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# Summer drought enhances diurnal amplitude of $CO_2$ in two German rivers of different size

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# ABSTRACT

Drought is becoming increasingly prevalent globally, stimulating research into its effects on river ecosystems. However, our understanding of how droughts affect riverine  $CO_2$  dynamics on a daily scale remains limited, particularly considering the likelihood of future drought occurrence. Here, we seize the opportunity to compare daily  $CO_2$  cycles between a non-drought summer and an unprecedented drought summer. We developed a new diel  $CO_2$  process model to examine how droughts affect diel change in riverine  $CO_2$ . Our findings reveal that summer drought amplifies diurnal  $CO_2$  fluctuations and the pattern holds true across rivers of varying sizes, with increases of 62% for the stream and 24% for the river during drought conditions. We demonstrate that, in comparison to higher radiation and temperature induced by droughts, diel amplitude is more sensitive to low water depths. A decrease in water depth by 43% and 44% corresponded to 13% and 25% less gas exchange in the studied stream and river, respectively, while decreasing ecosystem respiration by 26% and 57%. Our model effectively captures diel  $CO_2$  variations driven by drought considering river size, contributing valuable insights into aquatic ecosystem behavior and refining  $CO_2$  emission estimates. We emphasize the vulnerability of shallow rivers to drought, and carbon emissions from shallower waters should be explicitly assessed at sub-daily scales to improve the estimates of daily  $CO_2$  emissions.

#### 1. Introduction

Droughts, as one of the most dramatic consequences of ongoing climate change on the natural ecosystems, are becoming more intense worldwide (Treydte et al. 2023, Zhang et al. 2023a). Studies have consistently documented severe droughts and heatwaves in summer 2022 in Europe (Tripathy and Mishra 2023), the Yangtze River Basin (Ma et al. 2022), and North America (Zhang et al. 2023a). These events were marked by an unprecedented, exceptionally unusual spatial extent, duration, and intensity. Droughts would propagate through the water cycle with far-reaching effects on the structure and function of the rivers (Gómez-Gener et al. 2020). Intensifying heatwaves associated with droughts, causing a decrease in water levels and turbidity while increasing light availability and temperature, all of which have profound effects on biogeochemical processes and carbon cycles in river ecosystems (Gómez-Gener et al. 2015, Steward et al. 2012). Previous studies considered carbon cycling in transitional habitats, including dry

temporary streams (Bernal et al. 2022, Silverthorn et al. 2023) and exposed riverbeds (Koschorreck et al. 2024, Mallast et al. 2020, Marce et al. 2019), as well as the transitional processes, such as the effect of drying-rewetting on metabolic activity (Arce et al. 2021, Gallo et al. 2014). Yet little is known about how drought will influence river  $CO_2$  dynamics on shorter timescales.

Diurnal cycles in solar radiation impose a recognized periodicity on stream biogeochemical processes, resulting in diel patterns for dissolved  $CO_2$ . Several studies have reported diel fluctuations in  $CO_2$  in streams and rivers (Li et al. 2020, Rocher-Ros et al. 2020, van Bergen et al. 2019). Diel  $CO_2$  dynamics are acknowledged as a significant uncertainty source for  $CO_2$  flux estimation when using discrete measurements during the day (Gómez-Gener et al. 2021). A global estimate shows that nocturnal  $CO_2$  emissions are 27% greater than those estimated from daytime concentrations alone (Gómez-Gener et al. 2021). The constraints on light availability are the principal controls on diel  $CO_2$ variation (Bernal et al. 2022, Gómez-Gener et al. 2021, Reiman and Xu

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2019). The metabolic balance between photosynthesis and respiration is an important control of diel patterns (Demars et al. 2016, Gómez-Gener et al. 2021). Other processes, including interactions with the carbonate system, photochemical oxidation of organic matter, and diel changes in discharge and lateral CO2 input, can also vary at sub-daily scales. Rocher-Ros et al. (2020) observed that the diel CO<sub>2</sub> patterns in Arctic streams were primarily driven by in-stream metabolic processes, with the effect of photo-oxidation being overshadowed (Rocher-Ros et al. 2021, Rocher-Ros et al. 2020). Differences in CO<sub>2</sub> consumption/production rates and gas exchange velocity between day and night can further create day-night differences. The effect of carbonate buffering on CO2 dynamics becomes evident when an autotrophic system emits CO2 into the atmosphere (López Bellido et al. 2011, Marcé et al. 2015). Although this effect has been known for several decades, it has received far less attention in freshwater systems (Marcé et al. 2015, Stets et al. 2017). It partly uncouples diel dissolved inorganic carbon (DIC) dynamics from diel CO<sub>2</sub> (Butler 2019). CO<sub>2</sub> variation can be buffered by DIC pool - an effect highest in high-pH, high-alkalinity waters (Stets et al. 2017). Despite our awareness of the various processes that contribute to diel CO<sub>2</sub> patterns, there has been a lack of quantitative research into how these processes relate to diel changes in CO<sub>2</sub>. Considering the potential impact of drought on diel CO<sub>2</sub> patterns, we further prompt the question of how droughts can exert effects on diel CO<sub>2</sub> patterns and through what mechanisms.

We hypothesized that droughts could enhance diel CO<sub>2</sub> amplitudes,

thus increasing the uncertainty in estimating  $CO_2$  emissions. Droughtspecific parameters (e.g., water temperature, solar radiation, water depth) are expected to regulate the diel  $CO_2$  amplitude via C processing pathways (e.g., metabolic rates,  $CO_2$  evasion, carbonate buffering, Fig. 1a). The rationale is that droughts alter hydrological settings in rivers, leading to weakened gas exchange due to lower turbulence at low flow conditions. This also restricts exogenous respiration caused by limited transport of terrestrial  $CO_2$ . Droughts may enhance gross primary production (GPP) due to increased light availability. Moreover,  $CO_2$  can interact with the carbonate buffering system to structure  $CO_2$ dynamics and emissions (Leng and Koschorreck 2023, Stets et al. 2017), which can create a lag that allows for  $CO_2$  oversaturation in daily cycles.

