

DIEL CYCLING AND FLUX OF HCO_3^- IN A TYPICAL KARST SPRING-FED STREAM OF SOUTHWESTERN CHINA

DNEVNE SPREMEMBE IN TOK BIKARBONATA V TIPIČNEM KRAŠKEM POTOKU NA JUGOZAHODU KITAJSKJE

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Abstract

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Cheng Zhang, Jinliang Wang, Jun Yan & Jianguo Pei: Diel cycling and flux of HCO_3^- in a typical karst spring-fed stream of southwestern China

We investigated the diel variations of the dissolved inorganic carbon, isotopic composition, and partial CO_2 pressure from a karst spring (Guangcun Village, Guangxi, Southwest China) to the 1,350 m downstream profile of the stream. In addition, the carbon loss and CO_2 exchange flux at the water-gas interface were also estimated. The results showed that the pH value and DO in the stream varied regularly on a daily basis with the temperature of stream water, suggesting that the photosynthesis of aquatic plants and algae is the controlling factor for the diel variations of the pH and DO. During the monitoring period, while the DIC (mainly in HCO_3^-) input (at spring) was relatively stable at about 4.46 mmol L^{-1} , the concentrations of HCO_3^- and Ca^{2+} at downstream showed a diel cycle of daytime decrease and nighttime increase, with an amplitude of 22.4 %. We also found out that the CO_2 degassing mainly occurred in the upper reach of the surface stream right after groundwater is exposed to the surface. The total CO_2 exchange flux of the entire monitoring stream section was calculated to be 29.83 kg d^{-1} , accounting for 17.8 % of the DIC loss, which means that approximately 4/5 of the loss was converted into organic carbon or calcite precipitation. Compared with the total carbon input at spring, this carbon loss only accounts for 6.5 % of the total carbon amount (1.4 % of which was converted into organic carbon and 1.1 % of which was degassed to the atmosphere), indicating that the DIC of karst groundwater in low order surface stream of Guancun is stable in general, with 1 % being lost to the atmosphere. This suggests that on a daily timescale, carbon loss in the form of CO_2 of low order karst streams with lower gradient is much less pronounced.

Key words: inorganic carbon cycle, spring-fed stream, aquatic vegetation photosynthesis, CO_2 degassing, inorganic carbon flux, karst.

Izvleček

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Cheng Zhang, Jinliang Wang, Jun Yan & Jianguo Pei: Dnevne spremembe in tok bikarbonata v tipičnem kraškem potoku na jugozahodu Kitajske

Preučevali smo dnevno nihanje raztopljenega anorganskega ogljika, izotopsko sestavo in parcialni tlak CO_2 na 1350 m dolgem odseku kraškega potoka v vasi Guangcun, Guangxi na jugozahodu Kitajske. Ocenjevali smo tudi izgubo ogljika in izmenjavo CO_2 na stiku vodne gladine z ozračjem. Dnevna nihanja pH in raztopljenega kisika so očitno povezana s fotosintezo vodnih rastlin, saj so se v času spremljanja, ko je bil dotok DIC (raztopljen organski ogljik, predvsem HCO_3^-) skozi izvir relativno stabilen (4.46 mmol l^{-1}), koncentracije HCO_3^- in Ca^{2+} spreminjale v dnevnem ciklu. Največje dnevne in najmanjše nočne vrednosti so se razlikovale za 22,4 %. Razplinjanje CO_2 je največje v zgornjem toku, tik za izviro. Skupna izmenjava CO_2 za celoten odsek potoka je bila ocenjena na $29,83 \text{ kg CO}_2 \text{ d}^{-1}$, kar je 17,8 % celotne izgube raztopljenega organskega ogljika, iz česar je mogoče sklepati, da se približno 4/5 pretvorijo v organski ogljik oziroma v izločanje kalcita. Izguba predstavlja 6,5 % skupnega dotoka ogljika na, od katerega je 1,4 % pretvorjenega v organski ogljik, 1,1 % pa razplinjenega v ozračje. Vrednost anorganskega ogljika v potoku je relativno stalna, izhajanje ogljika v obliki CO_2 je v opazovanem potoku z relativno majhnim strmecem, precej neizrazito.

Ključne besede: spremembe anorganskega ogljika, izvorni potok, fotosinteza vodnega rastlinja, CO_2 razplinjevanje, tok anorganskega ogljika, kras.

