Quantification of carbopeaking and CO2 fluxes in a regulated Alpine river

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Abstract

Carbon dioxide (CO2) fluxes in regulated Alpine rivers are driven by multiple biogeochemical and anthropogenic processes, acting on different spatiotemporal scales. We quantified the relative importance of these drivers and their effects on the dynamics of CO2 concentration and atmospheric exchange fluxes in a representative Alpine river segment regulated by a cascading hydropower system with diversion, which includes two residual flow reaches and a reach subject to hydropeaking. We combined instantaneous and time-resolved water chemistry and hydraulic measurements at different times of the year identifying the main CO2 pathways through a one-dimensional transport-reaction model. The spatiotemporal distribution and drivers of CO2 fluxes depended on hydropower operations. Along the residual flow reaches, CO2 fluxes were directly affected by the upstream dams only in the first 2 km downstream of each dam, where the supply of supersaturated water from the reservoirs was predominant. Downstream of the hydropower diversion outlets, the magnitude and dynamics of CO2 fluxes were dominated by systematic sub-daily peaks in CO2 transport and evasion fluxes (‘carbopeaking’) driven by hydropoeaking. The additional input of CO2 released locally into the river at the hydropower diversion outlet during hydropeaking matched the amount of CO2 transported, metabolised, and exchanged with the atmosphere along the whole upstream reach. Hydropower operational patterns and regulation approaches in Alpine rivers significantly affect CO2 fluxes and their response to biogeochemical drivers across different temporal scales. This work contributes to understanding and quantifying these processes to clarify the role of natural and anthropogenic drivers in global carbon cycling.
Quantification of carbopeaking and CO$_2$ fluxes in a regulated Alpine river

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Key Points:

• Flow regulation in an Alpine river affects the spatiotemporal variability and drivers of CO$_2$ fluxes.
• Diel metabolism and carbonate dissolution sustained by lateral inflows dominate CO$_2$ dynamics in the residual flow reaches.
• Intense and localised peaks in CO$_2$ concentration and evasion rate are observed downstream of the hydropower outlets during hydropoeaking.

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Abstract

Carbon dioxide (CO\(_2\)) fluxes in regulated Alpine rivers are driven by multiple biogeochemical and anthropogenic processes, acting on different spatiotemporal scales. We quantified the relative importance of these drivers and their effects on the dynamics of CO\(_2\) concentration and atmospheric exchange fluxes in a representative Alpine river segment regulated by a cascading hydropower system with diversion, which includes two residual flow reaches and a reach subject to hydropeaking. We combined instantaneous and time-resolved water chemistry and hydraulic measurements at different times of the year identifying the main CO\(_2\) pathways through a one-dimensional transport-reaction model. The spatiotemporal distribution and drivers of CO\(_2\) fluxes depended on hydropower operations. Along the residual flow reaches, CO\(_2\) fluxes were directly affected by the upstream dams only in the first ~2 km downstream of each dam, where the supply of supersaturated water from the reservoirs was predominant. Downstream of the hydropower diversion outlets, the magnitude and dynamics of CO\(_2\) fluxes were dominated by systematic sub-daily peaks in CO\(_2\) transport and evasion fluxes ('carbopeaking') driven by hydropeaking. The additional input of CO\(_2\) released locally into the river at the hydropower diversion outlet during hydropeaking matched the amount of CO\(_2\) transported, metabolised, and exchanged with the atmosphere along the whole upstream reach. Hydropower operational patterns and regulation approaches in Alpine rivers significantly affect CO\(_2\) fluxes and their response to biogeochemical drivers across different temporal scales. This work contributes to understanding and quantifying these processes to clarify the role of natural and anthropogenic drivers in global carbon cycling.

Plain Language Summary

Rivers are crucial for the transport, processing and exchange of carbon and CO\(_2\) between land, atmosphere, and oceans. CO\(_2\) fluxes in rivers are influenced by biological, chemical, and hydraulic processes, which can be altered by the presence of hydropower dams. We studied these effects by measuring and modelling CO\(_2\) fluxes along an Alpine river over multiple days and across a year to account for the variability of processes in time and in space. In the river segment beneath the dams, where the flow is always kept low and constant, hydropower affected CO\(_2\) fluxes only for the first 2 km. Downstream of the power plant outlets, where the flow rate varies according to energy demand, CO\(_2\) concentration and emissions were much higher during the peaks in flow rate because of the release of water with high CO\(_2\) concentration from inside the reservoir. The CO\(_2\) released locally during these peaks equaled the amount processed and exchanged instantaneously by the whole part of the river where the flow was low and constant. Our findings highlight the need to consider CO\(_2\) variations in space and time for accurate quantification and understanding of the impact of human activity on CO\(_2\) processes in rivers.

1 Introduction

Rivers and streams play a fundamental role in the transport, processing, and exchange of organic and inorganic carbon along the river continuum (Battin et al., 2023). Unravelling and quantifying the processes that govern carbon fluxes along river networks is of paramount importance to understand and predict the response of the carbon cycle to global change. However, the drivers and dynamics of these fluxes are still largely unknown due to lack of data and inconsistent quantification approaches (Dean & Battin, 2024). Mountain rivers and streams, for instance, contribute disproportionately to global riverine greenhouse gas (GHG) emissions despite their relatively small surface area (Horgby, Segatto, et al., 2019). These rivers are characterised by high stream slopes, high turbulence intensities, and extensive occurrence of surface breaking and aeration. Overall, these factors yield higher gas transfer velocities and atmospheric exchange fluxes (Ulseth et al., 2019; Rocher-Ros et al., 2019), which are sustained by lateral inputs of organic...
and inorganic carbon and by the metabolic activity within the stream and across the watershed (Peter et al., 2014; Hotchkiss et al., 2015; Ulseth et al., 2018). The complex interplay between biogeochemical and geomorphological drivers induces a strong spatiotemporal variability of carbon and GHG fluxes across multiple scales, ranging from sub-diel (e.g., related to the ecosystem metabolism - Gomez-Gener et al. (2021)) and mesoscales (such as landscape-controlled hotspots - Rocher-Ros et al. (2019); Duvert et al. (2018)) to seasonal and full catchment-scales variations (e.g., related to hydrological connectivity - Peter et al. (2014); Duvert et al. (2018); Horgby, Boix Canadell, et al. (2019) - and/or metabolic regimes: Schelker et al. (2016); Bernhardt et al. (2018)). Such scale heterogeneity poses important challenges for the quantification of these fluxes (Ciais et al., 2014; Harmon, 2020).

In addition to the previously-mentioned ‘natural’ drivers, the widespread regulation of rivers for hydropower energy production exerts additional controls on carbon and GHG fluxes (Silverthorn et al., 2023). The relatively long residence time in reservoirs supports strong metabolic activity which can promote large GHG concentrations depending on nutrients and oxygen availability (Hertwich, 2013; Maavara et al., 2020). As a result, increased dissolved GHG (e.g., CO$_2$, CH$_4$, and N$_2$O) concentrations and evasion fluxes are often observed in the rivers downstream of hydropower reservoirs (Galy-Lacaux et al., 1997; Guérin et al., 2006; Kemenes et al., 2016; Soued & Prairie, 2020; Shi et al., 2023).

The fate of these additional GHG inputs depends on the physical and biogeochemical processes occurring along the river, which are affected by the design of the hydropower system and its operation. Hydropeaking is a widespread phenomenon resulting from the intermittent activation of the hydropower system according to energy market price and demand oscillations (Hauer et al., 2017; Hayes et al., 2023). The ensuing rapid fluctuations in flow discharge in the downstream reaches, sometimes accompanied by sudden variations in water temperature (‘thermopeaking’ - Toffolon et al. (2010); Zolezzi et al. (2011)), oxygen (Winton et al., 2019) and/or total gas saturation (‘saturopeaking’ - Pulg et al. (2016)), have large impacts on the aquatic ecosystem, which can be detected for many kilometres downstream of the hydropower outlets (Moreira et al., 2019; Hayes et al., 2022; Lennox et al., 2022). The increase in water depth and turbidity during hydropeaking can also limit light availability at the stream bed, affecting primary productivity (Hall et al., 2015; Deemer et al., 2022). In contrast, environmental flow regulation can reduce flow variability and dampen floods, thereby enhancing ecosystem respiration and primary productivity (Aristi et al., 2014).

Recently, Calamita et al. (2021) recorded a temporary increment in CO$_2$ evasion during hydropeaking (‘carbopeaking’) downstream of a tropical reservoir (the Kariba Reservoir on the Zambezi River). Carbopeaking resulted from the combination of two factors: the higher CO$_2$ concentration in the hypolimnetic water that supplied the hydropower system; and the higher gas transfer rate coefficient due to stronger turbulence during hydropeaking. Carbopeaking, which occurs with sub-daily frequency, is not typically accounted for in the computation of the reservoir carbon budget.

Because of the strong spatiotemporal gradients and high localisation of GHG sources, the characterisation of GHG fluxes downstream of hydropower reservoirs is challenging, especially in Alpine rivers where the ‘natural’ geomorphological and biochemical heterogeneity has been transformed by several centuries of anthropogenic pressure (Comiti, 2012), and where hydropower regulation is widespread. In this context, the use of diversion pipelines to connect a storage reservoir with a distant, lower-altitude, hydropower plant is a common approach for maximising the hydraulic head. In some cases, the by-passed river reach is regulated with a constant residual flow rate (baseflow). While the residual flow is still heavily affected by the presence of an upstream dam, the ecological impacts of hydropeaking dynamics are partially relieved (Bruno et al., 2023) and/or shifted downstream. In light of the rapid ongoing transformation of the hydrology and biogeochemistry of moun-
tain catchments driven by climate change (Hood et al., 2015; Boix Canadell et al., 2019; Brighenti et al., 2019) and of the increase in global demand for hydropower energy boosting dam construction (Zarfl et al., 2015), understanding and quantifying the drivers of carbon and GHG fluxes (including the anthropogenic ones) is paramount to predict the role of the Alpine ecosystem for global carbon cycling and to inform suitable management approaches.

The objectives of this work are to understand and quantify the CO$_2$ fluxes and their drivers across multiple temporal scales in a regulated Alpine river. Current measurement approaches are limited in their spatiotemporal resolution and coverage (Harmon, 2020), while numerical models suffer from a still incomplete description of the underlying processes (hence contributing to the epistemic uncertainty, sensu Beven and Westerberg (2011)) and from the dependence on a large number of parameters of influence, some of which are very difficult to determine (Battin et al., 2023). Inverse modelling, i.e., estimating the model parameters by fitting measured data, is a useful quantification approach to overcome at least in part these limitations (Saccardi & Winnick, 2021). The approach is often used for quantifying the ecosystem metabolism based on time series of dissolved oxygen concentration (Odum, 1956; Demars et al., 2015) also combined with CO$_2$ (Pennington et al., 2018). The extension to spatially resolved data has been proposed relatively recently to account for the spatial heterogeneity of physical and biological drivers. Segatto et al. (2023) developed a comprehensive framework to study fluxes of dissolved organic carbon and particulate organic carbon. Saccardi and Winnick (2021) employed a stream-network-scale model based on a steady-state one-dimensional CO$_2$ advection-reaction equation, quantifying groundwater inputs, runoff inputs, benthic hyporheic zone inputs, and water column respiration fluxes by optimising the fit with measurements. They neglected carbonate buffering, which can yield substantial effects in high-alkalinity waters (Stets et al., 2017). Winnick and Saccardi (2024) included carbonate buffering in the model of Saccardi and Winnick (2021), but they did not attempt a calibration with field data.

In the present work, we used an inverse modelling approach to quantify the main drivers of CO$_2$ fluxes along a segment of a regulated Alpine river located in the Italian Alps. The study site (Fig. 1) consists of a series of two reservoirs and two hydropower plants connected by a diversion pipeline system, running in parallel with two residual flow reaches. The diversion and the residual flow merge twice, first in the downstream reservoir, and then at the hydropower system outlets downstream of the bottom hydropower plant. The reach downstream of the hydropower outlets is subject to hydropoeaking. The juxtaposition of reaches subject to different regulation approaches provides an opportunity to identify the effects of differing approaches on CO$_2$ fluxes. We sampled the CO$_2$ and dissolved inorganic carbon (DIC) concentration and the main water quality parameters inside the upstream reservoir and at sixteen locations along the residual flow, and measured CO$_2$ concentration time-series at six sites distributed along the residual flow and in the reach subject to hydropoeaking, during four measurement campaigns in different times of the year. Then, we used the measured data to estimate the unknown terms of the CO$_2$ budget, i.e., lateral inputs, ecosystem metabolism, and gas transfer rate, by fitting a one-dimensional, steady-state transport-reaction model. To our knowledge, this was the first application of inverse modelling applied to CO$_2$ fluxes that included the effects of carbonate dissolution (speciation), motivated by the high alkalinity levels observed across our study site. With the aid of the model, we quantified the relative importance of the main drivers of CO$_2$ fluxes (transport, lateral inputs, surface exchange, chemical speciation, and metabolic processes) along the residual flow reaches, and compared them with the effects of carbopeaking observed downstream of the hydropower outlet to assess their relative importance.
2 Methods

2.1 Study site

We conducted multiple field measurement campaigns on the lower segment of the Noce River, the main right tributary of the Adige River, located in the Eastern Italian Alps. The Noce River is a fourth-order (Strahler stream order) highly-regulated Alpine stream with a total length of 105 km, that drains a catchment area of 1370 km² with river basin elevation ranging from 198 m a.s.l. (at the Adige River confluence) to 3769 m a.s.l. (Mount Cevedale). The river is regulated for most of its length (DEE, 2022) and has been the subject of several studies regarding the hydraulic, geomorphological, and biological alterations during hydropeaking (Bruno et al., 2009, 2010, 2023; Zolezzi et al., 2011). The present work focused on the lower segment of the river, downstream of the Santa Giustina reservoir (surface level 531.5 m a.s.l. at the maximum volume of 182.81×10⁶ m³ - DEE (2022)). This reservoir has been among the study sites of a previous work investigating near-surface CO₂ and CH₄ concentrations in 40 Alpine lakes and reservoirs (Pighini et al., 2018).