To test the hypothesis, we compiled sensor-based high-frequency  $CO_2$  time series data in two German rivers during the summers of 2021 (considered a 'non-drought' summer) and 2022 (considered a 'drought' summer). In 2022 Germany suffered one of the four warmest summers, the sunniest, and the sixth driest since 1881 (DWD 2022). A persistent lack of precipitation, along with higher-than-average temperatures and sunshine, caused a widespread and prolonged drought, with the 2022 European drought being described as 'worst in 500 years' (Henley 2022). Summer 2021 was  $1.3^{\circ}$ C cooler, rainier (114% more rainfall), and less sunny (25% fewer sunlight hours) than summer 2022, and closer to the 30-year averages ( $0.3^{\circ}$ C warmer, 27% more rainfall, and 6% fewer sunlight hours than the averages of 1991-2020). We leveraged a process modeling approach to simulate the diel CO<sub>2</sub> cycles. The



**Fig. 1.** Schematic diagram of the diel  $CO_2$  process model. a. The environmental drivers and processes that influence diel  $CO_2$  dynamics in the river ecosystem. Ecosystem gross primary production (GPP) and ecosystem respiration (ER) meld air-water exchange with terrestrial subsidies of inorganic carbon through carbonate buffering to impose diel  $CO_2$  dynamics in rivers. Orange arrows indicate the potential pathways that environmental drivers affect  $CO_2$  processes. b. Structure of the model at hourly timesteps.

primary goal was to disentangle the effect of potential drought drivers on the daily amplitude of  $CO_2$  in rivers of various sizes and understand the pathways through which these effects manifest. The findings can help to better understand the interaction of carbon processes on diel  $CO_2$ behavior and predict the effects of environmental change on temporal C variations. The model can serve as an effective tool to evaluate the priority for the high-frequency  $CO_2$  measurements in streams and rivers to reduce uncertainty in  $CO_2$  emission estimates.

# 2. Materials and methods

# 2.1. Site description

We selected two monitoring stations located in two rivers within the Elbe Catchment of Central Germany (Fig. S1). One site in the smaller river (hereafter named "stream") is situated in Gross Germersleben (114.8 km long to the upstream), within the 6<sup>th</sup>-order reach of the lower Bode River. The Bode River flows into the Saale River and subsequently into the Elbe River. It has a higher level of channelization, primarily for agricultural purposes. The riverbed substrate consists of mostly sand and small gravel, with an average width, discharge, and slope of 20 m. 8.04  $m^3 s^{-1}$ , and 0.4 ‰, respectively. The relatively open canopy allows high irradiance at the river surface and development of benthic algae while phytoplankton blooms are restricted to short periods primarily in spring (Huang et al. 2022). Additionally, the interaction between the river and groundwater is limited due to very low groundwater recharge in the surrounding area (Zhang et al. 2023b, Zill et al. 2023). The other site in the larger river (hereafter named "river") is located in Magdeburg (322 km long from the border of Germany and the Czech Republic) within the 8<sup>th</sup>-order reach of the Elbe River, which is the second-largest river in Germany. The studied river reach is less channelized, characterized by a considerably expansive floodplain, with an average width, discharge, and slope of 110 m, 554 m<sup>3</sup> s<sup>-1</sup>, and 0.2 ‰, respectively. Primary production is dominated by phytoplankton (Kamjunke et al. 2023). The climate in the Elbe Catchment is characterized by wet winters with spring floods in March and April during snowmelt and dry summers and autumns with base flow.

# 2.2. High-frequency monitoring

Dissolved CO<sub>2</sub> was measured using membrane-covered optical CO<sub>2</sub> sensors (AMT-CO<sub>2</sub> sensor, AMT Analysenmesstechnik GmbH, Germany) every 15 min at both sites between June and September 2021 and 2022 (hereafter referred to as "summer" given that the majority of the study period is during summer). Dissolved CO<sub>2</sub> concentrations in µmol L<sup>-</sup> were calculated from the mole fraction CO<sub>2</sub> in ppm provided by the CO<sub>2</sub> sensor according to its temperature-specific solubility coefficients at the respective temperature (Boehrer et al. 2021). The sensors were calibrated in the laboratory before deployment. The performance of CO<sub>2</sub> sensors was evaluated with lab measurements of CO<sub>2</sub> concentration every two weeks (see Supplementary material Text S1). Simultaneously, other environmental parameters, including dissolved oxygen (O2), pH, water temperature, and electric conductivity (EC), were monitored at the same time interval (15-min) at both stations by multi-parameter sensors (YSI 610 sensor, Yellow Springs, US). The time from all sensors was converted to UTC time zone.

Regarding the meteorological data, we obtained hourly weather data at Magdeburg station from the Germany Weather Service (DWD), including air pressure, air temperature, precipitation, and solar radiation (J cm<sup>-2</sup>). PAR (µmol m<sup>-2</sup> s<sup>-1</sup>) was calculated from solar radiation using a conversion factor of 4.56 µmol J<sup>-1</sup>. Since both sites are close to each other (24.3 km) in the lowland region, they experience similar weather conditions. In comparison to the non-drought summer, average air temperature in the drought summer was 1.1 °C higher (19.5 and 20.6°C). While the precipitation in drought summer (183.12 mm) was just 41% of the one in the non-drought summer (443.68 mm). The elevation at Elbe and Bode sites is 45.2 and 74.6 m above sea level, respectively.

# 2.3. Hydrological data, gas exchange velocity, and CO<sub>2</sub> evasion

Both sites have nearby gauging stations where hydrologic data can be obtained from the hydrologic service of the Saxony-Anhalt water authority (https://gld.lhw-sachsen-anhalt.de/) and the Elbe Waterways and Shipping authority (WSA) (https://www.wsa-elbe.wsv.de/). Discharge was calculated from continuous water level and monthly cross-section profile velocity measurements conducted by LHW (Landesbetrieb für Hochwasserschutz und Wasserwirtschaft) and WSA (Wasserstrassen- und Schiffahrtsamt Elbe), and discharge measurements were cross-referenced to ensure the precision of hydrological data (Kamjunke et al. 2021). Discharge and water level were obtained at both sites continuously at 15 min intervals. Since there was no continuous flow velocity data available, we calculated it by dividing the discharge by the area of the water cross section at the corresponding water level. The R package 'sf' (Pebesma 2018) was used to generate the area of the cross section at each water level (see *Supplementary material* **Text S2**).

