Hydrological and biogeochemical controls on temporal variations of dissolved carbon and solutes in a karst river, South China

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Abstract

Background: Understanding the responses of riverine dissolved carbon dynamics and chemical weathering processes to short-term climatic variabilities is important to understand the Surface-Earth processes under ongoing climate change. Temporal variations of solutes and stable carbon isotope of dissolved inorganic carbon (δ13C_DIC) were analysed during a hydrological year in the Guijiang River, South China. We aimed to unravel the chemical weathering processes and carbon dynamics in karst areas under ongoing climate changes.

Results: Significant positive relationships were found between weathering rates and climatic factors (i.e. temperature and discharge) over the hydrological year. The total flux of CO2 consumption (760.4 × 10^3 mol/km^2/year) in the Guijiang River was much higher than the global mean flux, with a higher CO2 consumption capacity in the Guijiang River relative to most other global rivers. Chemical weathering fluxes in this karst area showed high sensitivity to global climate change. CO2 evasion during the warm–wet seasons was much lower than those during cold–dry seasons. Light δ13C_DIC values occurred under high-flow conditions, corresponding with the high temperatures in high-flow seasons. IsoSource modelling revealed that biological carbon could account for 53% of all dissolved inorganic carbon (DIC), controlling the temporal carbon variabilities.

Conclusion: This study quantitatively evaluated the temporal variations in CO2 fluxes and carbon cycling of karstic river systems and demonstrated that riverine carbon cycling will have a higher sensibility to ongoing global climate change. High discharges accelerate solutes transport, with relatively large quantities of 13C-depleted carbon being flushed into rivers. Meanwhile, high temperatures also accelerate organic carbon mineralisation, producing high content of soil CO2, whose influx can shift the 13C-depleted values in the high-flow seasons. Taken together, biological carbon influx should be responsible for the temporal carbon dynamics.

Keywords: Dissolved carbon, Karst landscape, δ13C_DIC, CO2 outgassing, Carbon cycling

Background

Understanding the responses of carbon cycling to short-term climate variabilities (i.e. temperature and discharge) is necessary to investigate the effects of future global climate change on Surface-Earth processes [1, 2]. Of the different components within the global carbon cycle, the river system is the key channel, transporting dissolved carbon from the continents to the oceans [3]. Rock weathering is one of the main sources of dissolved carbon in river systems, which could consume atmospheric CO2 by converting it into dissolved inorganic carbon (DIC). Therefore, chemical weathering processes have a significant effect on modulating atmospheric CO2, and thereby affect global climate change.

Silicate weathering involves carbonic acid and leads to the net sequestration of CO2, which can be defined by Eq. (1). Carbonate rocks cover approximately 12%
of the Earth’s ice-free land area [4], with thin soil cover and well-developed conduit networks forming large underground drainage systems [5]. The dissolution of carbonate rocks consumes ~0.15 Pg of atmospheric CO₂ each year, based on the geochemical data from large rivers worldwide [6]. And the produced DIC is then transported to the ocean, which plays an important role as a carbon sink. On the other hand, as carbonate weathering can be consumed by other acids (e.g., nitric, sulfuric, and organic acids), it can lead to CO₂ release rather than CO₂ consumption [7], which can be expressed as Eqs. (3 and 4).

\[
\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{SiO}_2 \tag{1}
\]

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} \tag{2}
\]

\[
\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} + 2\text{N}_2\tag{3}
\]

\[
2\text{CaCO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SO}_4^{2-} \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{SO}_4^{2-} + \text{Ca}^{2+} \tag{4}
\]

Chemical weathering and related CO₂ consumption fluxes are highly affected by hydrological conditions. However, the coupled effects of hydrological and biogeochemical processes on CO₂ fluxes in river systems remain unclear. For example, the fluxes of CO₂ consumption are calculated by discharge and the dissolved solute content, yet the covariation between the above two variables could induce great uncertainty [21]. Additionally, seasonal and diurnal variations in CO₂ degassing may result from differences in solar radiation and temperature, causing changes in the content of DIC and CO₂ [22]. Thus, to reduce the overall uncertainty, high-frequency (monthly or even daily scales) sampling and analyses of hydrochemistry, isotopes, synchronous hydrology and meteorology of river systems are required.

The Guijiang River catchment is located in Southwest China, which is one of the largest karst regional centers in the world, exhibiting a high sensibility responding to chemical weathering processes under changing climate conditions. It is an ideal study object to understand carbon dynamics and weathering processes in response to various climatic conditions in karst rivers.