The reservoir feeds a cascade hydropower system through a diversion pipeline (see Fig. 1): water abstracted from the larger Santa Giustina reservoir (from hereon, upstream reservoir) supplies an upstream power plant, and is released in the smaller Mollaro reservoir (intermediate reservoir; 348 m a.s.l. at the maximum volume of 0.85×10⁶ m³) approximately 6 km downstream, with a maximum flow rate during peak energy production of 66 m³ s⁻¹; a second power plant at the bottom fed by the intermediate reservoir and by two streams (rio Pongaiola and rio Rinassico) releases a maximum flow rate of 60 m³ s⁻¹ back into the Noce River through a 900 m long open channel (223 m a.s.l.). The two consecutive reaches stretching between the upstream reservoir and the hydropower outlet, separated by the intermediate reservoir, extend for an approximate total length of 18 km. They are regulated as residual flow (minimum flow) reaches supplied by two small turbines installed at the bottom of the upstream and intermediate dams, respectively. The prescribed minimum discharge varies throughout the year (2.6 m³ s⁻¹ in December to March; 3.2 m³ s⁻¹ in August and September; 3.7 m³ s⁻¹ for the rest of the year, DEE (2022)). Small tributaries contribute to an additional flow rate of ~2.4-5.2 m³ s⁻¹ along the residual flow reaches (PAT, 2012). The reach downstream of the hydropower diversion outlet, extending for approximately 8 km until the confluence with the Adige River, is affected by hydropeaking. The average slope along the residual flow is 1.3 % in the upstream reach (between the upstream reservoir and the intermediate reservoir), and 0.9 % in the downstream reach (between the intermediate reservoir and the hydropower outlets), respectively. The average slope in the hydropeaking-affected reach is 0.4 %.

Field measurements and/or water sample collection were conducted at 18 sites in total (see Fig. 1). Site S0 was located within the upstream reservoir, at a distance of approximately 0.65 km from the dam. The intermediate reservoir was not accessible for measurements. Seven measurement sites (S1 to S7) were distributed along the upstream residual flow reach, and eight measurement sites (S8 to S15) were distributed along the downstream residual flow reach. Sites S16 and S17 were located along the hydropeaking-affected reach, 0.77 km and 7.14 km downstream of the diversion outlet, respectively. Measurements were conducted during four separate campaigns: Mar23 (21-03 to 14-04-2023), Jun23 (13-06 to 22-06-2023), Aug23 (21-08 to 08-09-2023), and Nov23 (17-11 to 29-11-2023). The campaigns were distributed in such a way as to capture the main seasonal patterns and reservoir stratification regimes. The measurements at site S8 and S17 were conducted only during Mar23 campaign.
Figure 1. Map of the study site with the location of measurement sites and the outline of the three main components of the system, i.e., the hydropower diversion system, the two residual flow reaches separated by the intermediate reservoir, and the hydropowering-affected reach downstream of the hydropower diversion outlet.

2.2 Measurement approach and instrumentation

2.2.1 Spot measurements and sample analysis

Water samples (500 ml) were collected at sixteen sites (S0 to S15) and analysed in the Hydraulics Laboratory of the University of Trento within 48 hours to determine the instantaneous pH, total alkalinity (TA), and dissolved CO$_2$ concentration ([CO$_2$]). All samples were collected during daytime. Alkalinity was determined by titration, while CO$_2$ concentration was measured with the headspace method (Koschorreck et al., 2020) using an EGM-4 environmental gas analyzer (PP Systems, USA), and further corrected for carbonate dissolution using the co2sys model (Lewis et al., 1998) implemented in Matlab (Sharp et al., 2020). Total alkalinity was relatively high (up to 6 mmol eq l$^{-1}$), therefore the correction was substantial (up to 160% for the samples with the lower CO$_2$ concentration of $\sim$ 10 $\mu$mol l$^{-1}$ for a 1:1 headspace-to-water-volume ratio).

In the upstream reservoir (site S0), the samples were collected at multiple (11 to 13) depths using a Niskin bottle sampler. Vertical profiles of water temperature, salinity, conductivity, and chlorophyll a were measured using a MicroCTD profiler (Rockland Scientific, Canada). The water level in the upstream reservoir changed by approximately 29 m throughout the period covered by the measurements, with the minimum depth (72 m at the sampling site) observed in Mar23 and the maximum depth (101 m) during Nov23.
measurement campaign. The vertical sampling and profiling covered the range from the water surface to less than 10 m above the bottom level.

2.2.2 Continuous logging

Time series of [CO₂], water level (h), water temperature (Tₜₚ), and incident light intensity (Iₖₑₚ) were recorded at six sites (S1, S7, S9, S15, S16, and S17 - see Fig. 1) distributed along the two residual flow reaches and downstream of the diversion outlet. The measurements were conducted simultaneously at two sites at a time employing two individual sets of loggers. Each set comprised a pressure/water-level logger (HOBO Water Level Data Logger - Onset Computer Corporation, USA; DCX-22AA - Keller, Switzerland), a temperature and relative light level logger (HOBO Pendant Temperature/Light 64K Data Logger, Onset Computer Corporation, USA), and a [CO₂] logger (Vaisala GM70, range 0-5000 ppm, Vaisala Oyj, Finland). To allow measurements of dissolved CO₂ concentration, the [CO₂] loggers were enclosed in a waterproof case, with their sensing head protected by a sheath made of hydrophobic sintered PTFE membrane (Virtek PMV27, Porex, USA) following Johnson et al. (2010). The loggers at sites S1, S7, and S9 recorded data with a sampling period of 15 minutes for at least 24 hours consecutively. A shorter sampling period (5 minutes) and longer duration (up to 72 hours) were employed at the most downstream sites S15, S16, and S17 to capture the rapid flow variations driven by hydropeaking. Further details about the sampling and continuous measurements and their uncertainties can be found in Text S3 of the supplementary information.

2.2.3 Ancillary meteorological and hydraulic data

Atmospheric pressure and air temperature data were retrieved from two meteorological stations operated by the Ufficio Previsioni e Organizzazione of the Autonomous Province of Trento located within 3 km from the hydropower diversion outlet (Mezzolombardo, Maso delle Part (Meteotrentino, 2023b)) and from the upstream dam (Cles, Maso Maiano (Meteotrentino, 2023a)), respectively. The flow rate was measured every 15 minutes at a gauging station managed by the Ufficio Dighe of the Autonomous Province of Trento (Mezzolombardo Ponte Rupe, PAT (2023)), located approximately 2.5 km downstream of the diversion outlet (1.6 km downstream of site S16, see Fig. 1). The gauging data was used to estimate the flow rate, cross-section averaged flow velocity, and water depth at site S16 based on a set of custom rating curves (see Text S1, supplementary information). The flow rate measured at the gauging station when the hydropower system was not operating (i.e., without hydropeaking) was defined as Q_{baseline}. Q_{baseline} varied from 6.0 m³ s⁻¹ for Mar23 data set to 10.0 m³ s⁻¹ for Nov23 data set. The wet channel width was measured at each site (S1 to S17) using a laser distance meter (Leica Geosystems, Switzerland). The residual flow reaches had an average width of 16.1 m (standard deviation 4.6 m). The widths at sites S16 and S17 in the hydropeaking affected reach were 36.1 m and 23.1 m, respectively.

Conditions inside the intermediate reservoir were unknown. Estimates of the representative values of [CO₂], water temperature, pH, and TA were obtained through a weighted average of the fluxes entering the reservoir during a characteristic time duration τ_r related to the residence time of the intermediate reservoir. These fluxes were the inflow from the upstream residual flow reach, and the inflow from the upstream segment of the diversion system. The former was estimated based on measurements at site S7 (approximately 1.5 km upstream of the intermediate reservoir), while the latter was calculated according to measurements at site S16 assuming that the upstream and downstream hydropower plants operated synchronously and with the same flow rate in both segments of the diversion line. For the details of the calculation and the definition of the characteristic time duration τ_r see Text S2 in the supplementary information.
2.2.4 CO₂ evasion fluxes

CO₂ evasion fluxes were modelled as follows (e.g., Wanninkhof, 1992):

\[ F_{\text{CO}_2} = k \Delta, \]  

(1)

where \( F_{\text{CO}_2} \) (mol s⁻¹ m⁻²) is the CO₂ flux intensity, \( k \) (m s⁻¹) is the gas-transfer rate,

\[ \Delta = [\text{CO}_2] - [\text{CO}_2]_{\text{eq}} \]  

(2)

is the CO₂ excess concentration, i.e., the difference between the dissolved CO₂ concentration in water, [CO₂] (mol m⁻³), and the concentration that would be in equilibrium with the atmospheric CO₂ concentration, [CO₂]_{eq}. The equilibrium concentration is evaluated as [CO₂]_{eq} = K_0 p_{\text{CO}_2\text{air}} (mol m⁻³), where \( p_{\text{CO}_2\text{air}} \) (Pa) is the CO₂ partial pressure in air, and \( K_0 \) (mol l⁻¹ Pa⁻¹) is the CO₂ solubility which depends on water temperature (Wanninkhof, 1992).

The distribution of the gas transfer rate \( k \) along the two residual flow reaches was estimated by fitting the measured [CO₂] distribution using a 1D transport-reaction equation (see section 2.3). In the reach subject to hydropeaking, the rapid variations in flow rate and [CO₂] prevented a direct comparison with the theoretical equation. There, \( k \) was quantified as \( k = k_{600} (600/Sc)^{0.5} \), where \( k_{600} \) (m day⁻¹) is the gas transfer rate standardised to a Schmidt number of Sc = 600. The Schmidt number, which represents the temperature-dependent ratio between water kinematic viscosity and mass diffusivity, was calculated according to Wanninkhof (1992). \( k_{600} \) was determined using the semi-empirical model of Ulseth et al. (2019),

\[ \log(k_{600}) = \begin{cases} 
3.10 + 0.35 \log(\varepsilon_d), & \text{if } \varepsilon_d \leq 0.018 \\
6.43 + 1.18 \log(\varepsilon_d), & \text{if } \varepsilon_d > 0.018 
\end{cases} \]  

(3)

where \( \varepsilon_d = g S V \) (m² s⁻³) is the total specific stream power which approximates the turbulent kinetic energy dissipation rate (Moog & Jirka, 1999), \( g \) (m s⁻²) is the gravity acceleration, \( S \) (−) is the bed slope, and \( V \) (m s⁻¹) is the mean flow velocity.

The model of Ulseth et al. (2019) was validated based on direct measurements obtained with an equilibration chamber mounted on a small anchored catamaran equipped with a CO₂ logger (K33 ELG, SenseAir, Sweden) and temperature and humidity sensors connected to an Arduino acquisition module following Bastviken et al. (2015) and Bastviken et al. (2020). The design of the chamber was optimised for minimal disturbance to near-surface turbulence (see Figure S1 and Text S4 in the supplementary information). The gas transfer rate \( k \) was determined by a least-squares fitting of the measured time series of CO₂ partial pressure inside the chamber (Vingiani et al., 2021). To observe the dependence of \( k \) on flow conditions, the chamber was deployed at multiple sites and on multiple occasions: 15 measurements were conducted at site S16 with different flow rates; 8 measurements were conducted at 8 different locations within a distance of approximately 500 m from site S15, where the morphological units of the wet channel varied between runs and riffles (e.g., Parasiewicz, 2007). At site S16, \( V \) was calculated based on the gauged flow rate using a rating curve. At site S15, the surface velocity \( V_s \) was measured with a hand-held surface velocity radar (SVR2-01, Decatur Electronics, USA) and \( V \) was estimated as \( V = \alpha V_s \), where \( \alpha = 0.85 \) is a typical value for the depth-averaged-to-surface-velocity index (Welber et al., 2016; Hauet et al., 2018).