To derive a time series of normalized gas transfer velocity ( $k_{600}$ ), we correlated  $k_{600}$  acquired from floating chamber measurements with flow velocity. Specifically, we conducted field chamber measurements near both monitored stations in April 2022 (spring high flow) and July 2022 (summer baseflow), along the Bode River reach (8.4 km long) and Elbe River reach (16.5 km long) to capture different flow conditions. We followed the method proposed by Lorke et al. (2015). Briefly, we freely drifted downstream on a boat by deploying a rectangular chamber connecting with the FTIR analyzer (GASMET 4010, Finland) for CO<sub>2</sub> flux measurement. Simultaneously, headspace samples were taken for determining dissolved CO<sub>2</sub> concentration for each chamber measurement (Koschorreck et al. 2021). Water temperature and barometric pressure were continuously recorded for the purpose of headspace calculation.

The bivariate relationship between flow velocity and  $k_{600}$  (m d<sup>-1</sup>) was established in both rivers with  $k_{600} = 1.92 \times V^{1.26}$  at Elbe (R<sup>2</sup> = 0.38, p < 0.001, n = 28) and  $k_{600} = 4.51 \times V^{0.47}$  at Bode (R<sup>2</sup> = 0.23, p = 0.014, n = 32), where V is water velocity in m s<sup>-1</sup> (see *Supplementary material* **Text S2** for the comparison of k estimates using empirical equations). Water velocity for each chamber deployment was calculated by dividing the length of the reach by the reach travel time. The gas transfer velocity for CO<sub>2</sub> ( $k_{CO_2}$ ) was then calculated from  $k_{600}$  using a temperature-corrected Schmidt number for CO<sub>2</sub> and a scaling factor of 0.5 (Raymond et al. 2012):

$$k_{CO_2} = \left(\frac{Sc_{CO_2}}{600}\right)^{-1/2} \times k_{600} \tag{1}$$

where  $Sc_{CO_2}$  is the Schmidt number for CO<sub>2</sub> at the water temperature calculated following the coefficients summarized in Raymond et al. (2012). Then CO<sub>2</sub> evasion was calculated as:

$$F_{CO_2} = k_{CO_2} \times \left( \left\lfloor CO_{2,water} \right\rfloor - \left\lfloor CO_{2,air} \right\rfloor \right)$$
(2)

where  $[CO_{2,water}]$  is the measured CO<sub>2</sub> concentration in water (µmol L<sup>-1</sup>), and  $[Co_{2,air}]$  is the CO<sub>2</sub> concentration in equilibrium with the ambient air (µmol L<sup>-1</sup>).

#### 2.4. Data analysis and modeling

# 2.4.1. Diel CO<sub>2</sub> process model

To better understand the potential effects of droughts on riverine diel  $CO_2$ , we modeled diel  $CO_2$  dynamics at hourly timesteps to determine how processes that change DIC and/or total alkalinity affect river  $CO_2$ . A data-driven model was developed that calculates time series of  $CO_2$ , alkalinity, and DIC based on the interplay of  $CO_2$  exchange with the

atmosphere, metabolic consumption/production, and carbonate buffering.

The model uses hypothetical starting  $CO_2$  concentrations and model conditions to generate time series. We assume that the water column is well mixed in both rivers. DIC change over time can be calculated by accounting for  $CO_2$  change due to air-water exchanges and then reequilibrating the DIC pool due to river metabolism at each time step. Thus, the governing equation for DIC dynamics is.

$$[DIC]_{t} = [DIC]_{t-1} + (F_{CO_{2}} + GPP_{DIC,t-1} - ER_{DIC,t-1})/z$$
(3)

where *t* is time, [*DIC*] is the dissolved inorganic carbon concentration (µmol L<sup>-1</sup>), and  $F_{CO_2}$  is the atmospheric CO<sub>2</sub> exchange (mmol m<sup>-2</sup> h<sup>-1</sup>), which can be modeled by Eq. 2. *GPP*<sub>DIC</sub> is DIC consumption via gross primary production and  $ER_{DIC}$  is the DIC production via ecosystem respiration both in µmol L<sup>-1</sup> h<sup>-1</sup>, respectively. *z* is the water depth (m).

As we determine  $[CO_2]_t$  from  $[DIC]_t$  and  $[ALK]_t$  (alkalinity, in µmol L<sup>-1</sup>) using the function *carbb()* from the R package *seacarb* (Gattuso and Epitalon, 2021), alkalinity is estimated to be constant (addition or removal of CO<sub>2</sub> does not affect alkalinity) if the change in the DIC pool could be attributed to CO<sub>2</sub> evasion or metabolic consumption/production (Aho et al., 2021),

$$\begin{bmatrix} ALK \end{bmatrix}_{t} = \begin{bmatrix} ALK \end{bmatrix}_{t-1}$$
  
if  $[CO_2]_{t-1} > -(F_{CO_2} + GPP_{DIC,t-1} - ER_{DIC,t-1})/z$  (4)

However, at moderate to high levels of GPP, when  $[CO_2]_t$  is less than the sum of atmospheric exchange and consumption of metabolism, alkalinity (mainly in forms of HCO<sub>3</sub>) will also be taken up via GPP,

$$\begin{aligned} & [ALK]_t = [ALK]_{t-1} - (F_{CO_2} + GPP_{DIC,t-1} - ER_{DIC,t-1})/z \\ & \text{if } [CO_2]_{t-1} < -(F_{CO_2} + GPP_{DIC,t-1} - ER_{DIC,t-1})/z \end{aligned}$$
(5)

Initial DIC and alkalinity (calculated from starting CO<sub>2</sub> and pH, Table 1) are an input to the model and then updated at each time step by the processes listed in the above equations. We used biweekly monitoring calcium and alkalinity data from each site and derived a range of possible calcite saturation indices (SI) using PHREEQC. For samples with SI > 1, thermodynamics will favor calcite precipitation, with 1 mol each of CaCO<sub>3</sub> and CO<sub>2</sub> produced from 2 mol of HCO<sub>3</sub>. Given that all calculated SI were <1, we did not consider a reduction in the carbonate pool via calcite precipitation in the mass balance.