Here, the Guijiang River catchment was selected to analyse the high-frequency contents of dissolved solutes and δ¹³CDIC, aiming to (1) depict the temporal variations of solute dynamics in a typical karstic catchment; (2) obtain information on the fluxes of chemical weathering and CO₂ consumption in response to climatic variabilities; (3) quantify the potential sources of DIC; and (4) estimate the vertical CO₂ fluxes from surface waters into the atmosphere.

Materials and methods

Site description and data source

The Guijiang River catchment (23° 28′–23° 55′ N, 110° 05′–110° 29′ E) is located in the northeastern Guangxi Province of South China. The study catchment has a length of 426 km from north to south, with a drainage area of 19,288 km². It originates from the Maoer Mountain, with an elevation of approximately 2141 m, and then flows southward through Guilin, where a typical karstic landscape is developed, finally entering the Xijiang River. Its landscape contains mainly hills and mountains with significant topographic relief. Karstic topography in the study catchment is well-developed (Fig. 1). Specifically, the upper–middle catchment is well-developed (Fig. 1). Additionally, seasonal and diurnal variations in CO₂ degassing may result from differences in solar radiation and temperature, causing changes in the content of DIC and CO₂ [22]. Thus, to reduce the overall uncertainty, high-frequency (monthly or even daily scales) sampling and analyses of hydrochemistry, isotopes, synchronous hydrology and meteorology of river systems are required.

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and Triassic carbonate rocks including sulfide-rich limestones and dolomites. The bedrocks distributed in the middle–lower catchment area are mainly Precambrian metamorphic rocks (gneiss) and igneous rocks (primarily granite). Few evaporites are scattered throughout the Guijiang River catchment, and no salt-bearing strata have been discovered [23–25].

The whole catchment is controlled by the subtropical monsoon climate. Here, the total annual precipitation varies from 1900 to 2700 mm, and most of the rainfall events (~80%) occur in the rainy season (April–September), while the mean annual temperature is ~19–21 °C [26, 27]. The study catchment is mainly hilly (40.8%) and highland (42.8%), has a low to medium degree of erosion, with a mean soil erosion rate of 157.7 t km$^{-2}$ year$^{-1}$ [28].

The main types of land use are forests (67.3%) and cultivated lands (10.8%) [28].

The sampling site was situated at the outlet of the Guijiang River (Fig. 1), which is ~39 km away from the mainstream of the Xijiang River. We collected 8 river water samples from October of 2013 to May of 2014 on monthly intervals during the low-flow season, while from June to September of 2014, 23 river water samples were collected based on the changing discharge conditions during the high-flow season. The sampling and analysis method for the content of major ions, dissolved organic carbon (DOC), and carbon isotopes ($\delta^{13}C_{\text{DIC}}$) were same to Liu et al’s study [29]. Daily river discharge ($Q$) was collected online from the Ministry of Water Resources (http://www.hydroinfo.gov.cn/), while water surface evaporation (WSE), water temperature (WT), daily precipitation (DP), and suspended sediment loads (SSL) were collected from the Hydrological Yearbook published by the Pearl River Conservancy Commission [30, 31].

Fig. 1 Map showing the sampling location and geological setting of the Guijiang River catchment, which is [16] modified from Zhong et al.
Data analysis

**LOADEST modelling**

The fluxes of major ions, DIC, and DOC contents with corresponding daily $Q$ were estimated by the Load Estimator (LOADEST) [32], which was performed using LoadRunner software [33]. According to the Akaike information criterion (AIC) in LOADEST [33], the following model was selected to calculate the daily loads of dissolved solutes and DIC:

$$\text{In Load} = a_0 + a_1\ln Q + a_2\sin(2\pi d\text{time}) + a_3\cos(2\pi d\text{time}) + a_4d\text{time},$$

(5)

while the DOC loads estimation uses the following model:

$$\text{In Load} = a_0 + a_1\ln Q + a_2\ln(Q^2 + a_3\sin(2\pi d\text{time}) + a_4\cos(2\pi d\text{time}) + a_5d\text{time} + a_6(d\text{time})^2,$$

(6)

where $Load$ is the content of constituents (kg/days), $a_0$ to $a_6$ are the model coefficients, $d\text{time}$ and $Q$ indicate the centre of decimal time and discharge, respectively. The LOADEST conducts calibrations and calculates fluxes based on an Approximate Maximum Likelihood Estimation (AMLE) algorithm. The values of $\delta^{13}\text{CDIC}$ were calculated based on the estimated $\text{HCO}_3^-$ content.