In Eq. (3), \( \varepsilon_d = 0.018 \) represents a threshold between low- and high-energy regimes. The conditions observed in the measurements were always within the high-energy stream range, with \( \varepsilon_d > 0.018 \) at all sites. The agreement between measured and predicted gas transfer rates (see Figure S2) was acceptable considering the large uncertainties of existing quantification approaches for \( k \), especially in highly turbulent flows (Hall & Ulseth, 2020).
2.3 Transport-reaction model

The evaluation and quantification of the drivers of carbon and CO$_2$ fluxes were based on a 1D solute transport-reaction equation for the dissolved inorganic carbon concentration ([DIC]). The equation is based on DIC conservation along a well-mixed river cross-section subject to longitudinal advection, lateral inflow, atmospheric exchange, and stream metabolism (Pennington et al., 2018), and was adapted from Bencala and Walters (1983) neglecting dispersion:

$$\frac{\partial}{\partial t} + \frac{Q}{A} \frac{\partial}{\partial x} [\text{DIC}] = \frac{qL}{A} ([\text{DIC}]_L - [\text{DIC}]) - \frac{W}{A} k\Delta - \frac{P_w}{A} \text{NEP},$$  \hspace{1cm} (4)

where $x$ (m) is the streamwise distance, $t$ (s) is time, $P_w$ (m) is the wetted perimeter, $W$ (m) is the wet channel width, $A$ (m$^2$) is the cross-sectional area, and $\text{NEP} = \text{GPP} - \text{ER}$ (mol m$^{-2}$ s$^{-1}$) represents the net ecosystem productivity, i.e., the fixation and mineralisation through gross primary production, GPP, and the ecosystem respiration, ER, respectively, $qL$ (m$^2$ s$^{-1}$) is the lateral flow-rate input per unit length, and $[\text{DIC}]_L$ is the DIC concentration in the lateral inflow. Unlike Saccardi and Winnick (2021), we did not distinguish between water column and hyporheic zone respiration fluxes. The DIC concentration is given by

$$[\text{DIC}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}],$$  \hspace{1cm} (5)

i.e., as the sum of the concentrations of CO$_2$ and of the main carbonate ion species. Expressing the model in terms of DIC allows for considering carbonate speciation, i.e., the variations in [CO$_2$] caused by the shift in chemical equilibrium between the different DIC species. In high-alkalinity waters ($\sim 2$ mmol l$^{-1}$), where the pool of ionised CO$_2$ (the carbonate buffer) is significant, the restoration of the chemical equilibrium dampens CO$_2$ variations driven by external drivers, i.e., it delays atmospheric equilibration, reduces the intensity of atmospheric evasion fluxes, and limits the apparent primary productivity (Stets et al., 2017).

The excess CO$_2$ mass transport flux along the river reach is defined as

$$\phi_{\text{CO}_2} = Q\Delta,$$  \hspace{1cm} (6)

with units of mol s$^{-1}$. The relative importance of transport and evasion fluxes is represented by a turnover length scale $\Lambda$, defined as

$$\Lambda = \frac{1}{W \frac{\phi_{\text{CO}_2}}{F_{\text{CO}_2}}} = \frac{Q}{kW}.$$  \hspace{1cm} (7)

Large values of $\Lambda$ indicate that DIC is transported a long distance downstream with minimal interaction with the atmosphere. Small values of $\Lambda$ are expected in turbulent mountain rivers where atmospheric exchange is predominant. Assuming steady state, introducing the definition of $\Lambda$ from Eq. (7), and approximating $P_w \approx W$ (wide cross-section), Eq. (4) can be simplified as follows:

$$\Lambda \frac{d}{dx} [\text{DIC}] = -\frac{qL}{Q} ([\text{DIC}] - [\text{DIC}]_L) - \Delta - \frac{\text{NEP}}{k}.$$  \hspace{1cm} (8)

$\Lambda$ has different physical meanings depending on the types of CO$_2$ sources and distribution. For instance, neglecting lateral inputs, metabolism, and carbonate speciation ($qL = 0$, NEP = 0, and $d[\text{DIC}] / dx = d[\text{CO}_2] / dx$), and assuming $W = \text{constant}$ for simplicity, the integration of Eq. (8) yields

$$\Delta(x) = \Delta(x_0) \exp \left(-\frac{(x - x_0)}{\Lambda}\right),$$  \hspace{1cm} (9)

i.e., $\Lambda$ represents the distance over which $\Delta$ approaches the asymptotic equilibrium $\Delta \rightarrow 0$ starting from an initial value $\Delta(x_0)$. Specifically, $\Delta(x)$ decreases by 63% relative to
its initial value $\Delta(x_0)$ over a distance $(x - x_0) = \Lambda$ (i.e., $(\Delta(x) - \Delta(x_0))/\Delta(x_0) = 1 - \exp(-1) = 63 \%$). If, instead, conditions are spatially homogeneous, e.g., $q_L = 0$, $[DIC] = \text{const.}$, then $\Delta = -\Lambda/k$, and

$$\Lambda = \frac{QA}{Wk\Delta} = -\frac{Q\Delta}{W\text{NEP}}, \quad (10)$$

i.e., $\Lambda$ represents the ‘turnover distance’ which is required by an initial CO$_2$ pool (represented by an upstream flux $Q\Delta$ (mol s$^{-1}$)) to be fully depleted to the atmosphere through evasion fluxes, $(AWk\Delta$, mol s$^{-1}$), and replaced with an equal amount of CO$_2$ originating from the ecosystem metabolism ($AW\text{NEP}$, mol s$^{-1}$).

Substituting $k$ from Eq. (3) into Eq. (7), $\Lambda$ can be related to the flow velocity and turbulent kinetic energy dissipation rate, revealing a different behaviour for low-energy and high-energy streams. Assuming Sc is constant and generalising Eq. (3) in the form $k = b(\varepsilon_d)a$, $(a = 0.35$ when $\varepsilon_d \leq 0.018$ and $a = 1.18$ when $\varepsilon_d \geq 0.018)$, one finds

$$\Lambda^* = \frac{\Lambda}{h_{\text{ref}}} = \frac{V}{k} \sim \frac{1}{b(gS)^a}V^{(1-a)}, \quad (11)$$

where $\Lambda^*$ is the non-dimensionalised $\Lambda$ based on a reference water depth $h_{\text{ref}} = Q/(VW)$. If $S = \text{constant}$ and $\varepsilon_d > 0.018$, the exponent of $V$ is negative and an increase in flow velocity is associated with a decrease in $\Lambda^*$, i.e., a larger relative weight of evasion fluxes compared to transport fluxes, and a more rapid turnover. In this case, the sensitivity of $\Lambda^*$ to variations in $V$ is rather small, $\Lambda^* \sim V^{-0.18}$ (see Figure S4 in the supplementary information). If $\varepsilon_d < 0.018$ the exponent of $V$ is positive, therefore, increasing the flow velocity yields an increase in $\Lambda^*$, meaning a longer non-dimensional travel distance before reaching equilibrium. An increase in river slope $S$ is always associated with a decrease in $\Lambda^*$ if the average flow velocity remains constant.

### 2.4 Data interpretation through the model

Equation (8) was used for quantifying the magnitude of the main contributors to the CO$_2$ mass balance along the residual flow reaches. A similar approach was used previously by Saccardi and Winnick (2021) to reconstruct CO$_2$ dynamics at watershed scales neglecting carbonate speciation. Following these authors, the ordinary differential equation (Eq. (8)) was approximated and solved numerically on a uniform grid (50 m resolution) using a first-order forward difference scheme. The integration was conducted along two separate computational domains representing the upstream $(x_{0}^{(us)}, x_1^{(us)}, \ldots, x_{12}^{(us)})$ and downstream $(x_{0}^{(ds)}, x_1^{(ds)}, \ldots, x_{12}^{(ds)})$ residual flow reaches, respectively. The upstream domain had a length of $L^{(us)} = 6$ km (121 nodes) and extended from the upstream dam $(x_0^{(us)})$ to the confluence of the upstream residual flow reach into the intermediate reservoir $(x_{\text{end}}^{(us)})$. The downstream residual flow domain had a length of $L^{(ds)} = 11.6$ km (233 nodes) and extended from the intermediate dam $(x_0^{(ds)})$ to the outlet of the hydropower diversion system $(x_{\text{end}}^{(ds)})$. The wet channel width was assumed constant within each reach ($W^{(us)} = 15.8$ m for the upstream reach and $W^{(ds)} = 16.4$ m for the downstream reach, corresponding to the average of local measurements at sites S1 to S15). Within both domains, the flow rate $Q(x_i)$ at the $i$-th node was assumed to be proportional to the drainage area upstream of the node, $DA_i(x_i)$ (m$^2$), following Conroy et al. (2023),

$$Q(x_i) = Q(x_0^{(us)}) + \left[Q_{\text{baseline}} - Q(x_0^{(us)})\right] \frac{DA_i(x_i)}{DA_0}, \quad (12)$$

where $DA_0$ (m$^2$) was the drainage area upstream of the gauging station (located in the reach subject to hydropeaking). $Q_{\text{baseline}}$ was the baseline discharge measured at the gauging station in the absence of hydropeaking, and $Q(x_0^{(us)})$ was equal to the minimum permissible residual flow discharge. $q_L$ was calculated as

$$q_L(x_i) = \frac{Q(x_i) - Q(x_{i-1})}{x_i - x_{i-1}}, \quad (13)$$
[DIC], [CO₂], pH, and TA are related by chemical equilibrium relations, which allow the calculation of any of these quantities if at least two of them are known (Dickson et al., 2007). Since the integration was conducted with respect to [DIC], either [CO₂], pH, or TA should have been determined iteratively. To reduce the computational effort, we avoided iterating by prescribing the conservation of total alkalinity in the form

\[ Q(x_i)TA(x_i) = Q(x_0)TA_0 + \sum_{j=1}^{i} (x_j - x_{j-1})q_L(x_j)TA_L, \]  \hspace{1cm} (14)

where TA_L was the total alkalinity in the lateral inflow, which was assumed to be constant in space, and TA_0 = TA(x_0) was the TA at the upstream boundary of each reach.

The assumption was justified by the fact that variations in CO₂ do not affect alkalinity, and variations in TA due to nutrient uptake or mineralisation are small (Stets et al., 2017; Winnick & Saccardi, 2024).

Temporal variations were neglected by assuming steady-state conditions for each quantity in Eq. (4), including the NEP. This was made possible by considering only the behaviour at peak daytime (when GPP reaches its maximum) and nighttime (when GPP = 0), separately, i.e.,

\[ \text{NEP}_{\text{peak,day}} = \text{GPP}_{\text{peak}} - \text{ER}, \]  \hspace{1cm} (15)
\[ \text{NEP}_{\text{peak,night}} = 0 - \text{ER}, \]  \hspace{1cm} (16)

Then, the parameters of Eq. (8) were estimated by fitting the model predictions and the measured distributions of [CO₂], pH, TA, and [DIC], using a multi-objective optimisation approach with an interior-point-convex optimisation algorithm (Nocedal et al., 2014). [DIC] was calculated as a function of the measured [CO₂] and TA using the co2sys model in Matlab (Lewis et al., 1998; Sharp et al., 2020). Measured daytime and night-time data were complemented by the estimated conditions in the upstream and intermediate reservoirs. Then, daytime measured data set included the sampling data at all 15 sites, the reservoir data, and the peak daytime data at the four continuous logging sites, S1, S7, S9, and S15 (21 data points per parameter and data set). Night-time measurements comprised only the reservoir data and peak nighttime values extracted from the continuous time series data (6 data points per parameter and data set).