# 2.4.2. Model simulation

We ran the model using our observations and modeled output variables to derive the diel  $CO_2$  variations (Table 1 and Fig. 1b). The estimates of ecosystem metabolism were discussed in greater detail in *Supplementary material* **Text S3**. Modeled GPP and ER were obtained as areal rates (g  $O_2$  m<sup>-2</sup> d<sup>-1</sup>) and were converted to C assuming a mol-tomol stoichiometric relationship between  $O_2$  and DIC, where 1 mol of  $O_2$  respired produces 1 mol of DIC, and inversely, 1 mol of DIC is photosynthesized into 1 mol of  $O_2$  (Berggren et al. 2012, Stumm and Morgan 2012). Daily GPP values were partitioned into hourly rates according to hourly average PAR compared to total daily PAR for each hour of the day

(Fig. S2). Daily ER values were partitioned equally into hourly rates. Days with daily discharge variations higher than 10% were removed during metabolism modeling to avoid extreme flows resulting in unrealistic metabolic rates. As the diurnal change of groundwater input was highly limited in both rivers (Zhang et al. 2023b, Zill et al. 2023), we can reasonably assume that any changes in river inorganic carbon pool were caused by carbon processes within river water (Fig. 1a). We ran the model over two summers at both rivers, assessing its performance by comparing the predicted and observed diel amplitudes of CO<sub>2</sub> concentrations. Evaluation of the CO<sub>2</sub> process model is based on the correlation coefficient ( $\mathbb{R}^2$ ), root mean square error (RMSE), and percentage of bias (PBIAS).

### 2.4.3. Scenario analysis on diel CO<sub>2</sub>

To quantify the effect of droughts on diel  $CO_2$  variations, we configured the model to mimic drought and non-drought river settings for both rivers in summer, using mean hourly water temperature, water depth,  $k_{600}$ , GPP, and ER, as well as mean starting pH and  $CO_2$  concentrations as model input from 2021 and 2022 (Table 1, Fig. 1b). We further selected two specific days in each year for each river where alkalinity was measured and compared it to the modeled alkalinity to assess the model's ability to represent the DIC pool in river ecosystems.

# 2.4.4. Quantifying the effect of droughts on CO<sub>2</sub> processes

Summer droughts influence diel changes in CO<sub>2</sub> primarily by altering rates of gas exchange, ER, and GPP. Based on the records, the summer drought was characterized by elevated water temperature and light availability, as well as reduced flow conditions (Table 1). We quantified the effect of each drought indicator on gas exchange and metabolic rates by using empirical regression models. Gas transfer velocity (k) was mainly driven by hydrologic regimes. It can be theoretically modeled based on physical characteristics of a site that correlates with surface turbulence (Raymond et al. 2012). Streams with a higher roughness-to-water-depth ratio tend to exhibit greater turbulence (Hall and Ulseth 2020). Since water depth is closely related to discharge, we used water depth as a proxy to estimate the effect of hydrology on k(Fig. S3). The thermal and hydrological regimes can profoundly change the stream ecosystem metabolism (Segatto et al. 2021). The effect of each predictor (water temperature, daily PAR, and water depth) on the metabolic rates (GPP and ER) was identified using the avPlots() function in R package car (Fox and Weisberg 2019) in the multiple regression model while holding constant the value of other predictors.

# 2.4.5. Sensitivity of the effect of droughts on diel $CO_2$

We designed a sensitivity analysis on diel  $CO_2$  in relation to drought indicators using two levels of water temperature, water depth, and solar radiation, based on the average measurements from both summers at both locations (Table 1). By substituting one of those indicators sequentially, we independently calculated the corresponding alterations in gas exchange and metabolic rates by employing the empirical models, followed by running the diel  $CO_2$  process model. We determined the sensitivity of the diel  $CO_2$  amplitude to drought indicators by comparing

Table 1

River characteristics during both summers (non-drought summer in 2021 in black and drought summer in 2022 in red). The mean values and standard deviations (in brackets) of each variable were reported. The mean values are used as the model inputs in scenario analysis.

Variable	Time interval	Source	Stream		River	
			Non-drought	Drought	Non-drought	Drought
Temperature,°C	Hourly	Measured	17.7 (2.0)	18.8 (2.8)	20.7 (2.3)	21.8 (2.9)
Water depth, m	Hourly	Measured	0.53 (0.16)	0.30 (0.06)	1.6 (0.5)	0.9 (0.2)
Daily PAR, mol m <sup>-2</sup> d <sup>-1</sup>	Hourly	Measured	64 (30)	93 (29)	73 (30)	91 (30)
Starting $CO_2$ concentration, µmol L <sup>-1</sup>	1st hour in a day	Measured	55 (5.4)	52 (9.0)	28 (21)	27 (17)
Starting pH	1st hour in a day	Measured	7.9 (0.05)	7.8 (0.13)	8.3 (0.5)	8.2 (0.4)
Gas exchange velocity, $k_{600}$ , m d <sup>-1</sup>	Hourly	Modeled from chamber measurement	2.5 (0.13)	2.3 (0.06)	2.9 (0.4)	2.2 (0.3)
Gross primary production, mmol $O_2 m^{-2} d^{-1}$	Hourly	Modeled from streamMetabolizer	124 (54)	145 (63)	114 (109)	86 (117)
Ecosystem respiration, mmol $O_2 m^{-2} d^{-1}$	Hourly	Modeled from streamMetabolizer	-172 (46)	-128 (31)	-135 (94)	-42 (100)

the original diel amplitude in non-drought summer and the one with replaced model inputs.