**The concentration–discharge (C–Q) relationships**

The $C$–$Q$ relationships of riverine materials express the transport and reactions of dissolved loads with changing discharge in catchments [13, 34, 35]. In this study, a power-law function was fitted to express the $C$–$Q$ relationships as follows:

$$C = a \times Q^b,$$

(7)

where $b$ is an index for mirroring the behaviors of solutes in response to discharge variabilities. If $b \approx 0$, $C$ is equal to the constant $a$, independent of variations in $Q$; when $-1 < b < 0$, dilution and chemostatic behaviors coexist. When $b = -1$, the solute content decreases with high water flux, and $Q$ is the only control on $C$, while if $b > 0$, the solute content increases as water flux increases and shows a flushing behavior.

The coefficients of variation of the solute contents and $Q$ ($\text{CV}_C$/CV$_Q$) are helpful to delineate the behaviors of solute contents responding to various water fluxes [36], and can be expressed as follows:

$$\text{CV}_C/\text{CV}_Q = (\mu_Q\sigma_C)/\left(\mu_C\sigma_Q\right),$$

(8)

where $\mu_C$ and $\mu_Q$ are the average values of solute contents and discharges, $\sigma_C$ and $\sigma_Q$ are their standard deviations. Chemostatic behavior ($b \approx 0$, CV$_C$/CV$_Q$$< 1$) can be defined as the buffering of variations in content as compared to the null hypothesis.

**Calculation of the calcite saturation, pCO2 and FCO2**

The calcite saturation index (SIc) and $p\text{CO}_2$ of water samples were calculated by mass action relationships described by water temperatures and corresponding thermodynamic constants [17]. The evasion of CO$_2$ from surface water to the atmosphere will happen when $p\text{CO}_2$ values of the river water are much larger than those in the ambient air. For the studied river, the CO$_2$ diffusion flux can be calculated as follows:

$$F_{\text{CO}_2} = k \times K_H \times \left(p\text{CO}_2(\text{aq}) - p\text{CO}_2(\text{air})\right),$$

(9)

where $F_{\text{CO}_2}$ (mmol/m$^2$/days) denotes the diffusion flux of CO$_2$ across the water–air interface, $k$ is the gas exchange rate (cm/h), $K_H$ represents Henry’s constant, $p\text{CO}_2(\text{aq})$ and $p\text{CO}_2(\text{air})$ are the partial pressure of CO$_2$ at the water surface and atmosphere. If $F_{\text{CO}_2} > 0$, CO$_2$ fluxes evasion from the water to the atmosphere, while if $F_{\text{CO}_2} < 0$, CO$_2$ invasion from atmosphere to water. 400 μatm for atmospheric CO$_2$ content was employed, and $k$ represents a temperature-dependent Schmidt number ($Sc_T$) of fresh water,

$$k = k_{600} \times (600/Sc_T)^{0.5},$$

(10)

With

$$Sc_T = 1911.1 - 118.11T + 3.4527T^2 - 0.04132T^3,$$

(11)

where $T$ represents the in situ water temperature (°C), and $k_{600}$ represents the $k$ for CO$_2$ at 20 °C in fresh water. The value of $k$ depends on river size [37], which is generally divided into two kinds, one is for the small river with a channel < 100 m, while the other is for the large river with a channel > 100 m. The main channel of the Guijiang River width is usually > 100 m, so $k_{600} = 4.46 + 7.11 \times u_{10}$ ($u_{10}$ represents the average wind speed at 10 m above rivers) was employed here. During the sampling period, the wind speed at Wuzhou ranged from 1.2 to 2.9 m/s, averaging 1.8 m/s, showing constant with previous related research [18, 19, 37].
Results

Hydrological parameters and hydrochemical characteristics

The hydrological parameters for the Guijiang River catchment are shown in Fig. 2. At the Pingle hydrological station, the WT records showed significant seasonal variations that followed meteorological trends. The highest WT reached 31.5 °C in the wet season, and intense evaporation at the water surface was in accordance with the high-temperature conditions (Fig. 2). In the dry season, as the WT dropped, evaporation at the water surface decreased accordingly. River water discharge was low in October of 2013, reaching two small peaks in November and December, and then declining rapidly and stabilizing at a minimal discharge from January to March of 2014. In April of 2014, there was a third small peak. Subsequently, discharge fluctuated mainly in the wet period, and reached its largest peak in June of 2014. The SSL also presented similar patterns with variations in discharge.