The T_w distribution was calculated separately for each data set by fitting an exponential function of the type \( T_w(x_i) = T_w(x_0) + c_2 \exp((x_i - x_0)/c_1) \). Nine additional parameters were estimated based on Eq. (8) and Eqs. (14)-(16): the upstream boundary values of [DIC] and TA ([DIC]_0 and TA_0) in the upstream reach, [DIC]_0 and TA_0 in the downstream reach; the DIC concentration and TA of the lateral inflow ([DIC]_L and TA_L, respectively); the daytime and nighttime NEP_peak (NEP_peak,day and NEP_peak,night, respectively); and \( \Lambda \). Except for \( \Lambda \) which was assumed to be constant throughout, each parameter was allowed to change across measurement campaigns. NEP_peak changed from daytime to nighttime according to Eqs. (15) and (16), while the other parameters were assumed to be independent of the time of day. \( \Lambda \), [DIC]_L, TA_L, NEP_peak,day and NEP_peak,night were represented by single average values representative of the two reaches. The choice of limiting the variability of the parameters in space and/or time in such a way was driven by the limited size of the data set, and followed a similar approach in previous studies (Saccardi & Winnick, 2021; Conroy et al., 2023). In the case of \( \Lambda \), fixing a unique representative value for all data sets was justified by the small variability of \( \Lambda^* \) for high-energy flows such as the one in the residual flow. Local values of \( k \) were calculated from the estimated values of \( \Lambda \) and \( Q \). In this way, we were able to account for \( k \) variability in space and across data sets in a physically realistic way with a relatively small number of degrees of freedom.
2.5 Calculation of CO2 inputs

The estimates of the [CO2] distributions and CO2 flux parameters along the residual flow reaches obtained by fitting the measurements with the model were employed for calculating the magnitude of the main CO2 fluxes, and to compare them with the effects of hydropeaking downstream of the hydropower diversion outliers. Positive fluxes were used to represent inputs of CO2 into the system. We distinguished seven main contributions to the budget of CO2:

\[ \text{EM} = -(W^{(us)}L^{(us)} + W^{(ds)}L^{(ds)})\text{NEP}_{\text{peak}} \]  

(17)

represents the CO2 production by the ecosystem metabolism (mol/s). EM is positive during the night but can be negative during the day if primary production dominates over respiration.

\[ \text{IN} = Q_x(x_0^{(us)})\Delta(x_0^{(us)}) - Q(x_{\text{end}}^{(us)})\Delta(x_{\text{end}}^{(us)}) + Q(x_0^{(ds)})\Delta(x_0^{(ds)}) \]  

(18)

represents the net excess CO2 input from the upstream boundaries of both residual flow reaches, where \(x_0^{(us)}\) and \(x_0^{(ds)}\) are the upstream boundary coordinates (i.e., the dam location) of the upstream and downstream reach, respectively, and \(x_{\text{end}}^{(us)}\) represents the downstream boundary of the upstream reach (i.e., the intermediate reservoir confluence location). The CO2 concentration inside the intermediate reservoir depends on (i) the input from the upstream reservoir through the diversion system and (ii) the input from the upstream reach at the confluence, approximated with \(Q(x_{\text{end}}^{(us)})\Delta(x_{\text{end}}^{(us)})\). This last term has been subtracted in Eq. (18) to isolate the contribution from the hydropower system.

\[ \text{OUT} = -Q(x_{\text{end}}^{(ds)})\Delta(x_{\text{end}}^{(ds)}) \]  

(19)

represents the excess CO2 outflow at the downstream end of the residual flow, \(x_{\text{end}}^{(ds)}\), located directly upstream of the diversion pipeline outlets. According to our sign convention, an outflow of undersaturated water \((\Delta(x_{\text{end}}^{(ds)}) < 0\) resulted in \(\text{OUT} > 0\).

\[ \text{LAT} = \sum_{i=0}^{\text{end}} (x_i^{(us)} - x_{i-1}^{(us)})q_L(x_i^{(us)})\Delta L(x_i^{(us)}) + \sum_{i=0}^{\text{end}} (x_i^{(ds)} - x_{i-1}^{(ds)})q_L(x_i^{(ds)})\Delta L(x_i^{(ds)}) \]  

(20)

represents the lateral input of excess CO2, where \(\Delta L\) was the excess CO2 concentration in the lateral inflow calculated based on [DIC]L and TA_L. LAT < 0 when \(\Delta L < 0\).

\[ \text{SURF} = -\sum_{i=0}^{\text{end}} (x_i^{(us)} - x_{i-1}^{(us)})k(x_i^{(us)})\Delta(x_i^{(us)})W^{(us)} + \sum_{i=0}^{\text{end}} (x_i^{(ds)} - x_{i-1}^{(ds)})k(x_i^{(ds)})\Delta(x_i^{(ds)})W^{(ds)} \]  

(21)

represents the CO2 exchange with the atmosphere. SURF < 0 indicates a flux of CO2 from water towards the atmosphere.

The CO2 balance in the residual flow is closed with the input of CO2 due to carbonate dissolution. We calculated it in terms of the net imbalance of HCO3− and CO32−, from which we subtracted any possible imbalance in DIC:

\[ \text{CHEM} = \text{IN}_{\text{HCO}_3^-} + \text{IN}_{\text{CO}_3^{2-}} - \text{IN}_{\text{DIC}} + \text{LAT}_{\text{HCO}_3^-} + \text{LAT}_{\text{CO}_3^{2-}} - \text{LAT}_{\text{DIC}} + \text{OUT}_{\text{HCO}_3^-} + \text{OUT}_{\text{CO}_3^{2-}} - \text{OUT}_{\text{DIC}} - \text{EM} - \text{SURF}. \]  

(22)

Lastly,

\[ \text{CPeak} = \left\langle Q(x_0^{(HP)}, t_j)\Delta(x_0^{(HP)}, t_j) \right\rangle_{\text{HP}} \]  

(23)
represents the net additional influx of excess CO$_2$ during hydropeaking calculated based
on the measurements at site S16, where $\langle \cdot \rangle_{HP}$ denotes conditional averaging during hy-
dropeaking events, and $x_0^{(HP)}$ indicates the location of the diversion outlet (here approx-
imated by the location of site S16). The addition of the term OUT is to subtract the baseline CO$_2$ flux coming from the residual flow reaches and to isolate the increase due to
carbopeaking.

Quantifying the different drivers of CO$_2$ in the hydropeaking-affected reach is chal-
lenging because of the rapid temporal variations in the CO$_2$ fluxes and hydraulic condi-
tions. It is possible, however, to quantify the scale of the CO$_2$ surface exchange that
occurs in this reach and that can be directly attributed to carbopeaking. To this end,
we considered a constant flow rate $Q_{HP} = < Q(x_0^{(HP)}, t) >_{HP}$ everywhere along the
hydropeaking-affected reach. Wet channel width ($W_{HP}$) and gas transfer rate ($k_{HP} =
Q_{HP}/(W_{HP} \Lambda_{HP})$) were assumed to be constant, as well. Lateral inputs, ecosystem metabolism,
and carbonate speciation were neglected ($q_L = 0$, NEP = 0, $d[\text{DIC}]/dx = d[\text{CO}_2]/dx$).
Under these conditions, $\Delta(x)$ follows Eq. (9). Then, the excess CO$_2$ mass flow rate en-
tering the hydropeaking-affected reach at its upstream boundary was $Q_{HP} \Delta(x_0^{(HP)}) =
\text{CPeak–OUT}$. The amount of CO$_2$ exchanged with the atmosphere during hydropeak-
ning between the location of the hydropower diversion outlet, $x_0^{(HP)}$, and a generic loca-
tion along the hydropeaking-affected reach, $x^{(HP)}$, can be calculated by integrating Eq. (1)
over the surface area, taking into account the relationships in Eq. (7)-(9),

$$
\int_{x_0^{(HP)}}^{x^{(HP)}} W_{HP} k_{HP} \Delta(x) dx = Q_{HP} \Delta(x_0^{(HP)}) \left[ 1 - \exp \left( - \frac{(x^{(HP)} - x_0^{(HP)})}{\Lambda_{HP}} \right) \right] = (\text{CPeak} - \text{OUT}) \left[ 1 - \exp \left( - \frac{(x^{(HP)} - x_0^{(HP)})}{\Lambda_{HP}} \right) \right].
$$

(24)

Only the term with CPeak is directly related to carbopeaking, and was defined as

$$
\text{SURF}_{HP} = \text{CPeak} \left[ 1 - \exp \left( - \frac{(x^{(HP)} - x_0^{(HP)})}{\Lambda_{HP}} \right) \right].
$$

(25)

According to Eq. (25), the percentage of carbopeaking that evades into the atmosphere
up to a distance $(x^{(HP)} - x_0^{(HP)}) = \Lambda_{HP}$ from the hydropower diversion outlet corre-
sponds to $\text{SURF}_{HP}/\text{CPeak} = 63 \%$.

3 Results

3.1 Measurements in the upstream reservoir

The profiles of CO$_2$ concentration and water temperature measured at site S0 in
the upstream reservoir (Fig. 2) displayed a marked seasonal variability. The [CO$_2$] was
higher at larger depths and lower near the water surface, except during Nov23 campaign
when it was approximately uniformly distributed following lake overturning. The depth-
averaged CO$_2$ concentration varied between a minimum of 26 μmol/l during Nov23 cam-
paign and a maximum of 53 μmol/l during Mar23 campaign. To highlight the poten-
tial evasion flux upon release into the river, [CO$_2$]$_{eq}$ was calculated at every depth based
on the local water temperature and average atmospheric CO$_2$ concentration ($p[\text{CO}_2]_{air} =
425$ ppm) at atmospheric pressure, and is not representative of pressure variations with
depth inside the reservoir. Thus, water was consistently supersaturated at the two in-
takes of the hydropower diversion system and of the penstock that fed the residual flow
reaches. Except for Nov23, values of [CO$_2$] near the water surface were well below the
equilibrium concentration, causing an influx of CO$_2$ from the atmosphere according to
Eq. (1). Near the surface, the decrease in [CO$_2$] was accompanied by an increase in chloro-
phyll a (see Figure S7 in the supplementary information), suggesting that the undersat-
Figure 2. Profiles of sampled dissolved CO$_2$ concentration [CO$_2$] (circles) and water temperature $T_w$ (colourmap) in the upstream reservoir, during the four measurement campaigns. White line: equilibrium concentration, [CO$_2$]$_{eq}$. Dashed line: diversion system intake level. Dashed-dotted line: residual flow intake level.

3.2 Measurements along the residual flow

Temporal variations in [CO$_2$] at the continuous monitoring sites (S1, S7, S9, and S15) along the residual flow reaches displayed a significant diel variability (Fig. 3), with lower daytime [CO$_2$] levels indicating the effects of primary production (e.g., Peter et al., 2014). Diel variations in [CO$_2$] were clearly visible at sites S7 and S15 located furthest downstream from the upstream and intermediate dams, respectively. The peak-to-peak [CO$_2$] range was very small during Nov23 campaign and was largest during Mar23 and Jun23 campaigns, when water became undersaturated ([CO$_2$] < [CO$_2$]$_{eq}$) during the daytime. The range was somewhat reduced at site S9 downstream of the intermediate dam, while variations were almost absent at site S1 closest to the upstream dam. The daily average of CO$_2$ excess concentration $\Delta$ was positive at all sites and varied between 2.94 $\mu$mol l$^{-1}$ (at site S9 for Aug23 data set) and 47.38 $\mu$mol l$^{-1}$ (at site S1 for Mar23 data set). The highest instantaneous value of $\Delta = 54.90$ $\mu$mol l$^{-1}$ was observed at 8:00 at site S1 for Mar23 data set, while the lowest value of $\Delta = -13.85$ $\mu$mol l$^{-1}$ was observed at 13:50 at site S7 for Jun23 data set.

The daytime spatial distributions of $T_w$ and $\Delta$ measured at the sampling sites S1 to S15 (Fig. 4a and b) indicated a decrease in $\Delta$ and an increase in $T_w$ (except for Nov23 data set) with the distance from the upstream dam, driven by the higher air temperature and lower CO$_2$ concentrations in the atmosphere compared to the hypolimnetic water in the upstream reservoir. The decay in $\Delta$ occurred rapidly within a distance of ap-
Figure 3. Temporal variation of $\text{[CO}_2\text{]}$ along the residual flow (sites S1, S7, S9, S15) as a function of the time of day, measured with the $\text{[CO}_2\text{]}$ loggers during the four measurement campaigns. For each campaign, the measurements at sites S1-S7 and S9-S15 were conducted on two separate consecutive days. Solid, black: $\text{[CO}_2\text{]}$ in the residual flow reaches. Dotted, black: $\text{[CO}_2\text{]}_{eq}$, Dashed, orange: sampled $\text{[CO}_2\text{]}$ in the upstream reservoir at the residual flow intake level (dotted lines bind the uncertainty interval). Background colours represent the logarithm of the measured light intensity (the dark blue colour indicates nighttime). Grey-shaded regions indicate periods for which measurements were not available.

proximately 2 km from the upstream dam, between sites S1 and S5, and was likely driven by the combined effects of atmospheric evasion and primary production. Beyond site S5, $\Delta$ showed limited spatial variation within each data set, but a clear variability across different data sets. During the day, water was undersaturated in CO$_2$ ($\Delta < 0$) for Mar23, Jun23, and Aug23 data sets, and supersaturated ($\Delta > 0$) for Nov23 data set. The lowest values of $\Delta$ were observed for Mar23 and Jun23 data sets. The pH distribution (Fig. 4c) mirrored the distribution of $\Delta$ as a consequence of chemical equilibrium. Total alkalinity (Fig. 4d) varied between 1.2 to 2.9 mmol l$^{-1}$ and increased along the residual flow most likely because of lateral influx from the watershed. The maximum in TA occurred during Nov23 campaign, although the strongest spatial variation in TA along the residual flow was observed during Aug23 campaign.