# 3. Results

# 3.1. Environmental characteristics

During the drought summer, discharge in the stream and river was primarily at baseflow (2.46 and 227  $m^3 s^{-1}$  on average), in comparison to 4.03 and 447  $m^3 s^{-1}$  in the non-drought summer (Fig. 2). Gauged water levels declined by nearly half compared to the non-drought summer (Table 1) and were closely correlated with discharge (Stream:  $R^2 = 0.77, p < 0.001$ , River:  $R^2 = 0.99, p < 0.001$ ). Gas exchange velocity significantly separated the two rivers (two-sample t-test, p <0.001), with the river being more turbulent ranging from 1.7 to 4.3 m  $d^{-1}$ , average of 2.6 m  $d^{-1}$ , compared to the stream (ranging from 2.1 to  $3.0 \text{ m d}^{-1}$ , average of  $2.4 \text{ m d}^{-1}$ ) due to its gentle slope and channelization. Meanwhile,  $k_{600}$  exhibited a substantial decrease from nondrought to drought conditions in both stream and river, declining from 2.5 to 2.3 m d<sup>-1</sup> and from 2.9 to 2.2 m d<sup>-1</sup>, respectively. Given the strong relationship between hydrologic conditions and  $k_{600}$ ,  $k_{600}$  can be predicted by water depth, with  $R^2$  being 0.74 and 0.99, respectively (Fig. S3). Water temperature was sinusoidally distributed (Fig. S2). Diel variability of water temperature in the stream and river elevated 1.0 and 0.4 °C relative to the non-drought summer (difference between maximum and minimum within each day, mean values reported). Light availability (daily PAR) followed a bell-shaped diel pattern, increasing by an average of 22% in the drought summer compared to the nondrought one.

# 3.2. River ecosystem metabolism

Both metabolic rates (GPP and ER) were of the same order of magnitude at both locations, and ecosystem metabolism varied markedly across both summers (Fig. S4). GPP and ER differed between stream and river (paired *t* test, GPP p = 0.03; ER p < 0.001). Mean GPP values increased from 124 to 145 mmol  $O_2 m^{-2} d^{-1}$  in the stream and fell from 114 to 86 mmol  $O_2 \text{ m}^{-2} \text{ d}^{-1}$  in the river during the non-drought and drought summers. There was a decrease of mean ER from the nondrought summer to the drought one (from -172 to -128 mmol  $O_2 m^{-2}$  $d^{-1}$  in the stream and from -135 to -42 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in the river). During the non-drought summer, both rivers were primarily heterotrophic (GPP<|ER|), with windows of autotrophy in the river in June. During summer, GPP was highest in July in the stream and in June in the river, which coincided with autotrophic days. Moreover, the dry summer had more autotrophic days in both systems. Compared to the nondrought summer, GPP increased in the stream but decreased in the river in the drought one. The correlations between GPP and environmental predictors revealed that GPP increased with warming waterflow and light, yet we found no significant effect of water depth on GPP (Fig. S5). ER was nicely predicted by water temperature, water depth, and daily PAR with lower water depths and increased light availability resulting in less negative ER. Among these, the response of ER to water temperature behaved differently between both locations, with a negative correlation in the stream and a positive one in the river. In general, those environmental drivers during drought summer (high water temperature, increased light availability, and low flow) resulted in higher NEP (GPP+ER) and lower ER.



**Fig. 2.** Hourly values in the stream (Bode River, left panel) and the river (Elbe River, right panel) sites in non-drought (2021, blue line) and drought (2022, red line) summer. (**a**, **b**) Flow discharge (m<sup>3</sup> s<sup>-1</sup>, solid line) and water level (cm, dashed line). (**c**, **d**) Water temperature (°C). (**e**, **f**) CO<sub>2</sub> evasion in river water (µmol L<sup>-1</sup>).

# 3.3. Diel patterns of CO<sub>2</sub> concentrations and emissions

Both rivers were oversaturated with CO<sub>2</sub> and thus a source of atmospheric CO<sub>2</sub> in summer, except for June in the river, where it was a sink. Although the overall pattern of diel shift was consistent, the average amplitude of diel CO<sub>2</sub> changes was clearly greater during the drought summer (62% for stream and 24% for river, Fig. 3). The daily mean CO<sub>2</sub> concentrations in the stream were 23.3 µmol L<sup>-1</sup> higher compared to those in the river. The daily mean CO<sub>2</sub> concentrations were slightly lower in the drought summer than in the non-drought one (2.6 µmol L<sup>-1</sup> for stream and 1.8 µmol L<sup>-1</sup> for river). Under minor daily changes in discharge, the diurnal CO<sub>2</sub> amplitudes could reach up to 150% and 125% of the daily mean CO<sub>2</sub> in the stream and river, respectively; however, when the daily amplitude of discharge was above 2 and 40 m<sup>3</sup> s<sup>-1</sup>, diurnal CO<sub>2</sub> amplitudes were <30% of the daily mean CO<sub>2</sub> in both rivers.

With respect to CO<sub>2</sub> emissions, the diurnal amplitude was comparable to that of concentrations with 33% and 8% higher mean evasion at midnight than noon (**Fig. S6**). CO<sub>2</sub> evasion between both rivers became comparable due to stronger gas exchange in the river (higher  $k_{600}$ ). Since the hydrologic variation was restricted ( $k_{600}$  varied within a small range), variations in CO<sub>2</sub> evasion were mostly induced by CO<sub>2</sub> concentrations, particularly in the drought summer. Changes in CO<sub>2</sub> evasion therefore essentially followed the temporal variations in CO<sub>2</sub> concentrations.

# 3.4. Modeled diel CO<sub>2</sub> change

The model succeeded in capturing the diel  $CO_2$  amplitude in the stream and river, with  $R^2$  of 0.79 and 0.50 and PBIAS of below 3%, respectively. The larger diel  $CO_2$  amplitudes during the drought summer in both rivers were primarily caused by decreased lowest  $CO_2$  values, which were well captured by the simulations (Fig. 4 a and b). Regarding

the diel  $CO_2$  concentration pattern, the model performed well in capturing the overall  $CO_2$  and alkalinity pattern, with the model underestimating the highest  $CO_2$  concentrations in the stream (see *Merits and limitations* for further discussion and **Fig. S7** for additional comparisons of diel  $CO_2$  changes and alkalinity between observations and simulations).