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INTRODUCTION

As one of three processes of the Earth's critical zone (Lin 2010), biogeochemical process connects biotic process with abiotic process. Coupled with hydrological process, it supports the sustainability of ecological process and in turn determines the overall morphology and function of the critical zone (Yang *et al.* 2014). In the fields of global change and karst carbon cycle, a better understanding of biogeochemical process, e.g. its influencing factors and mechanisms, are of vital importance to the study of the time-scale of karst processes and the stability of karst carbon sink (Martin *et al.* 2013; Zhang 2011). CO_2 consumed in carbonate dissolution, directly originated from rainfall as well as indirectly from decomposition of organic matter, are transferred into karst aquifers. The result is also chemical denudation of carbonate rocks (White 2013). During CO_2 transfer through karst aquifers, some portion of the carbon is released back to the atmosphere via the degassing of CO_2 , as well as CaCO_3 deposition as a result of speleothems deposition (e.g. stalagmites) and tufa downstream of karst spring. However, some inorganic carbon (mainly HCO_3^-) (Madsen 1983) is usually converted to organic carbon by aquatic vegetation photosynthesis and some, with the assistance of microbial carbon pump, might further become semi-labile dissolved organic carbon (SLDOC) or recalcitrant dissolved organic carbon (RDOC) in water bodies such as reservoirs or lakes (Jiao *et al.* 2013; He *et al.* 2010; Chen *et al.* 2012; Mermillod-Blondin *et al.* 2015). Hence, biogeochemical process in karst reservoirs and rivers can reflect weathering processes of watershed (Kanduc *et al.* 2007), and moreover could be counted as one of natural carbon sinks, that is, carbon sequestration. However, the research on the magnitude and mechanisms of its influence on carbon sink as well as the role of microbial processes in fresh water carbon storage is still in its infancy stage and we just start to gain some level of understanding.

Thanks to the development of high-resolution automatic online monitoring equipment and high-frequency automatic sampling techniques, more and more studies have been conducted on diel biogeochemical processes since the 1990s (Nimick *et al.* 2011). At least five processes have influence on the variations in amount and flux of dissolved inorganic carbon (DIC) in river waters: photosynthesis, respiration, water-gas exchange (degassing), groundwater recharge, and geochemical process (namely carbonate mineral precipitation or dissolution) (Tobias *et al.* 2011). Based on the findings from various studies in the past 20 years (Nimick *et al.* 2005; Nagorski *et al.* 2003; Waldron *et al.* 2007; Poulson *et al.* 2010; Liu *et al.* 2006; Liu *et al.* 2008), we now know that aquatic

vegetation activity can significantly affect the variations of hydrochemical parameters of stream waters, such as pH, DIC, dissolved oxygen (DO), and specific conductivity (SpC). The short time scale research on diurnal or seasonal variations is valuable to the investigation of the relatively rapid biogeochemical processes in waters (e.g. processes in stream flows). In addition, it also helps to reckon or to quantify watershed processes in upstream recharge areas. The existing studies (Dandurand *et al.* 1982; Spiro & Pentecost 1991; Guasch *et al.* 1998; Reichert 2001; Lorah & Herman 1988; Finlay 2003) on different stream orders show that biological processes (photosynthesis and respiration) and geochemical processes (bicarbonate equilibration and calcite precipitation) are two main controlling factors for diurnal variations of pH value, SpC, and concentrations of Ca^{2+} and HCO_3^- in streams. The majority of these studies focused on small tributary streams, particularly karst spring-fed small streams (discharge $< 0.1\text{m}^3/\text{s}$) as documented in Nimick *et al.* (2011), while some were conducted on streams with moderate flows (discharge $< 5\text{m}^3/\text{s}$) (Parker *et al.* 2010) or large rivers (discharge $> 10\text{m}^3/\text{s}$) (Hayashi *et al.* 2012).

During carbonate rock dissolution, CO_2 is consumed and HCO_3^- is generated. Accordingly, high amount of HCO_3^- is one of the distinctive characteristics of karst groundwater. It was found that carbon sink generated by karst processes could be an important part of the missing carbon sink on a global scale (Jiang *et al.* 2012). In karst areas, surface rivers are often rich in aquatic plants. Hence, the transformation of DIC to DOC caused by aquatic vegetation photosynthesis usually leads to the loss of DIC (mainly HCO_3^-) along rivers' course, which presents a natural sink of carbon (De Montety *et al.* 2011; Zhang *et al.* 2012). Nevertheless, the intensity, seasonal variation and major controlling factors of this carbon sink should be targeted by further investigation. The research on diel variations in hydrochemical composition and biogeochemical processes in surface karst rivers can not only reveal controlling factors for diel cycling of hydrochemical inorganic compositions, but also help us better understand the rate of transfer of inorganic and organic carbon in karst processes so as to provide insights about the biogeochemical nature (e.g. short time-scale features) of karst processes. The findings could significantly improve accuracy of karst carbon flux. Furthermore, they can help the implementation of long term water quality monitoring plan in drainage basins.

With a case study on a karst spring-fed stream at Guangcun Village, Guangxi, Southwest China, this paper

deals with the diel variations of the dissolved inorganic carbon, isotopic composition, and partial CO_2 pressure from the outlet to the 1,350 m downstream section of

the underground stream. In addition, it also estimates the carbon loss and CO_2 exchange flux at the water-gas interface.