3.3 Model fitting along the residual flow

We obtained an estimate of the nine unknown parameters $\Lambda$, NEP$\text{peak}_{\text{day}}$, NEP$\text{peak}_{\text{night}}$, $[\text{DIC}]_{L}$, $[\text{DIC}]_{\text{us}}$, $[\text{DIC}]_{\text{ds}}$, $\text{TA}_{L}$, $\text{TA}_{\text{us}}$, and $\text{TA}_{\text{ds}}$ by fitting the data measured along the residual flow reaches by means of Eq. (8) and Eq. (14)-(16) (see Fig. 5). The resulting estimates for these parameters are reported in Table 1. The estimated levels of $\text{TA}_{L}$ and $[\text{DIC}]_{L}$ (up to 6 mmol l$^{-1}$) were consistent with the scenarios considered by Winnick and Saccardi (2024) based on the range observed across streams in the United States (Stets et al., 2017). $\Lambda$ was estimated to be approximately 2.1 km, which was consistent with the rapid equilibration of $\Delta$ observed close downstream of the dams in Fig. 4. Local values of $k$ were calculated at each grid location based on $Q(x_i)$ and estimated $\Lambda$. The spatial average of $k$ varied between 8.7 m d$^{-1}$ for Aug23 data set in the upstream reach and 20.9 m d$^{-1}$ for Nov23 data set in the downstream reach, in agreement with the direct
Figure 4. Spatial daytime distributions of (a) water temperature, $T_w$, (b) excess CO$_2$ concentration, $\Delta$, (c) pH, and (d) total alkalinity, TA, measured along the residual flow, as a function of the distance from the upstream dam. Day-time measurements are representative of the daily minimum CO$_2$ concentrations (see Fig. 3) and maximum water temperatures at each site. Circles: sample measurements; stars: measurements at the residual flow intake inside the upstream reservoir; diamonds: average values inside the intermediate reservoir based on the weighted average of the input fluxes (see Text S2) (errorbars indicate diel minima/maxima); orange dashed-dotted line: atmospheric equilibrium conditions, $\Delta = 0$; solid blue lines: location of the upstream (0 km) and intermediate (6.6 km) dams; dashed blue line: location of the hydropower diversion outlet (18.2 km). Unless otherwise specified, errorbars indicate confidence intervals.

measurements at site S15. The higher estimated $k$ in the downstream reach compared to the upstream reach was consistent with the variation in flow rate along the residual flow reaches.

3.4 Measurements at the hydropower diversion outlet

Fig. 6 and Fig. 7 show the effects of hydropeaking on the flow rate, water temperature, and CO$_2$ fluxes, observed at site S16 for Jun23 and Nov23 data sets, respectively. The results for Mar23 and Aug23 data sets are shown in Figure S10 and Figure S11 of the supplementary information, respectively. Baseline conditions (i.e., without hydropeaking) were estimated based on the measurements at site S15 located upstream of the diversion outlet. Sharp increases in flow rate $Q$ (Fig. 6a and Fig. 7a) at site S16 were indicative of hydropeaking activity, which caused the flow rate to increase by a factor of $Q_{\text{peak}}/Q_{\text{baseline}} \approx 5.5$ in as little as 20 minutes. Hydropeaking events occurred regularly during Jun23, Aug23, and Nov23 measurement campaigns, preferentially during the
Table 1. Estimated CO$_2$ model parameters along the residual flow reaches. The values of $k$ reported here are the spatial averages calculated for each residual flow reach based on $\Lambda$ and $Q$. $F_{CO_2}$ were calculated separately for daytime and nighttime CO$_2$ distributions. The values reported here are the average along both residual flow reaches. ± indicates 95 % confidence intervals based on fitting.

<table>
<thead>
<tr>
<th></th>
<th>Mar23</th>
<th>Jun23</th>
<th>Aug23</th>
<th>Nov23</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER (µmol m$^{-2}$ s$^{-1}$)</td>
<td>2.52 ±1.36</td>
<td>4.97 ±1.42</td>
<td>3.07 ±0.94</td>
<td>2.17 ±1.20</td>
</tr>
<tr>
<td>GPP$_{peak}$ (µmol m$^{-2}$ s$^{-1}$)</td>
<td>6.01 ±2.23</td>
<td>7.94 ±2.57</td>
<td>2.93 ±1.71</td>
<td>1.35 ±2.10</td>
</tr>
<tr>
<td>DIC$_0^{(us)}$ (mmol l$^{-1}$)</td>
<td>2.09 ±0.12</td>
<td>1.81 ±0.13</td>
<td>1.54 ±0.13</td>
<td>2.04 ±0.13</td>
</tr>
<tr>
<td>DIC$_0^{(ds)}$ (mmol l$^{-1}$)</td>
<td>2.13 ±0.21</td>
<td>1.99 ±0.22</td>
<td>1.35 ±0.22</td>
<td>1.83 ±0.22</td>
</tr>
<tr>
<td>DIC$_L$ (mmol l$^{-1}$)</td>
<td>4.66 ±1.70</td>
<td>2.82 ±0.65</td>
<td>5.73 ±0.77</td>
<td>4.21 ±0.54</td>
</tr>
<tr>
<td>TA$_0^{(us)}$ (mmol l$^{-1}$)</td>
<td>2.02 ±0.12</td>
<td>1.78 ±0.13</td>
<td>1.52 ±0.13</td>
<td>2.03 ±0.13</td>
</tr>
<tr>
<td>TA$_0^{(ds)}$ (mmol l$^{-1}$)</td>
<td>2.10 ±0.21</td>
<td>1.95 ±0.22</td>
<td>1.30 ±0.22</td>
<td>1.81 ±0.23</td>
</tr>
<tr>
<td>TA$_L$ (mmol l$^{-1}$)</td>
<td>4.66 ±1.71</td>
<td>2.94 ±0.67</td>
<td>6.06 ±0.78</td>
<td>4.25 ±0.56</td>
</tr>
<tr>
<td>$\Lambda$ (km)</td>
<td>2.09 ±0.64</td>
<td>2.09 ±0.64</td>
<td>2.09 ±0.64</td>
<td>2.09 ±0.64</td>
</tr>
<tr>
<td>$k^{(us)}$ (m d$^{-1}$)</td>
<td>9.8 $^{+4.2}_{-2.3}$</td>
<td>10.3 $^{+4.5}_{-2.4}$</td>
<td>8.7 $^{+3.3}_{-2.0}$</td>
<td>10.6 $^{+4.7}_{-2.5}$</td>
</tr>
<tr>
<td>$k^{(ds)}$ (m d$^{-1}$)</td>
<td>11.8 $^{+5.2}_{-2.8}$</td>
<td>17.8 $^{+7.8}_{-4.2}$</td>
<td>13.6 $^{+6.0}_{-3.2}$</td>
<td>20.9 $^{+9.2}_{-4.9}$</td>
</tr>
<tr>
<td>$F_{CO_2}$ (µmol m$^{-2}$ s$^{-1}$) (day)</td>
<td>$-1.4$ $^{+1.2}_{-1.7}$</td>
<td>$-2.8$ $^{+1.5}_{-2.2}$</td>
<td>$-0.9$ $^{+1.0}_{-1.4}$</td>
<td>1.2 $^{+0.7}_{-0.9}$</td>
</tr>
<tr>
<td>$F_{CO_2}$ (µmol m$^{-2}$ s$^{-1}$) (night)</td>
<td>5.7 $^{+1.2}_{-1.5}$</td>
<td>6.2 $^{+1.1}_{-1.3}$</td>
<td>2.2 $^{+0.9}_{-1.3}$</td>
<td>2.8 $^{+0.9}_{-1.1}$</td>
</tr>
</tbody>
</table>
morning hours and in the late afternoon and through the evening. Mar23 campaign saw only two sporadic, shorter (less than 2 hours long), and less intense ($Q_{\text{peak}}/Q_{\text{baseline}} \approx 4.5$) events.

The measured water temperature patterns (Fig. 6b and 7b) displayed a periodic diel fluctuation in the baseline flow which was more marked for Jun23 data set, with higher $T_w$ during the day. The release of colder water from the diversion outlet during Mar23, Jun23, and Aug23 campaigns caused a decrease in $T_w$ (cold thermopeaking, see Zolezzi et al. (2011)), while warmer inflow from the hydropower system during Nov23 campaign caused warm thermopeaking. Thermopeaking was caused by the contrast between the variation of the water temperature along the residual flow and the relatively constant temperature of the water that circulated within the hydropower diversion system, close to the water temperature at the intake level in the reservoir. The magnitude of thermopeaking was largest (up to 4.5 °C for Jun23 data set) during the afternoon, when the baseline value of $T_w$ reached its maximum. The intermediate reservoir acted as a buffer for temperature fluxes, affecting the thermopeaking patterns. This became apparent after periods of inactivity in hydropower operation when the lack of input from the diversion system, and the subsequent increase in residence time, caused the conditions within the intermediate reservoir to become more similar to those in the residual flow. For this reason, the measured time series of $T_w$ for Jun23 data set had a small peak with a relative maximum at approximately 2.5 hours after the onset of hydropoeaking. Our simple mixing model to estimate the conditions inside the intermediate reservoir as the com-
Figure 6. Time series of (a): flow rate, $Q$; (b): water temperature, $T_w$; (c): excess CO$_2$ concentration, $\Delta$; (d): excess CO$_2$ mass flux, $\phi_{CO_2} = Q\Delta$; (e): gas transfer rate, $k$; (f): CO$_2$ evasion flux intensity, $F_{CO_2}$, recorded during Jun23 campaign in the baseline flow (site S15 - orange) and in the reach subject to hydropeaking (site S16 - black). Dashed-dotted line, black: conditions in the upstream reservoir, at the hydropower diversion intake. Dashed line, black: conditions in the intermediate reservoir.

The time series of the excess CO$_2$ concentration $\Delta$ (Fig. 6c and 7c) had a symmetric behaviour compared to the water temperature dynamics, i.e., higher CO$_2$ concentrations were observed during hydropeaking events or at night compared to the baseline. Diel [CO$_2$] fluctuations driven by the ecosystem metabolism governed the baseline [CO$_2$] dynamics like in the residual flow (Fig. 3). These fluctuations remained identifiable at site S16 at times when the hydropower system was inactive. Hydropeaking events were strongly correlated with rapid increases in CO$_2$ concentrations and therefore in $\Delta$ for...
Mar23, Jun23 (Fig. 6c) and Aug23 data sets, while no clear variation in $\Delta$ during hydropeaking could be observed for Nov23 data set (Fig. 7c). For Jun23 (Fig. 6c) and Aug23 (Fig. S11 of the supplementary information) data sets, the increase in $\Delta$ at the onset of hydropeaking was typically followed by a temporary drop with a minimum after approximately 2.5 hours, and by a subsequent second and higher surge lasting until the end of the hydropeaking event. This behaviour, which mirrored the $T_w$ patterns, could be explained similarly by buffering within the intermediate reservoir.

Figure 7. Time series of (a): flow rate, $Q$; (b): water temperature, $T_w$; (c): excess $\text{CO}_2$ concentration, $\Delta$; (d): excess $\text{CO}_2$ mass flux, $\phi_{\text{CO}_2} = Q\Delta$; (e): gas transfer rate, $k$; (f): $\text{CO}_2$ evasion flux intensity, $F_{\text{CO}_2}$, recorded during Nov23 campaign in the baseline flow (site S15 - orange) and in the reach subject to hydropeaking (site S16 - black). Dashed-dotted line, black: conditions in the upstream reservoir, at the hydropower diversion system intake. Dashed line, black: conditions in the intermediate reservoir.

$[\text{CO}_2]$ dynamics for Mar23 (Fig. S10 of the supplementary information) and Nov23 (Fig. 7c) data sets were more complex. In both cases, the predictions by our simple mixing model did not match the observations of $\Delta$ and $T_w$, suggesting that the dynamics of mixing in the intermediate reservoir were not adequately captured. As an example,
the Δ time-series measured during Nov23 campaign had an extremely sharp peak at around 8:00 of the first day, when Δ increased rapidly by around 40 μmol l⁻¹ in less than half an hour before going back to its initial value just as rapidly. Since this event occurred at the first occurrence of hydropoeaking after multiple days of hydropower inactivity, the difference from the predicted behaviour may have been caused by the asynchronous operation of the upstream and downstream power plants or by lateral influxes into the reservoir.

Excess CO₂ mass fluxes, φ₇ = QΔ, were considerably higher during hydropoeaking because of the combination of higher discharge and higher CO₂ concentration (Fig. 6d and Fig. 7d). The increase in flow rate during hydropoeaking was also associated with an increase in gas transfer rate according to Eq. (3) (Fig. 6e and Fig. 7e), and the combination of higher k and higher Δ yielded larger evasion fluxes F₇ (Fig. 6f and Fig. 7f). The baseline k and F₇ values represent the gas transfer rate and intensity that would occur in the hydropoeaking-affected reach in the absence of hydropoeaking. They were calculated with the baseline Δ concentration measured at site S15 but based on the hydraulic conditions and channel geometry of site S16 with the baseline flow rate. Table 3.4 summarises the variation in flow rate, water temperature, and CO₂ fluxes during hydropoeaking compared to baseline conditions, for all data sets. Evasion fluxes at site S16, F₇, were higher on average by a factor of 1.4 (Mar23) to 5.0 (Jun23) during hydropoeaking. Variations in Δ and k contributed similarly to the increase in F₇ except for Nov23 data set, when the increase in k was responsible for 98% of the average increase in F₇. Transport fluxes φ₇ increased more strongly during hydropoeaking than evasion fluxes, i.e., by a factor of 4 (Nov23) to 13 (Jun23) on average. As a result, Δ (evaluated according to Eq. (7)) increased from between 3.2 and 6.2 km in baseline flow conditions, to between 8.2 and 12.3 km during hydropoeaking. The increase in φ₇ was largely dominated by the flow rate, which contributed 76% (Jun23) to 99% (Nov23) of the variation.