The model provided evidence to elucidate the causes for the changes in diel CO<sub>2</sub> amplitude between both summers at both locations. Scenario analysis reveals that the mean diurnal CO2 amplitude for the stream and river during the non-drought summer were 23.7 and 11.5  $\mu mol~L^{-1},$ respectively. During drought summer, the diel amplitude increased to 45.3 (91% higher) for stream and 17.6  $\mu$ mol L<sup>-1</sup> (53% higher) for the river (Fig. 5). The diel amplitude clearly decreased with water depth (Fig. 4 c). When alkalinity was low, the diel  $CO_2$  amplitude varied widely and was favorably related to GPP rates; when alkalinity increased, however, the impact of GPP on diel amplitude and the variations of the amplitude were limited (Fig. 4 d). The scenario analysis assessed the effects of drought in such realistic conditions, considering all processes at once; however, there is limited evidence on the pathways by which drought affected diel CO<sub>2</sub> changes. We further explored hypothetically to what extent each environmental driver induced changes in diel CO<sub>2</sub> changes in both rivers.

The sensitivity analysis revealed that warming had a modest effect on diel CO<sub>2</sub> amplitude, driving ecosystem metabolisms primarily through increased GPP (increased by 15% and 13% in the stream and river, respectively, Fig. 5). Shallower water depth significantly influenced diurnal amplitude due to decreased gas exchange ( $k_{600}$ ) and lower ER. Specifically, diel amplitude increased by 99% and 52%, attributed to an 13% and 25% reduction in  $k_{600}$  from low flow conditions in the stream and river, respectively. Diel amplitude in the stream and river rose by 99% and 48% due to weakened respiration rates, which were 26% and 57% lower, respectively. High light input led to a 44% and 26% increase in diel CO<sub>2</sub> amplitude, primarily driven by elevated GPP (18%



Fig. 3. Diel variations in  $CO_2$  concentrations (panels **a**, **c**) and the averaged amplitude of the diurnal variations in  $CO_2$  for both locations (panels **b**, **d**). The bolder lines in panel **a** and **c** represent the average for non-drought and drought summer. The error bars in panel **b** and **d** are the standard deviation of the amplitude of diurnal  $CO_2$  change.



**Fig. 4.** Performance of the diel  $CO_2$  process modeling during both summers for both rivers. **a**. Time series of diel  $CO_2$  amplitudes from observations (dots) and simulated results (lines) from our model during the two summers. Four panels below compare the diel  $CO_2$  variations between observations (solid lines) and model outputs (dashed lines) on specific days where we measured alkalinity in the lab, as indicated by red dots in the time series plot. The green dots represent measured alkalinity. **b**. Comparison of the diel  $CO_2$  amplitude between field observations and simulated results with the linear regressions for both rivers, represented by different colors. The solid black line denotes a 1:1 line. **c**. The diel  $CO_2$  amplitude plotted against water depth for the two rivers. **d**. Diel  $CO_2$  amplitude and alkalinity values simulated by the model for each day for both rivers (indicated by point shapes; circle for the stream and triangle for the river). The different hues represent the rates of GPP.

and 22% higher).

#### 4. Discussion

Our process-based CO<sub>2</sub> model approach uncovers how droughts affect diel CO<sub>2</sub> patterns in two different-sized rivers. Summer droughts exacerbate diurnal CO<sub>2</sub> fluctuations in rivers, which are primarily caused by low water levels. This pattern is consistent for rivers of different sizes, but for different reasons. The findings highlight that future summer droughts, which are expected to occur more frequently around the world (Treydte et al. 2023), may induce higher levels of inaccuracy by discrete measurements of dissolved CO<sub>2</sub> during the day. Our model provides quantitative insight into how diel CO<sub>2</sub> patterns respond to a set of drought indicators, as well as how to estimate diurnal amplitudes in CO<sub>2</sub> utilizing hydrological and metabolic information. This helps us in identifying hotspots and moments of diurnal CO<sub>2</sub> variations, improving our estimates of temporal CO<sub>2</sub> patterns.

# 4.1. Impact of droughts on diel CO<sub>2</sub> changes

It is widely acknowledged that light availability is the principal control of diel  $CO_2$  variation by controlling rates of photosynthesis (Beaulieu et al. 2013, Segatto et al. 2021, Ulseth et al. 2018). Our findings align with this established understanding (Fig. S5). However, we emphasize that, rather than increased light availability and warming, a decrease in water depth induced by drought has an overweighting impact on the diel  $CO_2$  amplitude. This is due to its role in determining the water volume available for carbon processing and indicating the hydrologic condition for gas exchange (Fig. 5). Hydrological drought prolongs water residence time and decreases gas exchange



**Fig. 5.** Sensitivity of the effect of the environmental drivers characterizing summer drought on the diel  $CO_2$  amplitude in the stream and river. The panels summarize indirect effects of environmental drivers (higher water temperature, lower water depth, and higher solar radiation derived from daily PAR) on the diurnal  $CO_2$  amplitude as a result of direct effects on the gas exchange velocity (k) and metabolic rates (-ER and GPP, Fig S3). Arrows and the question mark symbolize the increasing, decreasing, and increase and/or decrease (unclear) effects. The light color of the bars is for the stream site and dark color for the river site. Values to the right of the bars demonstrate a percentage increase in diel  $CO_2$  amplitude compared to the non-drought summer. For instance, a decrease in gas exchange velocity due to reduced water depth increases the amplitude of diurnal  $CO_2$  change for the stream and river sites by 99% and 52%, respectively.

(Gómez-Gener et al. 2020), implying in-stream metabolism dominating diel  $CO_2$  dynamics, leading to a strong coupling between NEP and diel  $CO_2$  pattern. Lower hydrological disturbance impedes oxygen resupply from atmospheric exchange, further hindering aerobic respiration (Battin et al. 2023). GPP variations independent of water depth in our study corroborates with earlier findings (Segatto et al. 2021, UEH-LINGER 2006). Specifically, during low flow, low water depth enhances light availability for benthic primary producers and decrease water column mixing for phytoplankton (Hosen et al. 2019), both of which increase the capacity of autotrophs to utilize available light (Beaulieu et al. 2013). During high flow, light penetration depth may remain relatively constant due to increased turbidity, resulting in an insignificant correlation (Battin et al. 2023).