EC values had a wide range changing from 121 to 210 μS/cm, with a mean of 150 μS/cm. The amount of total dissolved solids (TDS) varied from 105 to 185 mg/L, with a mean discharge-weighted content (MDWC) of 118 mg/L, higher than the global discharge-weighted mean (97 mg/L) [38]. TZ+ is the total cationic charge \( (TZ^+ = 2Ca^{2+} + 2Mg^{2+} + Na^+ + K^+) \), and \( TZ^- \) is the total anionic charge \( (TZ^- = HCO_3^- + 2SO_4^{2-} + NO_3^- + Cl^-) \). The normalized ionic charge balances (NICB = \([TZ^+ - TZ^-] \times 100\% / (TZ^+ + TZ^-)\) were well-balanced (below 5%), implying that the unanalyzed ions amounted to negligible proportions. The MDWC values of cations were as follows, \( Ca^{2+} \) (22.7 mg/L) > \( Mg^{2+} \) (2.6 mg/L) > \( Na^+ \) (1.3 mg/L) > \( K^+ \) (0.9 mg/L), with the sum of \( Ca^{2+} \) and \( Mg^{2+} \) accounting for 94% of \( TZ^+ \). Meanwhile, the MDWC values of anions were as follows, \( HCO_3^- \) (67.9 mg/L) > \( SO_4^{2-} \) (9.3 mg/L) > \( NO_3^- \) (3.9 mg/L) > \( Cl^- \) (2.0 mg/L), with the sum of \( HCO_3^- \) and \( SO_4^{2-} \) accounting for 91% of \( TZ^- \). The Guijiang River yielded a predominance of \( HCO_3^- \), \( SO_4^{2-} \), \( Ca^{2+} \), and \( Mg^{2+} \), consistent with other karstic rivers (Fig. 3) [13, 14, 16, 27, 39].

Characteristics of dissolved carbon

In this study, the DOC contents fluctuated between 0.7 mg/L in the wet season and 2.4 mg/L in the dry season, with the MDWC value of 1.3 mg/L. Most of

![Fig. 2](image_url)  
Fig. 2 Hydrological parameters in the Guijiang River during the whole hydrological year, including daily water temperatures and surface evaporation, suspended sediment loads, and discharge and precipitation.
the river water samples contained less than 2 mg/L of DOC. Among the DIC species (i.e. carbonate (CO$_3^{2-}$), HCO$_3^-$, carbonic acid (H$_2$CO$_3$), and CO$_2$(aq)), HCO$_3^-$ was the predominant component, accounting for 95% (range of 84–98%) of DIC. The values of δ$^{13}$C$_{DIC}$ ranged from $-$16.9‰ during the wet season to $-$9.2‰ during the dry season (mean $-$13.6‰), exhibiting distinct temporal variations. The pCO$_2$ values ranged from 727 μatm to 6580 μatm, with a mean value of 1866 μatm, which were generally greater than the atmospheric pCO$_2$. The calcite saturation index (SIc) ranged from approximately $10^{-3.4}$ to $10^{-2.9}$ (mean $10^{-3.2}$). All river water samples had SIc values of > 0, and water samples were oversaturated with respect to calcite. F$_{CO2}$ values showed seasonal variations and ranged from 23 mmol/m$^2$/days (May of 2014) to 264 mmol/m$^2$/days (Jan of 2014), averaging 84 mmol/m$^2$/days in the study river.

**Discussion**

**Solute behaviors to hydrological variabilities**

For the Guijiang River, the content of most solutes displayed negative power-law relationships with discharge (Fig. 4a), showing that most solutes decreased with increasing discharge. However, CV$_C$/CV$_Q$<1 indicates that although the C–Q relationships showed different behaviors, the total solute content exhibited much less variability in response to changes in discharge (Fig. 4b). Geogenic ions (e.g. Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, Na$^+$, and K$^+$) consistently showed dilution but chemostatic behaviors in the study river, which are similar to those in the Xijiang River and Yujiang River [16, 29]. Ions from carbonate rocks (e.g. Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$) showed intense chemostatic behaviors when compared to those from silicate weathering (e.g. Na$^+$ and K$^+$), which may be due to the rapid kinetics of carbonate rock weathering [40]. Meanwhile, Na$^+$ and K$^+$ exhibited significant dilution patterns,
with higher \( CV_C/CV_Q \) ratios and more negative \( b \) values compared to \( Ca^{2+}, Mg^{2+}, \) and \( HCO_3^- \), suggesting that ions from silicate weathering have a higher sensibility to increasing water flux when compared to carbonate-sourced ions [16]. Another important source of \( K^+ \) was associated with the cation exchange between water and soil [40], especially during storm events [35]. \( Cl^- \) yielded lower \( b \) values and higher \( CV_C/CV_Q \) ratios, suggesting that \( Cl^- \) showed the strongest dilution effects among all solutes. The \( C–Q \) relationship for \( SiO_2 \) exhibited a slight flushing behavior, indicating that variations in discharge had little impact on variations in \( SiO_2 \) content, which is associated with secondary mineral precipitation [16]. A weathered zone can store or accumulate silica, until rapid flushing of the weathered zone by storm pulses induces dissolution and entrainment in rivers [41–43]. The \( C–Q \) patterns of \( SO_4^{2-} \) and \( NO_3^- \) showed similar behaviors, and both of them were greatly affected by anthropogenic inputs and biological activities. Sulfide-rich minerals in coal-bearing deposits within the bedrock formations underlay the study area, which serves as a geological source of \( SO_4^{2-} \) in this catchment [39]. Exogenous sources are often linked with \( SO_4^{2-} \) and \( NO_3^- \), which are generally correlated with chronic and elevated atmospheric precipitation, or with the application of chemical fertilizers during agricultural activities [35]. The Guijiang River catchment lies in South China, which is subject to intense acid rain [39, 44]. Additionally, it has been reported that the nitrogen fertilizer consumption budget accounted for \( \sim (7.25–7.47) \times 10^8 \) kg·N·year\(^{-1}\) from 2012 and 2014 [45]. Biologically associated solutes, such as DOC, further yielded the lowest \( CV_C/CV_Q \) and most negative \( b \), presented in Fig. 4b, showing a similar dilution behavior, and implying that the variability in DOC content was also predominantly controlled by variations in discharge in this study area.