Because of the increase in Δ during hydropoeaking, carbopeaking could be observed clearly at site S17, located 7 km downstream of the hydropower outlet, at least for Mar23 data set (see Text S5 and Fig. S3 of the supplementary information). The confluence with the River Adige, xₑ HP, was located 8.2 km downstream of the outlets, while Δ increased to between 8.2 and 12.3 km during hydropoeaking ((xₑ HP − x₀ HP)/Δ = 0.7 to 1.0). As a result, the percentage of carbopeaking that evaded into the atmosphere before the confluence according to Eq. (25), SURF HP(xₑ HP)/CPeak, varied between 49% (Nov23) and 63% (Mar23). The residual 51% to 37% was released into the River Adige. In the absence of hydropoeaking, only between 8% and 27% of the CO₂ flux entering the hydropoeaking-affected reach at its upstream end would be conveyed to the River Adige.

### 3.5 Quantification of CO₂ Inputs

The comparison between the estimated CO₂ fluxes integrated over the whole length of the residual flow reaches, summarised in Fig. 8, reveals different dominant drivers at different times of the year. The magnitude of atmospheric CO₂ inputs (SURF) was largest during the Jun23 campaign (0.44 mol s⁻¹ during the day and −0.88 mol s⁻¹ during the night - negative input values indicate a decrease in riverine CO₂ stock, i.e., evasion to the atmosphere). The residual flow was a sink of atmospheric CO₂ during the day, and a source during the night, except for Nov23 campaign. The magnitude of night-time evasion intensities was always higher than the daytime intake from the atmosphere. The net input from the dams (IN) was significantly smaller for Nov23 data set during lake over-turning (−0.04 mol s⁻¹ to 0.00 mol s⁻¹) compared to the other data sets (0.03 mol s⁻¹ to 0.27 mol s⁻¹). Lateral inputs (LAT) (−0.07 to 0.02 mol s⁻¹) were consistently small.

Metabolic drivers (EM) were predominant during all campaigns, especially for Jun23 data set (−0.85 mol s⁻¹ during the day and 1.41 mol s⁻¹ during the night). Daytime EM was negative for Mar23 and Jun23 data sets (ER< GPP peak). In Aug23 during day-
Table 2. CO₂ parameters and fluxes at the hydropower diversion outlet during baseline flow and hydropeaking. The gas transfer rate \( k \) was evaluated according to Eq. (3) and the turnover length scale \( \Lambda \) according to Eq. (7).

<table>
<thead>
<tr>
<th></th>
<th>Mar23 baseline h-peak</th>
<th>Jun23 baseline h-peak</th>
<th>Aug23 baseline h-peak</th>
<th>Nov23 baseline h-peak</th>
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<tr>
<td>( Q ) (m³ s⁻¹)</td>
<td></td>
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<tr>
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<td>49.0</td>
</tr>
<tr>
<td>( k ) (m d⁻¹)</td>
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<td></td>
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</tr>
<tr>
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<tr>
<td>( \Lambda ) (km)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>average</td>
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<td>8.2</td>
<td>4.8</td>
<td>11.9</td>
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<tr>
<td>( \text{SURF}<em>{\text{HP}}(\text{HP})/C</em>{\text{peak}} ) (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
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<td>50</td>
</tr>
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<td>( T_w ) (°C)</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>( \Delta ) (µmol 1⁻¹)</td>
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<td></td>
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**Figure 8.** Quantification of the main CO$_2$ inputs and drivers (mol s$^{-1}$): metabolic input (EM); upstream input from the dams (IN); lateral inputs (LAT); carbonate speciation (CHEM); downstream transport (OUT); atmospheric exchange (SURF); carbopeaking (CPeak). (a): daytime; (b): nighttime. 95% confidence intervals are shown in the smaller sub-cells.

<table>
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<table>
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<th>Nov23</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td>0.89</td>
</tr>
</tbody>
</table>

In daytime, EM was positive (ER$>$GPP$_{\text{peak}}$), but the residual flow still acted as a sink for atmospheric CO$_2$ (SURF$>0$). In this case, CO$_2$ undersaturation was driven by carbonate dissolution (CHEM) (see Fig. 9), which was responsible for a ‘carbonate sink’ of $-0.39$ mol s$^{-1}$ (daytime) to $-0.61$ mol s$^{-1}$ (night time). A smaller but significant CO$_2$ input due to carbonate dissolution was observed instead for Mar23 ($0.33$ µmol l$^{-1}$) and Jun23 ($0.11$ µmol l$^{-1}$) data set.

The CO$_2$ input due to carbopeaking (CPeak) varied from $0.22$ mol s$^{-1}$ (Mar23) to $1.41$ mol s$^{-1}$ (Jun23), and was close to the sum of all CO$_2$ exchange and processing along the two residual flow reaches. In fact, except for Mar23 when hydropeaking was limited, CPeak accounted for between 50 % (night time, c.i. 44 % to 54 %) and 100 % (daytime, c.i. 84 % to 138 %) of the L1 norm of all remaining terms of the CO$_2$ bud-
get \(|EM| + |IN| + |LAT| + |CHEM| + |OUT| + |SURF|\). The magnitude of CPeak was particularly significant since carbopeaking was concentrated in time, during hydropeaking events, and in space, at the confluence of the diversion pipeline into the river, while the dominant CO$_2$ inputs (EM, CHEM, SURF) were the result of an integration along the two residual flow reaches.

4 Discussion

4.1 Drivers and scales of CO$_2$ fluxes in the residual flow reaches

The quantification of the main CO$_2$ inputs across all data sets (Fig. 8 and Fig. 9) demonstrates the variability of the contribution from different drivers across time scales. CO$_2$ fluxes along the residual flow reaches were dominated by metabolic inputs (EM), with a marked seasonal and diel dependence. Peak ecosystem activity was observed in Mar23 and Jun23 data sets, when the residual flow acted as a CO$_2$ sink during daytime. While the CO$_2$ input by respiration remained high throughout the year, we found that NEP was strongly reduced for Aug23 data set and Nov23 data set, when the CO$_2$ daytime NEP sink disappeared. The decrease in productivity for the Aug23 campaign can be explained by a storm (85 mm of rain over 24 hours) occurring 2 to 4 days before the measurements, causing substantial bed mobilisation and a reduction in light penetration owing to increased water turbidity (Peter et al., 2014; Bernhardt et al., 2018). The concurrent increase in lateral CO$_2$ input (indirectly, through carbonate dissolution) indicates a good lateral connectivity along the residual flow reaches.

The significant ‘carbonate sink’ (CHEM) observed for Aug23 data set was driven by a lateral inflow with high TA (6.06 ± 0.78 mmol l$^{-1}$), high pH (9.2 ± 0.1), but low CO$_2$ concentration ($\Delta_L = -12.0$ µmol l$^{-1}$), which mixed with the less alkaline water of the stream driving a shift of the carbonate equilibrium and hence a decrease in un-ionised [CO$_2$]. The strong contribution of CHEM for Aug23 data set was associated with a higher longitudinal gradient in TA and DIC along the residual flow (relative increase of 64% between the upstream dam and the diversion pipeline outlet, compared to an average of 30% for the other data sets), which was likely connected to the same storm event that affected NEP. The Mar23 data set had a relatively large (0.33 µmol l$^{-1}$) positive CHEM input which could not be explained by lateral inflow, since the Mar23 campaign followed a period of sustained lack of precipitation when the estimated increase in flow rate and TA due to lateral inputs were at a minimum (30% and 25% along the whole residual flow length, respectively). For this data set (and similarly but with lesser magnitude for Jun23 data set), the CHEM input was sustained by the carbonate buffer, which counteracted the rapid decrease in daytime [CO$_2$] driven by atmospheric evasion within a few kilometres downstream of the dam. Under conditions of relatively low [CO$_2$] and high alkalinity, in fact, carbonate buffering can account for up to 90% of emissions (Winnick & Saccardi, 2024).

The consumption or production of CO$_2$ by the ecosystem metabolism and to a lesser extent by carbonate dissolution were mostly compensated by the exchange with the atmosphere (SURF). The relatively large contribution of evasion fluxes despite the small magnitude of $\Delta$ along most of the residual flow was justified by the high gas transfer rate and consistent with the relatively short $\Lambda$ compared to the reach length. In fact, the overall length of the residual flow was approximately 8 × $\Lambda$, meaning that the whole CO$_2$ stock was renewed around 8 times through mostly metabolic activity and surface exchange.

$\Lambda$ is also representative of the distance from the upstream boundary of each reach where the CO$_2$ input from the dams (IN) vanished, approximately 2 km. The magnitude of IN changed according to the [CO$_2$] distribution inside the upstream reservoir but also according to the hydropower operation patterns. Specifically, sporadic hydropower activity during Mar23 resulted in a smaller input from the intermediate reservoir for this
data set, despite the higher CO$_2$ concentration inside the upstream reservoir. Almost
homogeneous CO$_2$ distribution and low CO$_2$ concentration in the upstream reservoir ex-
plained the lowest CO$_2$ input for Nov23 data set. For all measurements, the combined
input from the dams (IN), lateral inflow (LAT), and downstream export (OUT), led to
a relatively small net positive CO$_2$ influx into the system, which was compensated by
NEP (EM), surface evasion (SURF), and/or carbonate dissolution (CHEM).

4.2 Scaling and generality

Hydropower regulation can impact CO$_2$ fluxes by introducing additional inputs of
CO$_2$ in the tailwaters of the dam or during hydropeaking, and by altering the spatiotem-
poral scales of the fluxes. In the residual flow, the input of CO$_2$ from the dams was sig-
nificant but limited to a short distance of approximately 2 km. Beyond this distance, the
main drivers of CO$_2$ fluxes were those typical of non-regulated mountain streams, i.e.,
lateral inputs, ecosystem metabolism, and carbonate dissolution (Horgby, Boix Canadell,
et al., 2019; Horgby, Segatto, et al., 2019; Boix Canadell et al., 2021; Saccardi & Winn-
nick, 2021). We quantified peak primary productivity (GPP$_{peak}$) and respiration rates
(ER) between 2.52 to 4.97 $\mu$mol m$^{-2}$ s$^{-1}$ and between 1.35 to 7.94 $\mu$mol m$^{-2}$ s$^{-1}$, re-
spectively (see Table 1). A direct comparison with previous data sets in terms of GPP
and NEP (see Table S1 of the supplementary information) is difficult since these data
are typically integrated over at least 24 hours, whereas our estimates were representa-
tive of daily minima or maxima. ER, in contrast, is often assumed constant throughout
the day. Our estimates of ER were slightly higher than global average expectations for
temperate streams (1.56 $\mu$mol m$^{-2}$ s$^{-1}$; Battin et al. (2023)) and than measurements
in prealpine stream networks (Saccardi & Winnick, 2021; Roberts et al., 2007), but they
were within the range of other Alpine streams (0 to 19.6 $\mu$mol m$^{-2}$ s$^{-1}$; (Ulseth et al.,
2018)) and close to observations in regulated reaches in the Pyrenees (Aristi et al., 2014).

Expectations for the evasion flux intensity vary greatly in the literature because
of the strong heterogeneity of the drivers of CO$_2$ concentration and gas transfer rate. Our
estimates of average $F_{CO_2}$ in the residual flow reaches (~2.8 to 1.2 $\mu$mol m$^{-2}$ s$^{-1}$ at day-
time and 2.2 to 6.2 $\mu$mol m$^{-2}$ s$^{-1}$ at nighttime) were generally within the expected range
for mountain rivers (see Table S2 of the supplementary information for a detailed com-
parison with previous studies). In fact, global average expectations vary between 3.57 $\mu$mol m$^{-2}$ s$^{-1}$
(2.75 to 4.49) for streams and small rivers in the temperate zone (Lauerwald et al., 2015)
and 2.9 $\mu$mol m$^{-2}$ s$^{-1}$ (~1.43 to 137.4) in global mountain rivers (Horgby, Segatto, et
al., 2019). Higher evasion rates (18.0 to 43.1 $\mu$mol m$^{-2}$ s$^{-1}$ - Horgby, Boix Canadell, et
al. (2019)) were measured in Swiss Alpine streams with significantly steeper slopes than
in our study case.

CO$_2$ concentrations in the upstream reservoir were one order of magnitude smaller
than previously observed in tropical and subtropical reservoirs (Guérin et al., 2006; Kemenes
et al., 2016; Calamita et al., 2021; Wu et al., 2024), but comparable to the concentra-
tions observed in other Alpine reservoirs (Diem et al., 2012; Pighini et al., 2018). The
observed seasonal variations in average concentration and vertical distributions within
the reservoir were similar to those recorded in a sub-tropical reservoir (Wu et al., 2024).