STUDY AREA

The three monitoring sites are located along the stream section from the outlet of an underground stream at Guancun Village (in Daliang Town, Rongshui County, Guangxi Province, China) to the junction of its lower reach at Leiya Village. This stream section is 1,350 m long

(Fig. 1) and 2–5 m wide, with a depth of 0.2–1.0 m (generally 0.5 m). The flow velocity in this section is about 0.2 m s^{-1} and the average hydraulic gradient is less than 2 m/km . This stream is about 60 km away north from Liuzhou City, a major industrial city in Southwest China.

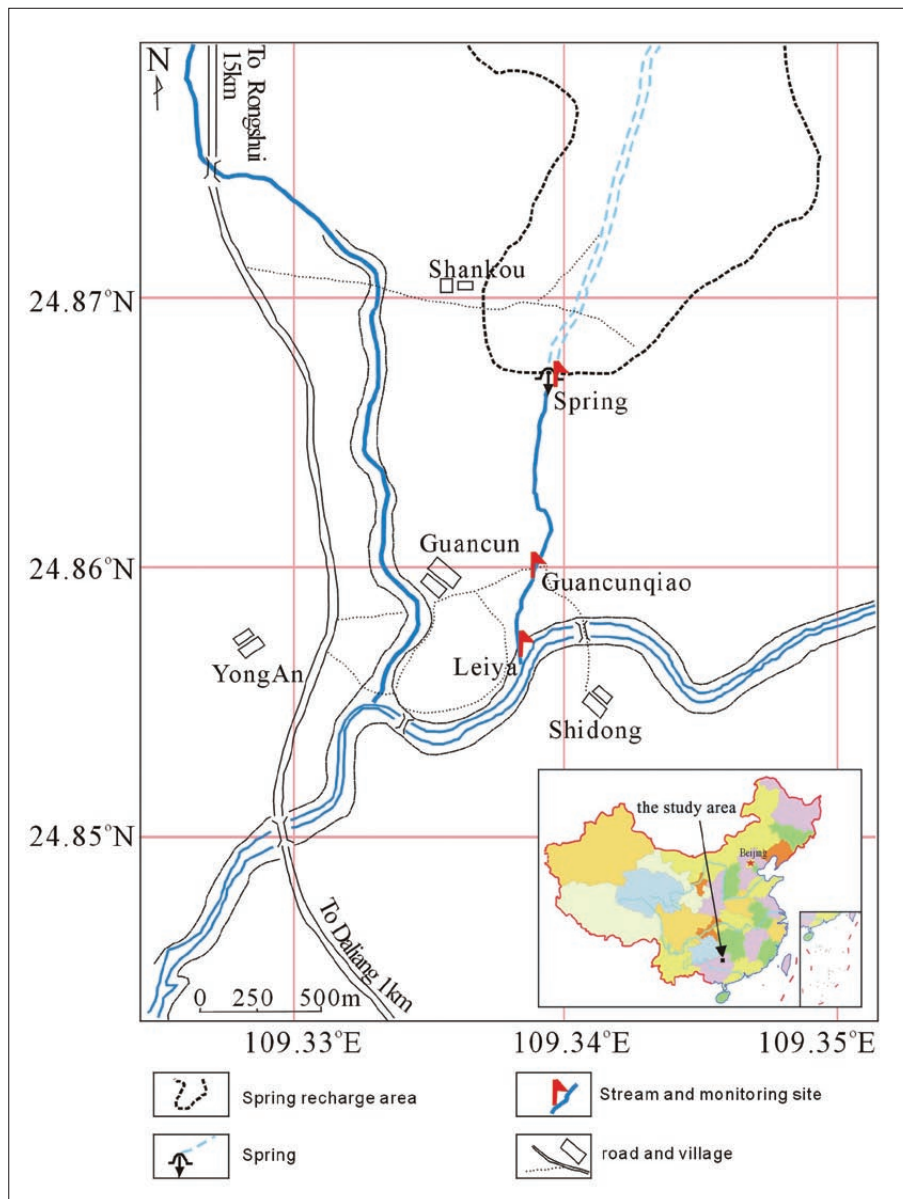


Fig. 1: Locations of the study area and monitoring sites.

Tab. 1: Diel variations and mean values of concentration of major ions at spring (mg L^{-1}).

Ion	Maximum	Mean	Minimum	Maximum–Minimum
K^+	0.55	0.53	0.5	0.05
Na^+	0.72	0.70	0.68	0.04
Ca^{2+}	85.85	84.78	83.22	2.63
Mg^{2+}	10.37	10.21	9.96	0.41
Cl^-	2.76	2.74	2.72	0.04
SO_4^{2-}	14.58	14.54	14.46	0.12
HCO_3^-	278.45	272.30	265.8	12.65
NO_3^-	9.83	9.54	8.24	1.59
TOC	1.41	0.65	0.39	1.02
DOC	0.79	0.52	0.38	0.41

