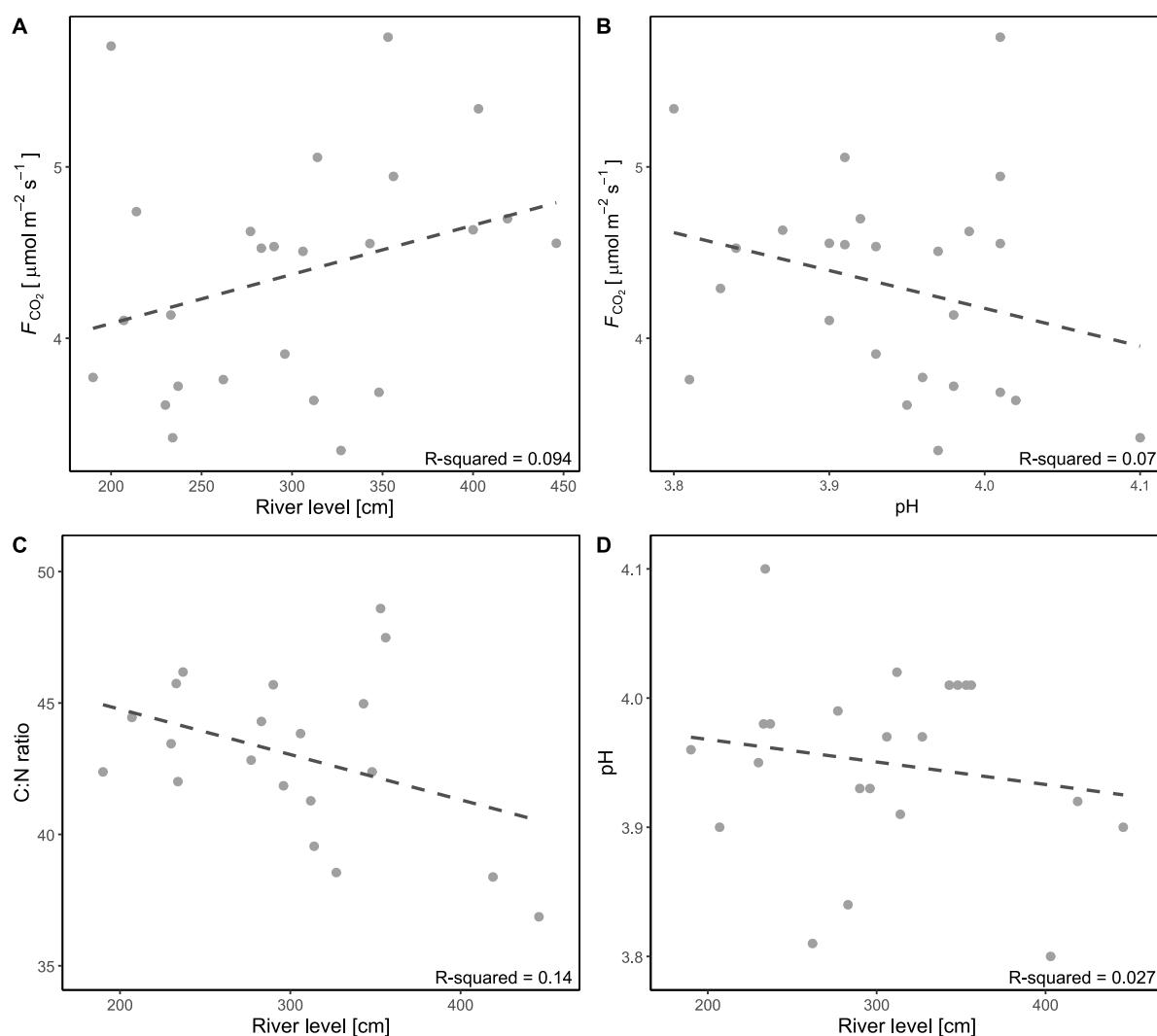
Fig S 7. Aquatic CO2 fluxes correlated with the river level at the gauging station (A), and pH (B); C:N ratio (C) and pH (D) correlated with the river level. Non significant linear regression lines are displayed as dashed black lines. R-squared values are displayed at the bottom of the respective graphs.

References

Bastviken, D., Sundgren, I., Natchimuthu, S., Reyier, H., and Gålfalk, M.: Technical Note: Cost-efficient approaches to measure carbon dioxide (CO2) fluxes and concentrations in terrestrial and aquatic environments using mini loggers, Biogeosciences, 12, 3849–3859, https://doi.org/10.5194/bg-12-3849-2015, 2015.

Dong, L. F., Nedwell, D. B., and Stott, A.: Sources of nitrogen used for denitrification and nitrous oxide formation in sediments of the hypernutrified Colne, the nutrified Humber, and the oligotrophic Conwy estuaries, United Kingdom, Limnol. Oceanogr., 51, 545–557, 2006.

Roper, J. D., Burton, D. L., Madani, A., and Stratton, G. W.: A simple method for quantifying dissolved nitrous oxide in tile drainage water, Can. J. Soil Sci., 93, 59–64, https://doi.org/10.4141/cjss2012-021, 2013.