Compared to a previous study by Calamita et al. (2021) focused on CO$_2$ fluxes and
dynamics downstream of a tropical reservoir, the drivers and the scales of CO$_2$ fluxes
in our study case were markedly different, as they were directly influenced by the design
of the hydropower system and by the different spatiotemporal scales and drivers of moun-
tain rivers. In the Kariba reservoir there were no residual flow reaches. The river slope
was much smaller (0.01 % to 0.03 %), and the discharge was much larger (~1500 m$^2$ s$^{-1}$),
therefore transport was expected to dominate over surface exchange. The variation in
CO$_2$ concentration downstream of the dam was by large the dominant component (~80%)
of carbopeaking (Calamita et al., 2021). Such a variation was caused by the selective ac-
Figure 9. Schematic representation of the main CO$_2$ fluxes (arrows) contributing to CO$_2$ river balance. The arrows width is proportional to the magnitude of the fluxes. The upper pathway (dashed rectangle) represents the two residual flow reaches subject to multiple CO$_2$ fluxes: input from the dams (IN); carbonate speciation (CHEM); lateral input (LAT); atmospheric exchange (SURF); metabolic input (EM); downstream transport (OUT). The lower pathway represents the hydropower system (diversion pipeline and intermediate reservoir) insulated from external inputs. The upstream reservoir and the diversion pipeline outlet constitute the upstream and downstream boundaries of the system, respectively, where the two pathways merge. Changes in the magnitude and direction of the fluxes indicate different dominant CO$_2$ processes in different seasons and times of day. In the residual flow reaches, ‘vertical’ (e.g., CHEM, LAT, SURF, and EM) fluxes are closely interconnected and predominant over ‘horizontal’ (IN and OUT) fluxes, as expected given the relatively short turnover length scale Λ. CO$_2$ inputs from the reservoir bypass the residual flow effectively through the diversion pipeline but become largely predominant during hydropeaking in the hydropeaking-affected reach.
tivation of multiple turbine intakes located above and below a strong vertical [CO₂] gra-

dient inside the reservoir.

In our study case, carbopeaking was governed by the increase in flow rate (76% to
99%) rather than concentration. Although the intakes that supplied the residual flow
and the hydropower system were located at different depths like in the Kariba reservoir,
this difference had a marginal effect on carbopeaking. Instead, the discontinuity in CO₂
concentration during hydropeaking was caused primarily by the decoupling of CO₂ fluxes
along the residual flow and the hydropower diversion pathways. This was the result of
(i) the spatial separation between the dam and the hydropower release outlet and (ii)
the disparity of temporal scales (e.g., transit time) between the residual flow and the di-
version system: the spatial separation drove a substantial drift of the CO₂ concentra-
tion along the long (relative to Λ) residual flow, leading to a very different concentra-
tion directly upstream of the hydropower diversion outlet; the scale disparity allowed min-
imal CO₂ leakage and equilibration within the hydropower system (including the inter-
mediate reservoir) so that the outflow from the diversion pipeline was still considerably
 supersaturated in CO₂. Our data revealed the importance of these two contributions to
the occurrence of carbopeaking: for Nov23 data set, the little metabolic activity in the
residual flow and the low supersaturation inside the reservoir limited the streamwise gra-
dient in CO₂ concentration along the residual flow making the spatial separation inef-
fective; for Mar23 data set, the magnitude of carbopeaking was inhibited by prolonged
inactivey of the hydropower system which drove an increase in transit time in the di-
version pipeline. In both cases, CPeak was smaller than in Jun23 and Aug23. Since the
mode of operation and geometry of the hydropower system in our study site is fairly com-
mon at least across the Alpine area, we expect these controls of carbopeaking to have
widespread relevance in this context.

5 Conclusions

Hydropower regulation can significantly alter the spatiotemporal distribution of
carbon and CO₂ fluxes by introducing shorter sub-daily variations and highly localised
inputs and by breaking the space-time continuity of the river network. These alterations
add to the natural heterogeneity and complexity of CO₂ drivers across river systems, es-
pecially in Alpine rivers, posing additional challenges for the quantification and under-
standing of CO₂ fluxes. We combined spatially and temporally resolved field data with
numerical modelling to quantify the main drivers of CO₂ fluxes along an Alpine river reg-
ulated by a cascading hydropower diversion system, which includes two reaches subject
to residual flow (minimum flow) regulation, and a reach subject to hydropoeaking. CO₂
drivers and dynamics in the residual flow were similar to those observed in non-regulated
rivers, except in the first ~ 2 km downstream of the dams where the reservoir released
a substantial additional CO₂ input. In contrast, carbopeaking had a strong impact on
the magnitude and dynamics of CO₂ fluxes across the whole hydropeaking-impacted reach.
We quantified an effect of carbopeaking comparable to the cumulative magnitude of all
CO₂ fluxes integrated along both residual flow reaches at peak daytime and night-time.
One of the main scientific objectives to enable the quantification and understanding of
the role of rivers in global carbon cycling is to determine to what degree direct (e.g., damming)
and indirect (e.g., climate change) anthropogenic perturbation affects riverine carbon
fluxes (Dean & Battin, 2024). Our work contributed to this objective by shedding new
light on the fundamental processes governing CO₂ fluxes in a regulated river within the
Alpine context, where the separation between natural and anthropogenic drivers is sub-
tle, and where climate change is rapidly transforming the hydrology and biogeochem-
istry of catchments. Upscaling and integrating our combined measurement/modelling
approach into future long-term observation systems will help clarify and predict changes
in riverine carbon cycling on a regional and global scale.
Open Research Section

All data sets for this research are openly available at the following URL: https://doi.org/10.5281/zenodo.11032052 (Dolcetti, 2024).

Acknowledgments

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References


Supporting Information for "Quantification of carbopeaking and CO$_2$ fluxes in a regulated Alpine river"

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2. Table S1 to S2

3. Figures S1 to S14
Text S1: Hydraulic measurements

The flow rate, cross-section-averaged flow velocity, and average water depth at the two measurement sites located upstream (S15) and downstream (S16) of the hydropower diversion outlet were calculated as follows:

i. the water level time series measured with loggers was referenced to a fixed datum and defined as \( h_{\text{ref}}(t) \);

ii. \( h_{\text{ref}}(t) \) and the water level measured at the gauging station were cross-correlated in order to find a representative lag delay \( \tau_d \) between the two data sets, representative of the physical separation between the measurement locations (for site S15, upstream of the hydropower outlet, only the portion of gauging data below a certain threshold - when it could be assumed that the outflow from the hydropower diversion system was negligible - was used for the correlation);

iii. the instantaneous average water depth was approximated as \( h(t) = (h_{\text{ref}}(t) - a_1) \), where \( a_1 \) was the unknown water depth datum;

iv. the parameters \( a_1, a_2, \) and \( a_3 \) were determined by fitting the rating curve \( Q(t) = a_2 h(t)^{a_3} \) against the time-shifted gauging flow rate data, \( Q_{\text{gauge}}(t + \tau_d) \), and measured water level, \( h_{\text{ref}} \);

v. the cross-section-averaged flow velocity was estimated as \( V(t) = Q(t)/(h(t)W) \), where \( W \) was the channel width at the measurement site.

For site S15, \( a_3 \) was fixed as \( a_3 = 5/3 \) per Manning’s formula to reduce the uncertainty due to the small observed range of variation in water level and flow rate. The estimated 95% confidence intervals for \( a_1 \) (water depth datum) and for the flow rate were ±2 cm and ±0.12 m\(^3\) s\(^{-1}\) (at site S15), and ±4 cm and ±0.24 m\(^3\) s\(^{-1}\) (at site S16), respectively. The
estimated velocity uncertainties were ±4 % at site S15 and ±10 % at site S16. The measurements of the flow rate at the gauging station at the times when the hydropower plant was not operating was employed to estimate $Q_{\text{baseline}}$. $Q_{\text{baseline}}$ varied between 6.0 m$^3$ s$^{-1}$ for the Mar23 data set and 10.0 m$^3$ s$^{-1}$ for the Nov23 data set, respectively. Temporal variations of $Q_{\text{baseline}}$ were found to be smaller than 10 % for each data set.

**Text S2: Estimate of the conditions in the intermediate reservoir**

The value of each scalar quantity $X$ (e.g., $X = [\text{CO}_2], T_w$, or TA) at time $t$ in the intermediate reservoir, $X_{\text{IR}}(t)$, was estimated based on a simple 0-dimensional mixing model:

$$X_{\text{IR}}(t) = \frac{\int_{t-\tau_r}^{t} [Q_{S7}X_{S7}(t) + Q_{\text{HP}}(t - \tau_d)X_{\text{HP}}] \, dt}{\int_{t-\tau_r}^{t} [Q_{S7} + Q_{\text{HP}}(t - \tau_d)] \, dt},$$

where $Q_{S7}X_{S7}(t)$ represents the input rate of the scalar $X$ coming from the upstream residual flow reach, approximated with the values at site S7, and $Q_{\text{HP}}(t - \tau_d)X_{\text{HP}}$ represents the input coming from the hydropower system. $Q_{S7}$ was calculated with Eq. (12) of the main text, while $X_{S7}(t)$ was measured. $X_{\text{HP}}$ was the value of the scalar $X$ measured at the hydropower intake level inside the upstream reservoir, and was assumed to be constant in time. Assuming that the two cascading hydropower diversion systems operated synchronously and with the same flow rate, $Q_{\text{HP}}$ was approximated with $Q_{\text{HP}} = Q_{\text{gauge}} - Q_{\text{baseline}}$, i.e., with the increase in flow rate observed downstream of the hydropower outlet. The integration time $\tau_r$ was related to the residence time of the intermediate reservoir, which varied between 3.6 hours (when $Q_{\text{HP}} = 66$ m$^3$ s$^{-1}$) and 87.1 hours (when $Q_{\text{HP}} = 0$), and was defined implicitly as follows:

$$\int_{t-\tau_r}^{t} [Q_{S7} + Q_{\text{HP}}(t)] \, dt = \beta V_{\text{IR}},$$

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where $V_{IR}$ was the volume of the intermediate reservoir (provided by DEE (2022)) and $\beta$ is an empirical correction factor ($\tau_r$ coincides with the residence time if $\beta = 1$). We used an empirical value of $\beta = 1/3$, which provided a reasonable agreement with the observed time series of $[\text{CO}_2]$ and $T_w$.

**Text S3: CO$_2$ measurements**

The water samples were all collected during the daytime. The air-tight sample containers were filled completely with water, and stored in a cold and dark environment before the analysis, which was performed in the laboratory within 48 hours of the collection. The pH was measured with a calibrated WTW pH315i analyzer (Xylem Analytics, Germany). The alkalinity was measured by manual titration on multiple 50 ml sub-samples using a 0.05M HCl solution. CO$_2$ concentration was measured with the headspace method (Koschorreck et al., 2020): five 30 ml water sub-samples were extracted from each sample with a syringe and equilibrated with 30 ml of air at known atmospheric CO$_2$ concentration; the dissolved CO$_2$ concentration in the original samples was then quantified based on the equilibrium headspace concentration measured with an EGM-4 environmental gas analyzer (PP Systems, USA), and further corrected for the effects of the carbonate system equilibration based on the measured alkalinity, using the *co2sys* model in Matlab (Lewis et al., 1998; Sharp et al., 2020). For a 1:1 headspace-to-water-volume ratio, the correction was as large as 160% for the samples with a lower CO$_2$ concentration $[\text{CO}_2] \sim 10$ $\mu$mol l$^{-1}$, and larger alkalinity TA $\sim 6$ mmol eq l$^{-1}$. Without carbonate system correction, the estimated dissolved CO$_2$ concentrations would display a spurious dependence on the headspace-to-water-volume ratio (Koschorreck et al., 2020). The accuracy of the correction was validated by analysing the same samples using different headspace-to-water-volume ratios.
between 0.5 and 2.0, which resulted in a residual \([\text{CO}_2]\) variability smaller than \(\pm 6\%\) for all samples, after the correction. Random error uncertainties of the alkalinity and \([\text{CO}_2]\) measurements were quantified in terms of the maximum variation within each set of sub-samples. The uncertainty of the alkalinity measurements was generally less than 0.1 mmol eq l\(^{-1}\), and comparable to the maximum resolution allowed by the titration procedure with the chosen protocol and instrumentation. The uncertainty of the \([\text{CO}_2]\) headspace measurements was typically less than 3 \(\mu\text{mol l}^{-1}\).

The \([\text{CO}_2]\) loggers were enclosed in a waterproof case, with their sensing head protected by a sheath made of hydrophobic sintered PTFE membrane (Virtek PMV27, Porex, USA) following Johnson et al. (2010) (Fig. S1a). The membrane was bonded and sealed onto a perforated steel cap using low-surface-energy double-sided adhesive tape (93015LE, 3M, USA). The head of the logger was encapsulated in a perforated protection case made of plastic and further covered with plastic mesh to prevent fouling. The \([\text{CO}_2]\) loggers were factory-calibrated. A cross-comparison test showed differences between the two loggers of less than \(\pm 1\ \mu\text{mol l}^{-1}\) for dissolved \(\text{CO}_2\) concentrations between 20 \(\mu\text{mol l}^{-1}\) and 145 \(\mu\text{mol l}^{-1}\).