Its spring is located at $109^\circ 20' 3.41''$ E and $24^\circ 52' 5.34''$ N with an elevation of 160 m. The drainage area is about 30.5 km^2 with higher elevations in the northeast and northwest. This section is characterized by karst peak-cluster depressions, with well-developed dolines and sinkholes. This underground stream is developed from

the recharge area and composed of limestone and dolomite of Rongxian Formation (D_{3r}). The annual average temperature of the study area is 20°C and the annual average rainfall is 1,750 mm, with the wet season from May to July and the dry season from September to February. The rainfall in six months of the dry season accounts for only 11 % of the total of the whole year. The water of this underground stream is rich in calcium and bicarbonate with low contents of Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} and NO_3^- . The ranges and mean values of their concentrations can be seen in Tab. 1, showing relatively low variations in the monitoring period. Ca^{2+} , HCO_3^- and Mg^{2+} mainly come from the Devonian limestones and dolomites of Rongxian Formation while K^+ and Na^+ are from soil.

During the monitoring period, the discharge at spring, the source of the underground stream was relatively stable, with a range of 149.5–156.4 L/s. Water temperature (T), pH, SpC, and dissolved oxygen (DO) remained about the same as well (21.26°C , 7.47, 418 $\mu\text{S/cm}$, and 7.18 mg L^{-1} respectively) during the monitoring period.

MATERIALS AND METHODS

MONITORING, SAMPLING, ANALYTICAL METHODS

Diel monitoring was carried out during August 21–26, 2011, a total of six days. Three monitoring sites were set up along the stream section: (1) the outlet site of the underground stream (CK): the input section site to obtain the physiochemical indicators as the initial values of the water; (2) the Guangcun Bridge site (GCQ): 880 m downstream from the outlet; (3) the junction site just before confluence with Shimen river at Leiya Village (LY): 1,350 m downstream from the outlet, which is used to evaluate the variations, diel cycling and ranges of the biogeochemical parameters along the flow path, and ultimately how biological processes influence variations of bicarbonates temporally and spatially. An automatic online monitoring instrument was installed at each monitoring site. The in-situ titration analysis and sampling work were started at the outlet site first. It lasted only one day (Tab.1) at the outlet site because of the relatively constant ion concentrations. The work conducted at the Guangcun Bridge site and the junction site at Leiya Village lasted all six days.

T, pH, SpC, water level, and DO were monitored by a YSI 6920 at 5-minute intervals with the accuracies of 0.1 $^\circ \text{C}$, 0.2, 1 $\mu\text{S cm}^{-1}$, 0.01 m, and 0.01 mg L^{-1} respectively. The concentrations of Ca^{2+} and HCO_3^- were

obtained through in-situ titration analysis using Aquamerck testing box at 1-hour intervals with the accuracy of 0.05 mmol L^{-1} . Hydrochemical samples and carbon isotopic samples for chemical and isotopic analysis were collected at 1-hour intervals by an automatic sampler ISCO. Three flow discharge measurements were conducted on August 21, 23, and 26 respectively. In line with the standards of GB/T8538–2008 and DZ/T 0184.1-0184.22-1997 (geological sample isotopic analytical methods), the determination of hydrochemical compositions and $\delta^{13}\text{C}$ isotopes was performed in the Karst Geological Resources, Environmental Monitoring and Testing Center, Ministry of Land and Resources of China using an IRIS Intrepid II XSP plasma spectrometer and a MAT253 stable isotope mass spectrometer.

DATA PROCESSING

The values of calcite saturation indices (SIc) and partial pressure of dissolved CO_2 ($p\text{CO}_2$) were calculated using the program WATSPEC (Wigley 1977). The water temperature and the pH were extracted from the available online monitoring data. The concentrations of Ca^{2+} and HCO_3^- were determined by in-situ titration data and the ion concentrations of Mg^{2+} , K^+ , Na^+ , Cl^- and SO_4^{2-} were the analytical data tested from the water samples in the laboratory.

The CO₂ exchange flux at the water-gas interface was estimated by the molecular diffusion model:

$$F = k \times \Delta C = k \times (C_{\text{water}} - C_{\text{air}}) \quad (1)$$

where F is the exchange flux at the water-gas interface (mmol m⁻² d⁻¹). When F > 0, water releases CO₂ to the atmosphere, while water absorbs CO₂ from the atmosphere when F < 0. C_{water} and C_{air} are the CO₂ concentrations (ppm) in water and gas respectively and hence ΔC represents the difference of gas concentrations across the interface (Cole *et al.* 1994; Galy-Lacaux *et al.* 1997; Jones *et al.* 2001), k, the gas exchange coefficient, is a function of the boundary diffusion layer thickness (z), i.e. k=D/z, where D is the diffusion coefficient of gas. Cole *et al.* (1994) found that the k value for CO₂, was 0.5 m d⁻¹ in most lakes and the corresponding boundary diffusion layer thickness was equivalent to 300 μm (in summer) and 200 μm