Responses of weathering processes to climatic variabilities

Riverine materials are mainly sourced from atmosphere inputs, rocks weathering, and anthropogenic activities (e.g. coal combustion). Based on the forward model using Additional file 1: Eqs. (S1–S10), we found that dissolved solutes in this studied river were mainly derived from carbonate weathering, which accounted for a mean of 56.8% of total cations in the Guijiang River, followed by atmospheric inputs (28.1%), anthropogenic activities (7.8%), sulfide oxidation (3.1%), silicate weathering (2.6%), and gypsum dissolution (1.5%). The contributions of sulfide oxidation and gypsum dissolution were generally <5% in this study area.

For most end-members, especially atmospheric inputs and silicate weathering, the contributions
generally showed significant dilution behavior in response to increases in discharge. Meanwhile, the percentage of carbonate sources was shown to be relatively stable for the hydrological year (Figs. 5a, b). These behaviors can be attributed to the dissolution kinetic characters of carbonate weathering, which may be enhanced by the generation of soil CO$_2$ and associated biological processes under warm and wet conditions [46]. Similar observations have been reported in monsoonal rivers worldwide [16, 47].

The products of silicate weathering, such as, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, and dissolved SiO$_2$, were used to calculate the silicate weathering rate (SWR), while the Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$ contents from carbonate dissolution produced by carbonic and sulfuric acids were used to estimate the carbonate weathering rate (CWR). The equations for these rates are presented in Additional file 1 as equations (S11) and (S12), respectively. The SWR ranged from 0.4 t/km$^2$/year in the dry period to 78.6 t/km$^2$/year in the wet period, averaging 6.5 t/km$^2$/year, which was lower than the River Rhône (14.4 t/km$^2$/year).

**Fig. 5** a mean monthly contributions from all end-members; b rates of physical and chemical weathering; c variations in temperature and discharge; d the CO$_2$ consumption fluxes of silicates and carbonates; e linear relationships between CO$_2$ consumption fluxes of silicates and carbonates versus discharge in the Guijiang River during the hydrological year.
and Yujiang (7.6 t/km²/year) [29], but much higher than the River Seine (1.2–2.6 t/km²/year) [48]. Simultaneously, the CWR ranged from 5.8 t/km²/year in the dry period to 802.5 t/km²/year in the wet period, averaging 88.1 t/km²/year, which was also higher than the River Seine (48 t/km²/year) [48] and Yujiang (69.7 t/km²/year) [29], but was similar to the River Rhône (89 t/km²/year) [47]. The results suggest that to reduce the uncertainties in SWR and CWR estimations, high-frequency temporal sampling strategies and geochemical analyses with synchronous discharge are necessary.

The average total chemical weathering rate (TWR = CWR + SWR) in this study was 105.9 t/km²/year, much higher than the global mean (24 t/km²/year) [15], but lower than the value reported in a previous study (129 t/km²/year) [27]. The mean rate of physical erosion was 148.0 t/km²/year, which increased by ten or even hundreds of times relative to the TWR in the wet period. However, there were significant positive relationships between the total weathering rates (i.e. rates of physical erosion and chemical weathering) and variabilities of temperatures and discharge over the hydrological year (Fig. 5c), consistent with the observations in the Yujiang River [29]. The reason for this is that high discharge accelerates the transport of suspended sediments and further exposes reactive mineral surfaces. Meanwhile, high temperatures accelerate biological activities, which may enhance soil CO₂ content, thereby accelerating rock weathering in the catchment [16]. Hence, physical and chemical weathering are two complementary processes at the catchment-scale controlling the morphology of the Earth’s surface [16, 49]. Coupled physical and chemical weathering processes in crushed rocks provide weathered rocks and chemically reactive surfaces are easily fractured under various climatic conditions [49]. Additionally, biogeochemical processes are modified by physical processes, so dissolved solutes present diverse behaviors in response to variations in climatic conditions (i.e. discharge and temperature) [13, 50].