The temperature dependency of ER and GPP remains equivocal across different studies. Our study observed a positive thermal dependency of GPP for both rivers, which is in line with a number of studies (Demars et al. 2011, Song et al. 2018). However, in the partial regression plot (Fig. S5) we observe the temperature drives ER in opposing directions across the two systems. The temperature dependence of ER and GPP can vary considerably from one stream to another. due to the nonlinear nature of temperature dependence and substantial variability in the activation energies of GPP and ER within and across biomes (Beaulieu et al. 2013, Segatto et al. 2021, Song et al. 2018, Ulseth et al. 2018). Moreover, a complex interplay between temperature and other environmental variables that may covary might suppress or enhance the temperature sensitivity at the ecosystem level (Hosen et al. 2019). Nevertheless, using the temperature dependency of GPP and ER for individual streams, rather than applying the same relationship across all streams, is more reasonable in weighing the importance of the thermal response of stream metabolism.

We acknowledge that all environmental drivers and processes interact in complex ways, making it challenging to isolate one effect on diel CO<sub>2</sub> amplitude from the others (Fig. 1). For example, photosynthesis can be enhanced by warmer temperature and greater light incidence simultaneously (**Fig. S5**); the physical exchange rate is regulated by diel changes in water temperature (Demars and Manson 2013) and by hydrological regimes (Raymond et al. 2012). We address the issue by focusing on a single driver while controlling for the effects of others in the sensitivity analysis. These findings add to further evidence that droughts stimulate diel CO<sub>2</sub> amplitudes primarily through low gas exchange and high NEP (towards autotrophy) for both rivers. Furthermore, environmental drivers can be responsible for the difference in diel amplitudes between the two rivers.

# 4.2. Effect of river size on diel $CO_2$ patterns

Temporal patterns in river CO<sub>2</sub> differed not only between nondrought and drought summers, but also spatially by river size. The river experienced significant across-day variations, which can be attributed to its high hydrologic variability. In contrast, the stream primarily displayed diel variations. The stream was extensively managed by the drinking water reservoir upstream and for agricultural purposes, leading to limited hydrologic change. Furthermore, streams typically receive a higher percentage of terrestrially derived carbon than rivers, which can explain the lower DIC concentrations in the stream during drought summer (mean DIC of 2921 and 2031  $\mu$ mol L<sup>-1</sup> in nondrought and drought summers, respectively, as estimated by the model). The contribution of stream heterotrophs can be constrained due to hydrological disconnection between the stream channel and riparian zone (Bernal et al. 2022, Rocher-Ros et al. 2020), resulting in low ER. It is well established that smaller rivers receive a greater proportion of external DIC input and have a more negative NEP (Hotchkiss et al. 2015, Stets et al. 2017), which is also observed in our systems.

Despite the fact that hydrologic connectivety plays a more important role in CO<sub>2</sub> variations in the stream, water depth differentially affects the metabolisms that process C in both rivers. Theoretically, in the benthic primary producer dominated stream, GPP increases at low water depth due to better light penetration through the water column. In the pelagic primary producer dominated river, GPP decreases at low water depth if the entire water column is euphotic (the upper layer of water allowing phytoplankton to perform photosynthesis) (Rocher-Ros et al. 2020). If the river has a non-photic zone, GPP will remain constant as the water depth decreases until the entire water column becomes euphotic (Julian et al. 2008, Martin et al. 2017). Furthermore, given lower turbidity during drought, GPP could be even higher. Our findings that GPP remains similar in the stream but decreases substantially in the river confirm the pattern (Fig. S5). With respect to the effect on ER, low water depth first reduces allochthonous OC respiration (Gómez-Gener al. 2020). OC respiration remains constant in the et periphyton-dominated river since it occurs at the river bottom, but decreases in the phytoplankton-dominated river due to a smaller water column (Martin et al. 2017). Our model does not distinguish between autochthonous and allochthonous sources or between autotrophic and heterotrophic respirations; instead, it utilizes ecosystem respiration, which integrates both types. While ecosystem respiration rates are sufficient for our study, disentangling the various respiratory processes requires a more complex model that considers different depth layers and the vertical distribution of pelagic and benthic primary producers across the water column. Our observations demonstrate that ER decreases largely with decreasing depth, especially in the river. Thus, low flow and high light availability are critical for altering the balance between GPP and ER, driving NEP positive during drought. The knowledge that shallow streams have higher CO2 concentrations and larger diel amplitudes underscores the need to focus research on shallow waters since they are more vulnerable to droughts.

The carbonate buffering system influences the effect of GPP on the diel CO<sub>2</sub> amplitude. Despite the principal control of GPP over diel CO<sub>2</sub> change, an increase in alkalinity results in a narrower range of diel CO2 amplitude (Fig. 4 d). In higher alkalinity waters, atmospheric equilibration occurs more slowly since CO2 removed through evasion is replaced by CO<sub>2</sub> from the pool of HCO<sub>3</sub> present in the water column (Stets et al. 2017). Meanwhile, photosynthetic  $HCO_3^-$  uptake can also support GPP, imparting additional controls on CO<sub>2</sub> dynamics, but this only becomes important when CO<sub>2</sub> is depleted (Aho et al. 2021). Furthermore, low alkalinity consistently correlates with high GPP (Fig. S8), indicating that limited external input leads to a tight coupling of CO<sub>2</sub> with productivity. Compared to the stream, the river typically has alkalinity levels below 1000 µmol L<sup>-1</sup>, implying a more conservative external contribution to diel CO2 dynamics. This suggests that as alkalinity increases, GPP may be constrained, leading to a more stable diel amplitude (Fig. S8). This highlights the influence of the buffering system in smaller rivers with higher percentages of external input.

#### 4.3. Merits and limitations

We rely on a CO<sub>2</sub> process model for post-hoc analysis to estimate how riverine CO<sub>2</sub> evolved within a day and to distinguish between drought and non-drought effects in diel CO<sub>2</sub> changes in rivers. The field observations validate the credibility of our simulation, suggesting that the model effectively captured the discrepancy in diel CO<sub>2</sub> amplitude induced by drought and different river sizes. It also implies that our model considers all relevant parameters. Consequently, as a data-driven model, the model approach demonstrates its potential to generate and investigate mechanism-based hypotheses regarding the future behaviour of aquatic ecosystems, which is impractical by experimental approaches. The model can estimate diurnal CO<sub>2</sub> amplitude in the absence of high frequency  $CO_2$  monitoring. It demonstrates that it is applicable to rivers dominated by periphyton and phytoplankton, where the underlying mechanism may differ in how metabolic rates can be impacted by light attenuation with changing water depth.