(in winter). Researchers from the UK (Galy-Lacaux *et al.* 1997) and Germany (Schmidt & Conrad 1993) used 100 μm (in winter) and 200 μm (in summer) as the values of boundary diffusion layer thickness when studying water reservoirs and lakes. Some researchers adopted a unified boundary layer thickness of 200 μm for estimating (Jones *et al.* 2001; Wang *et al.* 2012). The underground stream basin in Guancun Village, Rongshui County, Guangxi, is located in low-elevation karst peak-cluster depressions with low perennial wind speeds, accordingly, a unified boundary diffusion layer thickness of 200 μm was used for this research. The diffusion coefficient of CO₂ in water were 1.26 × 10⁻⁵ cm² s⁻¹ (in winter with the water temperature of 10°C) and 1.93 × 10⁻⁵ cm² s⁻¹ (in summer with the water temperature of 25°C), and the corresponding CO₂ exchange coefficient was 0.5–0.8 m d⁻¹ (Wang *et al.* 2012).

RESULTS

WATER TEMPERATURE, pH, and DO

The water average temperature, pH and DO were constant at the outlet site of the underground stream, 21.3 °C, 7.5 and 7.17 mg/L respectively (Fig. 2). In contrast, these parameters at the Guancun Bridge site (GCQ) and the Leiya Village site (LY) showed prominent diel variations (Fig. 2). At GCQ, the pH value increased to 7.9–8.3 and the average daily values of the water temperature, pH and DO (from August 21 to 25) were 23.2 °C, 8.0 and 8.41 mg L⁻¹ respectively, with the respective diel amplitudes of 5.0 °C, 0.4 and 4.83 mg L⁻¹. As the water temperature rose during daytime, the pH and DO values of the water increased simultaneously, with the maximum values of 8.3 and 11.85 mg L⁻¹ (13:00–14:30). Low val-

ues occurred at nighttime, with the minimum values of 7.87 and 6.69 mg L⁻¹, respectively (Tab. 2 and Fig. 2), thus showing typical diel variations of pH and DO led by photosynthesis. Comparatively, similar variations occurred at LY. The pH increased to 8.0–8.3 and the average daily values of water temperature, pH and DO (from August 22 to 25) were 23.6 °C, 8.1 and 8.11 mg L⁻¹ respectively, with the respective diel amplitudes of 5.0°C, 0.3 and 3.58 mg L⁻¹. The variation amplitudes of pH and DO were smaller slightly at LY when compared to those at GCQ. The maximum values during daytime were 8.3 and 10.59 mg L⁻¹ and the minimum values at night were 8.0 and 6.61 mg L⁻¹.

Tab. 2: Diel variations of water parameters at the Guancun Bridge monitoring site and the Leiya Village monitoring site.

Index	Spring(LY)	Guancun Bridge(GCQ)				Leiya Village(LY)				Note
	Mean	Min	Max	Max-Min	Mean	Min	Max	Max-Min	Mean	
T _{water} (°C)	21.3	21.5	27.5	6.0	23.7	21.8	28.0	6.2	24.3	monitoring data on August 22, 2011
SpC (μS cm ⁻¹)	418	412	452	40	438	395	454	59	433	
pH	7.5	7.9	8.3	0.4	8.0	8.0	8.3	0.3	8.1	
DO (mg L ⁻¹)	7.18	6.69	11.85	5.16	8.51	6.61	10.59	3.98	8.15	
Ca ²⁺ (mg L ⁻¹)	84.8	73.0	87.1	14.1	80.7	69.0	84.9	15.9	77.8	monitoring data on August 25, 2011
Mg ²⁺ (mg L ⁻¹)	10.2	10.3	10.7	0.5	10.5	10.1	10.5	0.4	10.3	
HCO ₃ ⁻ (mg L ⁻¹)	272.3	222.6	279.5	56.9	259.1	227.8	278.5	50.6	254.7	
δ ¹³ C _{DIC} (‰)	-15.31	-14.55	-11.95	2.60	-13.50	-14.40	-11.30	3.10	-13.21	
Slc	0.32	0.74	1.07	0.33	0.88	0.85	1.12	0.27	0.96	
pCO ₂ (μatm)	8494	1137	3355	2218	2305	946	2166	1220	1652	