The CO₂ consumption fluxes from carbonate weathering (FCO₂carb) and silicate weathering (FCO₂sil) were deducted from the sulfuric acid involved with carbonate and silicate weathering, described by Additional file 1: Equations (S13 and S14), respectively. The mean monthly FCO₂carb values showed strong positive relationships with discharge and temperatures, increasing from 3.2 × 10⁹ mol/year (March of 2014) to 3.2 × 10¹⁰ mol/year (June of 2014), averaging 14.3 × 10⁹ mol/year, as shown in Figs. 5d, e. Meanwhile, FCO₂sil values increased from 0.1 × 10⁹ mol/year (December of 2013) to 0.9 × 10⁹ mol/year (June of 2014), averaging 0.4 × 10⁹ mol/year, which displayed positive relationships with changing discharge and temperatures during the hydrological year (Figs. 5d, e). These findings showed that the FCO₂carb had a higher sensitivity to variations in temperature and discharge relative to FCO₂sil, exhibiting similar behaviors with the contributions of silicate and carbonate weathering in response to changing discharge and temperature conditions. The FCO₂carb and FCO₂sil for the Guijiang River accounted for around 0.1% and 0.01% of the global CO₂ consumption fluxes by carbonate and silicate rocks weathering, respectively [6]. These results in this study were much lower than those previously reported (e.g. 21.1 × 10⁹ mol/year and 1.86 × 10⁷ mol/year) [27], which may be due to the uncertainties caused by limited sampling frequency in the previous study.

The total rates of CO₂ consumption (ΦCO₂ = [ΦCO₂carb] + [ΦCO₂sil]) were defined as FCO₂ per unit area. Although the total ΦCO₂ (760.4 × 10³ mol/km²/year) do not show obvious advantages in those of global catchments, the CO₂ consumption capacity in this study river was much higher than the global mean (Fig. 6). Worldwide, rivers with large catchment areas generally had lower ΦCO₂, while rivers yielding higher ΦCO₂ values usually had small areas and low discharges [6]. The Changjiang River, Huanghe River, and the Xiijiang River were all located near the global mean line [6].

**Carbon dynamics under various climate variabilities**

Previous studies had demonstrated that carbonate weathering via carbonic and sulfuric acids generated a large amount of DIC in karst areas [27]. Carbonate weathering involving carbonic and sulfuric acids may also lead to different elemental ratios, with the molar ratios of [HCO₃⁻]/[Ca²⁺ + Mg²⁺] = 2 or 1 [46]. As shown in Fig. 7a, carbonate weathering involved with carbonic acid...
was the primary reaction, though sulfuric acid also acted an important role. For carbonate-sourced carbon, the isotopic values were assumed to be 0‰. However, this was accompanied by clear relationships between the isotopic signals and climatic parameters (e.g. discharge and temperature), with heavy $\delta^{13}$CDIC values occurring under low-flow conditions and light $\delta^{13}$CDIC values occurring under high-flow conditions, which is in accord with related studies \[16, 46, 54\]. One hypothesis is that the contribution of lighter $\delta^{13}$CDIC carbon stored in matrix porosity is higher under warm and wet conditions during the wet period than that found during the dry period \[46\].

The influx of soil CO$_2$ produced by soil organic matter degradation can shift $^{13}$C-depleted DIC values. As shown in Fig. 7b, there were positive correlations between the content of DIC and DOC during the hydrological year. On the other hand, C$_3$ plants are widely distributed in this study area, with a mean $\delta^{13}$C value of $-27\%$. So the $\delta^{13}$C of soil CO$_2$ in the study area is around $-22.6\%$, after accounting for the +4.4\% isotopic enrichment caused by molecular diffusion \[54\]. Hence, light $\delta^{13}$CDIC values occur under high-flow conditions, corresponding with higher temperatures than those in the low-flow seasons (Fig. 7c), which may suggest that $^{13}$C-depleted DIC can be influenced by soil CO$_2$, especially under warm and wet conditions. Additionally, DIC contents decreased with increasing discharge (Fig. 7c), which should be ascribed to the shortened fluid transit time during the high-flow seasons, consistent with previous studies in Southwest China \[15, 29, 55\].