**Text S4: Measurements of the gas transfer rate**

The calculation of the gas transfer rate \(k\) was based on Ulseth’s formula (Eq. (3) in the main text), where \(\varepsilon_d\) was estimated as \(\varepsilon_d = gSV\), \(g\) is the acceleration due to gravity, \(S\) is the channel slope, and \(V\) is the mean flow velocity. This formula was validated based on direct measurements of \(k\) conducted at site S16 and various locations between approximately 800 m and 600 m upstream of the outlet (Fig. S2). In these locations, the bed slope varied relatively rapidly in a range between 0.37 \% and 0.91 \%, and the river
alternated relatively calm waters with shallow rapids with considerable whitewater and aeration. At site S16, \( V \) was calculated through the rating curve derived according to Text S1. At the other locations upstream of the hydropower outlet, \( V \) was calculated as \( V = \alpha V_s \), where \( V_s \) was the surface velocity measured with a hand-held surface velocity radar (SVR2-01, Decatur Electronics, USA), and \( \alpha = 0.85 \) is a typical value of the surface-velocity-to-depth-averaged-velocity index (Hauet et al., 2018; Welber et al., 2016). The uncertainty of the estimates of \( \varepsilon_d \) reflects the variability of the velocity measurements across 10 repetitions.

Evasion fluxes were measured using an equilibration chamber mounted on a small anchored catamaran (Fig. S1b). The chamber was made of plastic, had an internal volume of 8.9 dm\(^3\), and was able to exchange CO\(_2\) with water through a bottom opening with an area of 7.56 dm\(^2\). Air-tight sealing with respect to the external atmosphere was ensured by a U-shaped folded sheath of plastic film running along the side of the chamber, in contact with the water surface. The volume between the folds of the sheath was filled with water, to maintain contact with water while minimising the disturbance to the flow. The chamber was equipped with a CO\(_2\) logger (K33 ELG, SenseAir, Sweden) with embedded temperature and humidity sensors, which was complemented by an additional pair of temperature and humidity sensors and connected to an Arduino acquisition module, as described by (Bastviken et al., 2015) and (Bastviken et al., 2020). The time series of CO\(_2\) partial pressure inside the chamber, \( p_{CO_2}(t) \) (Pa), recorded with a sampling period of 30 seconds, were fitted with the following exponential function of time \( t \) (Vingiani et al., 2021),

\[
p_{CO_2}(t) = \frac{1}{K_0} \left\{ [CO_2] + [K_0 \cdot p_{CO_2}(t_0) - [CO_2]] \exp \left( -k A_e \frac{p_{atm} K_0}{n} (t - t_0) \right) \right\},
\]

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where $A_c$ is the area of the chamber opening (m$^2$), $p_{\text{atm}}$ is the atmospheric pressure (Pa), $n$ is the number of CO$_2$ moles in the chamber volume (mol m$^{-3}$), and $t_0$ is the initial time of deployment of the chamber (s). The CO$_2$ solubility $K_0$ was calculated according to Wanninkhof (1992). The gas transfer rate $k$ and initial time $t_0$ were calculated by a least-squares fitting of the measured data, assuming $p\text{CO}_2(t_0) = p\text{CO}_2\text{air}$.

The 95% confidence intervals for $k$ were calculated based on the Jacobian of the least-squares fitting procedure. Larger uncertainties at the higher $k$ were due to the smaller number of degrees of freedom when the equilibration inside the chamber was faster, and to the presence of relatively steep water waves. The latter were found to cause sharp discontinuities in the $p\text{CO}_2$ time series which were attributed to the leakage of atmospheric air into the chamber, either through small gaps between the plastic sheath and the deformed water surface caused by the surface motion and internal pressure transients, or through bubbles entrained by the overturning and breaking of water waves, escaping below the sheath. The data were trimmed to avoid such discontinuities, limiting the proportion of data (degrees of freedom) that could be used for the fitting and increasing the uncertainties. Rigid chamber walls protruding further into the water would have reduced the air leakage but increased the disturbance to the turbulent mixing dynamics.

**Text S5: Measurements at site S17**

Simultaneous continuous measurements of CO$_2$ fluxes at sites S16 and S17 (located 0.77 km and 7.14 km downstream of the diversion outlet, respectively) were conducted during the Mar23 campaign. These measurements were conducted 13 days after the measurements at sites S15 and S17, shown in Fig. S10. Two separate hydropeaking events could be identified, although only the first event was associated with an observable
increase in CO\textsubscript{2} concentration at both sites. This anomaly was attributed to the mixing dynamics in the intermediate reservoir, which will have been particularly complex given the pulsed hydropeaking pattern during the second event and due to a precipitation event during the 12 hours preceding the measurements. Precipitation was also responsible for the irregular pattern of \( \Delta \) observed at site S16 during the second day of measurement. The peak in CO\textsubscript{2} observed at site S17 during the first hydropeaking event was delayed and slightly longer in duration than at site S16, suggesting the presence of dispersion. Diel fluctuations in [CO\textsubscript{2}] were also larger in amplitude at site S17 compared to site S16, with higher nighttime concentrations. This was justified by the low (compared to the residual flow reaches) gas transfer rate in the reach between sites S16 and S17, which sustained higher values of \( \Delta \) with equal external lateral inputs and/or biogeochemical input.

**Open Research Section**

All data sets for this research are openly available at the following URL: https://doi.org/10.5281/zenodo.11032052 (Dolcetti, 2024).

**References**


Attermeyer, K., Casas-Ruiz, J. P., Fuss, T., Pastor, A., Cauvy-Fraunié, S., Sheath, D., ... others (2021). Carbon dioxide fluxes increase from day to night across european streams. *Communications Earth & Environment, 2*(1), 118.

Table S1. Summary of published ecosystem metabolism data. For the present study, GPP and NEP indicate peak values (at daytime and nighttime). For all the remaining studies, GPP and NEP are integrated over 24 hours, therefore the values expressed in mol/m²s are representative of daily averages of the instantaneous fluxes.

<table>
<thead>
<tr>
<th>Reference</th>
<th>GPP (µmol/m²s)</th>
<th>ER (µmol/m²s)</th>
<th>NEP (µmol/m²s)</th>
<th>location</th>
<th>notes</th>
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<td>Present study</td>
<td>1.35 to 7.94</td>
<td>2.17 to 4.97</td>
<td>−2.97 to 0.82</td>
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<td>peak values</td>
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<td>(Boix Canadell et al., 2021)</td>
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<td>high-altitude Alpine streams</td>
<td>annual average</td>
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<td>(Saccardi &amp; Winnick, 2021)</td>
<td>0.04 to 1.00</td>
<td>0.00 to 1.50</td>
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<td>prealpine streams</td>
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<tr>
<td>(Battin et al., 2023)</td>
<td>0.87</td>
<td>1.56</td>
<td></td>
<td>global temperate streams</td>
<td>annual average</td>
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<td>(Ulseth et al., 2018)</td>
<td>0.00 to 10.51</td>
<td>−0.01 to 19.60</td>
<td>−14.9 to 5.68</td>
<td>Austrian Alps</td>
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<td>(Aristi et al., 2014)</td>
<td>0.20 to 0.83</td>
<td>0.33 to 1.74</td>
<td>−0.31 to −0.13</td>
<td>Spanish Pyrenees</td>
<td>non-regulated reach</td>
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<td>(Roberts et al., 2007)</td>
<td>0.48 to 10.52</td>
<td>1.28 to 1.63</td>
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<td>headwater stream</td>
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<td>Reference</td>
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<td>7.38 to 10.2</td>
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<tr>
<td>Austrian Alps</td>
<td>Peter et al., 2014</td>
<td>4.16 (3.7 to 5.7)</td>
<td>3.60 to 6.21</td>
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<td>Prealpine river network</td>
<td>Crawford et al., 2015</td>
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<td>(daytime)</td>
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<tr>
<td>Italian Alps</td>
<td>Saccardi &amp; Winnick, 2021</td>
<td>3.57 (2.3 to 4.9)</td>
<td>2.15 to 6.23</td>
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<td>Prealpine river network</td>
<td>Scholker et al., 2016</td>
<td>0.89 to 1.11</td>
<td>(daytime)</td>
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<td>NW Sweden</td>
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<td>Swiss Alps</td>
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<td>European streams</td>
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<td>Peter et al., 2014</td>
<td>9.78 (2.3 to 69.9)</td>
<td>(daytime)</td>
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**Table S2.** Gas transfer rate and CO2 surface evasion intensity in the residual flow regions compared to published data.
Facilitating the use of low-cost methane (CH$_4$) sensors in flux chambers—calibration, data processing, and an open-source make-it-yourself logger. *Biogeosciences, 17*(13), 3659–3667.


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Figure S1. Pictures of the CO$_2$ measurement instrumentation. (a): [CO$_2$] logger, with hydrophobic PTFE membrane sheath; (b): anchored catamaran equipped with the CO$_2$ chamber.
Figure S2. Comparison of measured (symbols) and predicted (solid line - based on Eq. (3) of the main text) gas transfer velocity as a function of turbulence kinetic energy dissipation rate, $\varepsilon_d$. Blue circles: measurements in the residual flow. Yellow triangles: measurements at site S16. Dashed line: transition between low-energy ($\varepsilon_d < 0.018 \text{ m}^2 \text{ s}^{-3}$) and high-energy ($\varepsilon_d > 0.018 \text{ m}^2 \text{ s}^{-3}$) stream regimes according to Ulseth et al. (2019).
Figure S3. Time series of (a): flow rate, $Q$; (b): water temperature, $T_w$; (c): excess CO$_2$ concentration, $\Delta$; (d): excess CO$_2$ mass flux, $\phi_{CO_2} = Q\Delta$; (e): gas transfer rate, $k$; (f): CO$_2$ evasion flux intensity, $FCO_2$, recorded during the Mar23 campaign at sites S16 and S17 in the hydropeaking-impacted reach.
Figure S4. Variation of the non-dimensionalised turnover length scale $\Lambda/h$ with the turbulent kinetic energy dissipation rate, $\varepsilon_d$, according to Eq. (11) in the main text. Dashed line: transition between low-energy ($\varepsilon_d < 0.018 \text{ m}^2 \text{s}^{-3}$) and high-energy ($\varepsilon_d > 0.018 \text{ m}^2 \text{s}^{-3}$) stream regimes according to Ulseth et al. (2019).
Figure S5. Temporal variation of the water temperature $T_w$ at multiple sites (S1, S7, S9, S15) along the residual flow as a function of the time of day, measured with the [CO$_2$] loggers during the four measurement campaigns. Solid, black: measured $T_w$. Dashed, orange: sampled $T_w$ inside the upstream reservoir (dotted lines bind the uncertainty interval). Background colours represent the logarithm of measured light intensity (dark blue colour indicates nighttime). Shaded regions indicate periods for which measurements were not available.
Figure S6. Water temperature profiles in the upstream reservoir. Dashed line: diversion pipeline intake level. Dashed-dotted line: residual flow intake level.

Figure S7. Chlorophyll $a$ profiles in the upstream reservoir. Dashed line: diversion pipeline intake level. Dashed-dotted line: residual flow intake level.

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Figure S8. pH profiles in the upstream reservoir. Dashed line: diversion pipeline intake level. Dashed-dotted line: residual flow intake level.

Figure S9. Total alkalinity profiles in the upstream reservoir. Dashed line: diversion pipeline intake level. Dashed-dotted line: residual flow intake level.
Figure S10. Time series of (a): flow rate, $Q$; (b): water temperature, $T_w$; (c): excess CO$_2$ concentration, $\Delta$; (d): excess CO$_2$ mass flux, $\phi_{CO_2} = Q\Delta$; (e): gas transfer rate, $k$; (f): CO$_2$ evasion flux intensity, $F_{CO_2}$, recorded during the Mar23 campaign in the baseline flow (site S15 - orange) and in the reach subject to hydropeaking (site S16 - black). Dashed-dotted: conditions in the upstream reservoir, at the hydropower diversion intake. Dashed line: conditions in the intermediate reservoir.
Figure S11. Time series of (a): flow rate, $Q$; (b): water temperature, $T_w$; (c): excess CO$_2$ concentration, $\Delta$; (d): excess CO$_2$ mass flux, $\phi_{CO_2} = Q\Delta$; (e): gas transfer rate, $k$; (f): CO$_2$ evasion flux intensity, $F_{CO_2}$, recorded during the Aug23 campaign in the baseline flow (site S15 - orange) and in the reach subject to hydropoeaking (site S16 - black). Dashed-dotted: conditions in the upstream reservoir, at the hydropower diversion intake. Dashed line: conditions in the intermediate reservoir.
Figure S12. Example of modelled (lines) and measured (triangles) parameters distribution along the residual flow, based on the Mar23 data set. The grey shaded areas indicate 95% confidence intervals of fitting. (a): DIC concentration, [DIC]; (b): CO₂ excess concentration, Δ; (c) pH; (d): total alkalinity, TA; (e): water temperature, $T_w$. 
Figure S13. Example of modelled (lines) and measured (triangles) parameters distribution along the residual flow, based on the Aug23 data set. The grey shaded areas indicate 95% confidence intervals of fitting. (a): DIC concentration, [DIC]; (b): CO$_2$ excess concentration, $\Delta$; (c) pH; (d): total alkalinity, TA; (e): water temperature, $T_w$. 

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Figure S14. Example of modelled (lines) and measured (triangles) parameters distribution along the residual flow, based on the Nov23 data set. The grey shaded areas indicate 95% confidence intervals of fitting. (a): DIC concentration, [DIC]; (b): CO₂ excess concentration, Δ; (c) pH; (d): total alkalinity, TA; (e): water temperature, T_w.