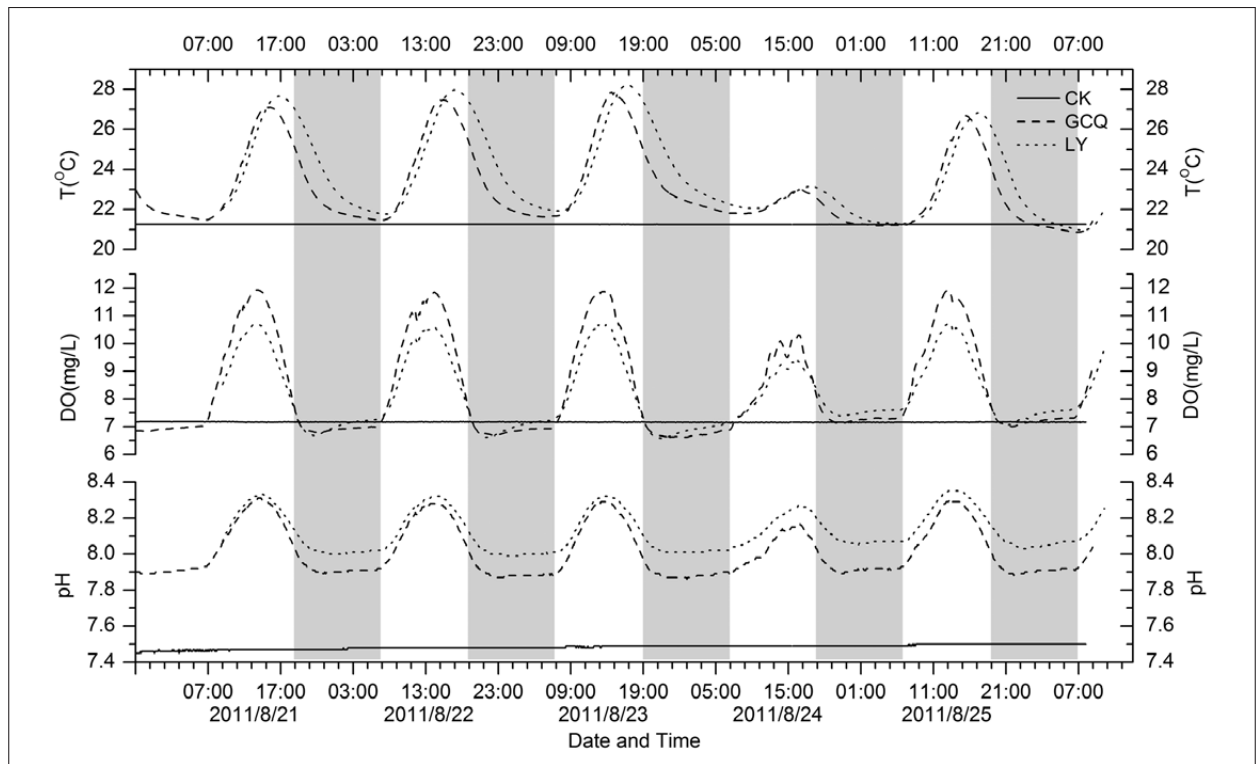


Fig. 2: Diel variations in water temperature, pH, and DO. CK-the outlet monitoring site of the underground stream (spring). GCQ-the Guancun Bridge monitoring site. LY-the Leiya Village monitoring site. The grey areas represent nighttime.