In comparison with atmospheric CO$_2$, the pCO$_2$ in the Guijiang River was generally supersaturated, causing large amounts of CO$_2$ outgassing into the atmosphere. Therefore, the relatively heavier $\delta^{13}$CDIC values under dry conditions, as compared to those under wet conditions, might be partially attributed to CO$_2$ outgassing \[54\]. Because of high CO$_2$ outgassing with longer residence times during low-flow seasons, the $\delta^{13}$CDIC values under low-flow conditions are much heavier, whereas there is a shorter residence time during high-flow seasons that may weaken isotopic exchange \[54\].
The mixing model (i.e. IsoSource) [56] was used to constrain the carbon sources according to the $\delta^{13}\text{C}$ values of distinct carbon end-members. The isotopic values were assigned as $-22.6\%$ for biological carbon and $0\%$ for carbonate-derived carbon as endmembers, as well as deducting the enrichment of $14.7\%$ caused by kinetic fractionation of CO$_2$ outgassing [57]. The contributions of each source to DIC can be estimated by the following expressions (12–13):

$$
\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{bio}} \times a + \delta^{13}\text{C}_{\text{carb}} \times b - \delta^{13}\text{C}_{\text{out}} \times c
$$

$$
a + b + c = 1,
$$

where $\delta^{13}\text{C}_{\text{bio}}$, $\delta^{13}\text{C}_{\text{carb}}$, and $\delta^{13}\text{C}_{\text{out}}$ represent the carbon isotopic compositions of biological carbon (DIC$_{\text{bio}}$) and carbonate (DIC$_{\text{carb}}$), and CO$_2$ outgassing, respectively, $a$ and $b$ indicate the ratios of carbon from biological and carbonate endmembers, and $c$ is the ratio of lost carbon via CO$_2$ outgassing.

The calculated results showed that the contribution of DIC$_{\text{bio}}$ increased from 38% (January of 2014) to 65% (June of 2014), with a mean value of 53% during the hydrological year, displaying a clear positive relationship with increasing discharge (Fig. 7d). These results showed that DIC$_{\text{bio}}$ was the dominant factor controlling the behaviors of riverine DIC, and provided strong evidence to support the argument that the exogenous DIC during high-flow seasons was mostly contributed by 13C-depleted soil CO$_2$. The contribution of DIC$_{\text{carb}}$ ranged from 28 to 48%, with a mean of 37%, and showed nearly chemostatic behavior with increases in discharge. The carbon loss from CO$_2$ outgassing decreased from 26% (January of 2014) to 2% (June to August of 2014), with a mean of 10%, which may be due to the more limited exchange between water and gas during the wet period relative to that occurring during the dry period [54]. Therefore, DIC in the study river was dominantly controlled by soil CO$_2$ and its reaction with carbonates. The contributions of various endmembers to DIC can be affected by variations in climatic conditions. These observations were similar to those in other karstic monsoonal rivers [16, 29, 46]. Hence, additional high-frequency sampling (both spatial and temporal) should be conducted to study the isotopic fractionation of DIC under CO$_2$ outgassing, which have an important impact on the transport of riverine DIC.

### Evasion of CO$_2$ from the river system

To estimate CO$_2$ evasion flux, the hydrological year was divided into three periods: Period I (October–November of 2013), Period II (January–April of 2014), and Period III (May–September of 2014). Pronounced seasonal variations in CO$_2$ evasion fluxes were observed throughout the hydrological year. Period II exhibited the strongest CO$_2$ evasion fluxes (averaging 211 mmol/m$^2$/days) among the study periods. Meanwhile, a much lower efflux was estimated in Period I (averaging 53 mmol/m$^2$/days) and the lowest efflux occurred during Period III (averaging 36 mmol/m$^2$/days) (Table 1). In the Guijiang River, the average value of $F_{\text{CO}_2}$ (84 mmol/m$^2$/days) is similar to the Beipan River (78 mmol/m$^2$/days) [58], but lower than those of the Xijiang River (189.0–356.2 mmol/m$^2$/days) [19], Amazon River (345.2 mmol/m$^2$/days) [1], and the Mississippi River (269.9 mmol/m$^2$/days) [59]. These results further demonstrated that biological