The model has some limitations with respect to its general applicability. First, our model encompasses both observation and process errors, as well as uncertainty resulting from the assumptions, potentially leading to slight divergence of our simulations from observations. GPP and ER in our model are simulated with both observation and process errors (Supplementary material Text S3) (Appling et al. 2018). The inclusion of both error types is further passed to diel CO2 process modeling. All simulations include noise in high frequency measurements of pH, O<sub>2</sub>, and CO<sub>2</sub>, which capture noisy random signals and create errors when calculating carbon process rates. Among these, pH is probably the most sensitive measurement, with the potential to introduce significant errors (Fig. S9). Moreover, the links between metabolism and environmental factors are site-specific. It relies on the understanding of ecosystem metabolism in the studied system. Therefore, it is understandable that simulations cannot completely reflect the dynamics of real data (Fig. S7). In addition, our study focuses on low flow periods and is only able to demonstrate that low flow coincides with large changes in light and temperature. Future work with varying climatic and catchment settings can be used to identify whether our findings can be generalized.

Second, the uncertainty from the chosen quotient to convert the unit of metabolic rates from mmol  $O_2 m^{-2} d^{-1}$  to mmol  $CO_2 m^{-2} d^{-1}$  could be critical in evaluating diel  $CO_2$  amplitude (Berggren et al. 2012, Trentman et al. 2023). In our case, increasing  $CO_2$ :  $O_2$  from 1 to 1.2 causes diel  $CO_2$  amplitudes to increase by 21-40% in the river. The respiration quotient depends on the organic substrate in question, the degree of its oxidation, and the metabolic pathway used (Honkanen et al. 2021). The photosynthesis quotient may also vary if the assimilation of nutrients (especially nitrate) is considered in the stoichiometric photosynthetic reaction (Stumm and Morgan 2012). The  $CO_2$ :  $O_2$  quotient that we used is based on the relationship between DIC and  $O_2$  from field observations, which probably diminishes the possible uncertainty.

Third, caution is needed with respect to the sensitivity of the model results to pH values in the model input. pH measurement is well-known for inducing error when attempting to determine the carbonate system (Koschorreck et al. 2021). When the pH value increases from 7.5 to 8.5 in both rivers, the diel  $CO_2$  amplitude decreases by 101% and 155% in the stream and river, respectively (**Fig. S9**). This reflects the importance of proper pH measurement for the model, as well as how the carbonate system would interact with metabolism, resulting in varying diel  $CO_2$  amplitude.

Fourth, flow conditions ( $k_{600}$ ) and metabolic rates are covaried in reality. Our sensitivity analysis can only capture the effect of a single pathway on diel CO<sub>2</sub> variation. However, the reality of the drought summer demonstrates the cumulative effects of all drought drivers. Our model is biased toward low and steady flow conditions. Variations in flow discharge caused by rainfall or evaporation will only affect water gain or loss from the system, not the carbon mass balance in our model. However, groundwater input can be more complex because groundwater can introduce abundant CO<sub>2</sub> into river water (Duvert et al. 2018). Further detailed investigation into hydrologic fluctuations is needed before applying our model to groundwater affected systems.

#### 4.4. Implications for assessing river CO<sub>2</sub>

Droughts duration and intensity are projected to increase in Europe and globally (Tripathy and Mishra 2023). Our findings indicate that such droughts amplify diel  $CO_2$  variations, potentially increasing uncertainty in riverine  $CO_2$  emission quantification in the future. During drought conditions, a bias derived from discrete samplings is expected to worsen, with evidence that diurnal amplitudes reach up to 150% of daily averages in our study. Our findings uncover important consequences for global estimates of CO<sub>2</sub> dynamics in fluvial systems. Despite ongoing uncertainties in predicting global carbon emissions from these systems (Gómez-Gener et al. 2021), our work shows that the modeling approach can be employed to constrain this uncertainty even in the absence of high frequency monitored CO<sub>2</sub> data. We found that moderate alkalinity systems with warmer temperatures, increased light incidence, and low flow conditions have larger diel CO<sub>2</sub> amplitudes. We imply that, of all of these environmental changes, diel CO<sub>2</sub> variations are most sensitive to water depth changes, with shallow streams contributing more to the uncertaintv in CO<sub>2</sub> estimation. Consequently, prioritizing high-frequency CO2 monitoring in open-canopy low-order streams during low-flow summers is essential, along with focusing on sampling in shallow areas to further reduce uncertainty in riverine CO<sub>2</sub> estimates.

# 5. Conclusions

- Our results imply that drought, which is coupled with increased light availability and low flow, can elevate diel CO<sub>2</sub> amplitudes in rivers, primarily driven by a decrease in water depth. Therefore, we speculate discrete measurement during daytime may have induced larger underestimation of CO<sub>2</sub> concentrations and emissions in drying rivers.
- Our model simulation confers to current opinions that the diel CO<sub>2</sub> pattern is predominantly influenced by GPP. Drought amplifies the diel CO<sub>2</sub> amplitude primarily through decreased respiration and weaker gas exchange due to low flow. In addition, lower carbonate buffering capacity further strengthens the diel amplitude.
- Our study offers a tool that is capable of refining the estimates of the CO<sub>2</sub> emission magnitude on the temporal scale. It connects the diel CO<sub>2</sub> patterns with abiotic environmental components in aquatic ecosystems.
- Undoubtedly, more high-frequency monitoring will significantly reduce uncertainty in riverine CO<sub>2</sub> emission estimates and will enhance our understanding on the response of CO<sub>2</sub> emissions from streams to global change.

# Appendix A. Supplementary material

The *supplementary material* is available online. Text (Text S1-S3) and figures (Figure S1-S7) are included in the *Supplementary material*. Text S1-S3 provides methods for data quality control, river profile area computation, and metabolic rate estimation. Figure S1-S9 shows the map of the study sites, the times series and diel patterns of various observations and metabolic rates, the correlations between different variables, and the process-based model results.

# CRediT authorship contribution statement

**Peifang Leng:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis. **Michael Rode:** Writing – review & editing, Project administration. **Matthias Koschorreck:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.122870.

#### Data availability

Datasets for this research can be found online at https://doi.org/10.6084/m9.figshare.25918825">

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