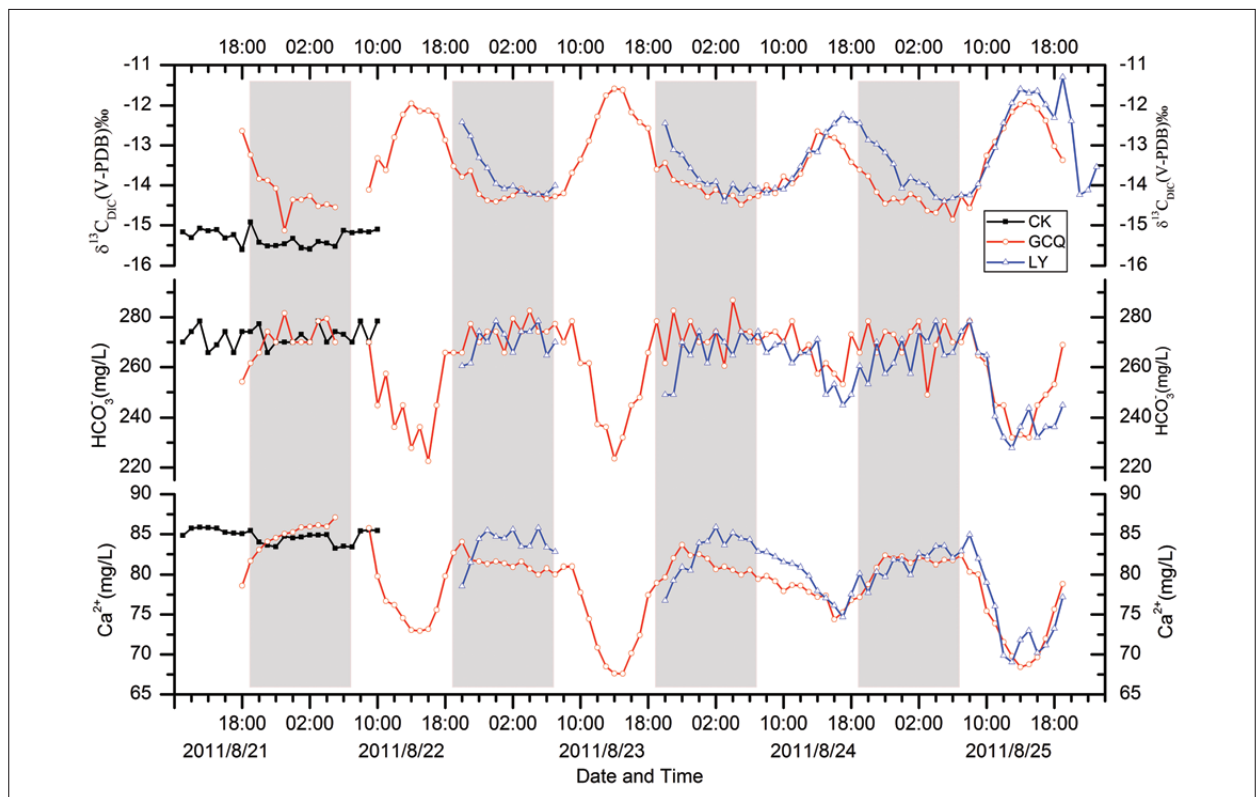


Fig. 3: Diel variations in HCO_3^- , Ca^{2+} and $\delta^{13}\text{C}_{\text{DIC}}$

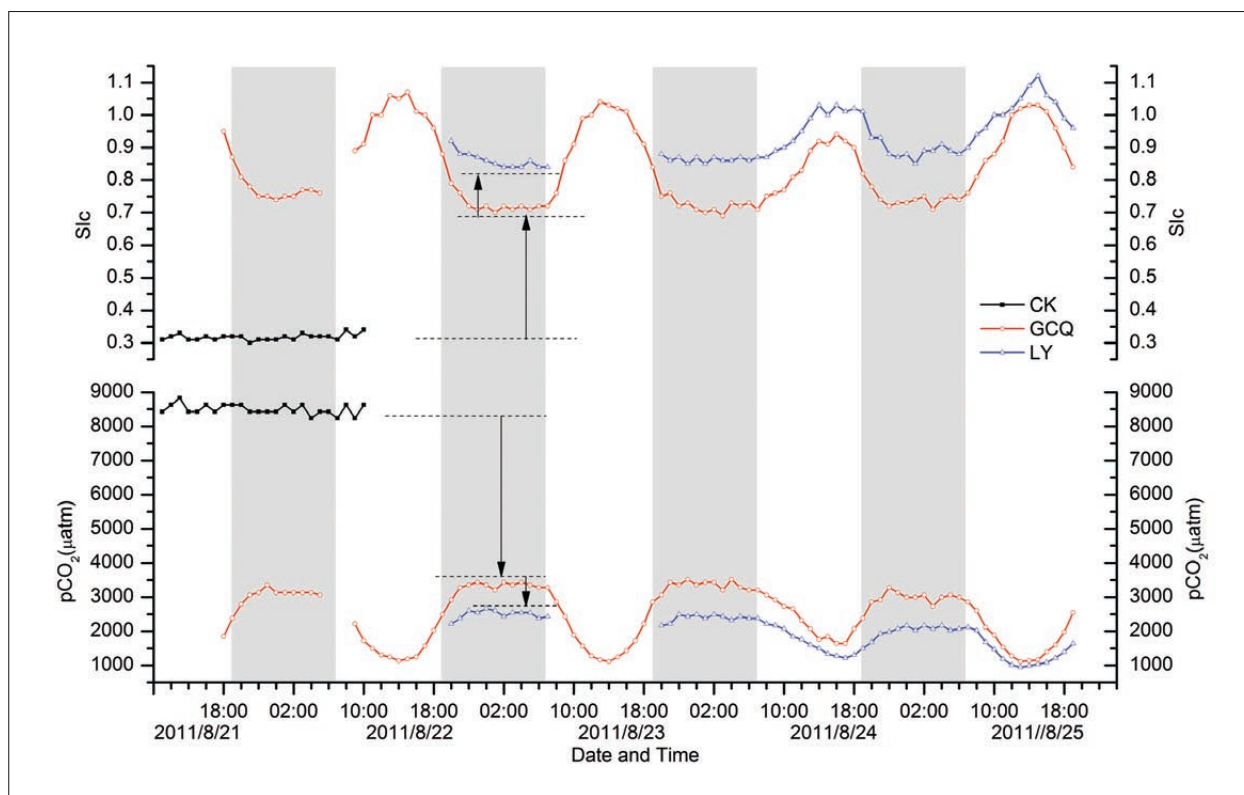


Fig. 4: Diel variations in Sicc and pCO_2 .

The underground stream has a flow path of 880 m from CK to GCQ. As shown in Fig. 2, the increased range of the pH values along this flow path can be divided into two parts: from 7.5 (which is the constant pH value at CK) to 7.9, and a diel range from 7.9 to 8.3. This may suggest that the degassing and the photosynthesis of aquatic plants and photosynthetic organisms both affect the increase of the pH values.