### Table 1 Comparison of $p\text{CO}_2$ and CO$_2$ outgassing of the Guijiang River with rivers worldwide

| River | Location | Climate | K (cm/h) | $p\text{CO}_2$ mean (μatm) | $F_{\text{CO}_2}$ (mmol/m$^2$/days) | Sources |
|-------|----------|---------|----------|---------------------------|---------------------------------|---------|
| GJR (I) | China | Subtropical | 11 | 2083 | 53 | This study |
| GJR (II) | China | Subtropical | 16 | 5162 | 211 | This study |
| GJR (III) | China | Subtropical | 13 | 1460 | 36 | This study |
| Beipan | China | Subtropical | 8 | 1287 | 78 | [58] |
| Xijiang | China | Subtropical | 8–15 | 2600 | 189.0–356.2 | [19] |
| Yangtze | China | Subtropical | 8 | 1297 | 38.4–147.9 | [60] |
| Huanghe | China | Subtropical | 42.1 | 2770 | 856 | [61] |
| Amazon | Brazil | Tropic | 15 | 3320 | 345.2 | [37] |
| Mississippi | USA | Temperate | 16.3 | 1335 | 269.9 | [59] |
| Hudson | USA | Temperate | 4 | 1125 | 16–37 | [62] |
| Ottawa | Canada | Temperate | 4 | 1200 | 80.8 | [8] |
| Gäddtjärn | Sweden | Boreal | 2.1 | 2266 | 983 | [63] |
| Lower Mekong | Canada | Boreal | 26 | 611 | 16 | [10] |
| Auchencorth Moss | UK | Boreal | – | 25,418 | 2.6 | [64] |
| Krycklån | Sweden | Boreal | – | 722–24,167 | 1 | [65] |

GJR, Guijiang River; I, from October–November of 2013; II, from January–April of 2014; III, from May–September of 2014.
activities increased with the higher temperatures during high-flow seasons, resulting in accelerated chemical weathering rates, and then consuming more soil CO₂. A conceptual model of the seasonal variations in the DIC production, weathering processes, and CO₂ evasion in karst rivers is shown in Fig. 8. Hence, the DIC dynamics under short-term climate variabilities show the significant negative feedback between chemical weathering and global climate change, which needs more attention in future studies.

Conclusions
Based on temporal distributions of riverine dissolved solutes and δ¹³C_{DIC} values throughout a hydrological year in the Guijiang River, we found that the dissolved solutes showed obvious temporal variabilities over the hydrological year. Most dissolved solutes with different sources (e.g. geogenic, anthropogenic, and biological solutes) behaved differently with respect to variations in discharge. Our results support the generality of most solutes’ C–Q patterns, reflecting chemostatic behaviors and implying consistent source generation and hydro-biogeochemical processes, despite the considerable variations in lithologies and human activity.

Carbonate weathering was the main source of dissolved solutes, and weathering products from carbonates (e.g. Ca^{2+}, Mg^{2+}, and HCO₃⁻) showed strong chemostatic behavior when compared to those from silicate weathering (e.g. Na⁺ and K⁺) in response to changing discharge, which may be due to the rapid dissolution kinetics of carbonate weathering. Meanwhile, both Na⁺ and K⁺ exhibited dilution effects, implying that silicate-sourced ions are more sensitive to various hydrological conditions than carbonate-sourced ions. Significant positive relationships existed between the weathering rate and variations of climatic conditions, which may be attributed to the presumption that high discharge accelerates solutes transport and high temperature facilitates soil CO₂ production, enhancing rock weathering. Based on the LOADEST program, the CO₂ consumption rates of carbonate and silicate weathering were 14.2 × 10⁹ mol/year and 0.4 × 10⁹ mol/year, respectively. Although the CO₂ consumption rate in the Guijiang River only contributed to a small part of the global CO₂ consumption rate, its CO₂ consumption capacity far exceeded the global mean.

Fig. 8 Mean monthly values of F_{CO₂} under different climatic conditions in the Guijiang River during the hydrological year
The IsoSource model was applied to constrain the DIC sources, which demonstrated that soil CO2 content and its reactions with carbonates were the predominant factors controlling riverine DIC. Meanwhile, compared to the dry period, biological activities increased during the wet period, resulting in high soil CO2. Temporal variations were also observed in CO2 fluxes through CO2 outgassing ($F_{CO2}$), showing that CO2 evasion in the wet season was less than that in the dry season, demonstrating further that biological effects become increasingly important with high temperatures. This study provides valuable insights into the carbon dynamics in karst rivers, which can help to improve the understanding of regional and global carbon balance.

**Supplementary Information**
The online version contains supplementary material available at https://doi.org/10.1186/s12302-021-00495-x.

**Additional file 1.** Calculation method of the forward model(A), Rates of silicate and carbonate weathering(B), and Flux of CO2 consumption by silicate and carbonate weathering(C).

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**Authors’ contributions**
JL and JZ were involved in the investigation, experiments, and manuscript writing. JL, SC, and SX were involved in the data curation and validation. JZ and SL contributed to the study design and review. All authors read and approved the final manuscript.

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**Availability of data and materials**
The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

**Declarations**

**Ethics approval and consent to participate**
Not applicable.

**Consent for publication**
Not applicable.

**Competing interests**
The authors declare that they have no competing interests.

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