HCO_3^- , Ca^{2+} , and $\delta^{13}\text{C}_{\text{DIC}}$

The hydrochemical indices at CK were relatively constant. The average daily concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- were 84.8, 10.2 and 272.3 mg L^{-1} respectively, with the respective amplitudes of 2.6, 0.4 and 12.7 mg L^{-1} . The diel average value of the inorganic carbon isotope ($\delta^{13}\text{C}_{\text{DIC}}$) in water was -15.31‰ , with an amplitude of 0.68 ‰. The average daily concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- at GCQ were 78.6, 10.2 and 262.7 mg L^{-1} respectively, with the respective amplitudes of 13.1, 0.6 and 49.0 mg L^{-1} . The diel average value of $\delta^{13}\text{C}$ was -13.56‰ , with an amplitude of 2.55 ‰. The average daily concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- at LY were 79.4, 10.3 and 259.3 mg L^{-1} respectively, with the respective amplitudes of 13.6, 0.6 and 40.1 mg L^{-1} . The diel average value of $\delta^{13}\text{C}$ was -13.34‰ , with an amplitude of 2.64 ‰.

Contrary to the diel variations of pH and DO, the concentrations of Ca^{2+} and HCO_3^- at GCQ and LY showed a daytime decrease and nighttime increase cycling (Fig. 3), but the peaks were not completely synchronized with each other. The low values appeared at around 17:00 with the minimum values of 69.0 mg L^{-1} and 222.6 mg L^{-1} respectively, which may be consistent with the high values of water temperature, almost 3 hours later than the time when the maximum values of pH and DO appeared. After that, the concentrations of Ca^{2+} and HCO_3^- at GCQ and LY gradually increased and the maximum values appeared in the early morning of the following day. The diel variations of the $\delta^{13}\text{C}_{\text{DIC}}$ were the total opposite to those of the HCO_3^- , showing a daytime increase and nighttime decrease. The high $\delta^{13}\text{C}_{\text{DIC}}$ value corresponds to the low DIC. The maximum diel amplitude of the isotope was around -3.10‰ (from the minimum value of -14.40‰ at night to the maximum value of -11.30‰ during daytime).

Sicc and pCO_2

At CK, the calcite saturation index (Sicc) and partial CO_2 pressure (pCO_2) were relatively constant, with the average values of 0.32 and 8,494 μatm respectively and the amplitudes of 0.04 and 397 μatm respectively. The values of Sicc and pCO_2 showed sharp increases and decreases

downstream, respectively. At GCQ, the average daily values of SIc and $p\text{CO}_2$ were 0.84 (range 0.69–1.07) and 2500 μatm (range 1,110–3,510 μatm) and the average diel amplitudes were 0.31 and 2144 μatm , a significant increase in variation amplitude compared to those at CK. At LY, the average daily values of SIc and $p\text{CO}_2$ were 0.94 (range 0.85–1.12) and 2360 μatm (range 950–2,490 μatm) and the average diel amplitudes were 0.23 and 1,245 μatm . Possibly influenced by rainfall (early morning in the day of 23rd August), these diel amplitudes showed slight decreases when compared to those at GCQ.

The diel variation of $p\text{CO}_2$ was the opposite of that of pH, showing a decrease during daytime, with the minimum value of 946 μatm . The dissolved CO_2 partial pressure rose at night, with the maximum value of 2,487 μatm and the diel amplitude amounts of 1,220–1,270 μatm (Fig. 4). Due to the consumption of CO_2 by photosyn-

thesis in the morning at 7:00, $p\text{CO}_2$ decreased and the water gradually became supersaturated, suggesting that Ca began to precipitate. After 17:00, $p\text{CO}_2$ gradually rose again and reached a relatively constant high value after midnight. The values of SIc were larger than 0, indicating that the water stayed in the state of supersaturation. The values showed a daytime increase and nighttime decrease cycling, with the maximum of 1.12 and the minimum of 0.85. SIc rose steadily in the morning from 8:00, with an associated decrease of Ca^{2+} and HCO_3^- (Fig. 3). The maximum value occurred around 14:00 and then decreased slowly during 14:00–17:00, corresponding to the constant low values of Ca^{2+} and HCO_3^- . After that, SIc sharply dropped while concentration of Ca^{2+} and HCO_3^- sharply increased. After 22:00, SIc reached a relatively constant low value but Ca^{2+} and HCO_3^- increase gradually.

DISCUSSION

VARIATIONS IN WATER TEMPERATURE, pH, and DO

Karst groundwater is characterized by high alkalinity as a result of high concentration of HCO_3^- and Ca^{2+} . In this weakly alkaline environment, the geochemical processes that influence the diel variations of river hydrochemistry mainly include: photosynthesis and respiration of aquatic plants and algae (Odum 1956), biomass, heat exchange at the water-gas interface, water $p\text{CO}_2$ values and related CO_2 degassing, etc. During daytime, high air temperature and strong daylight make rise of the water temperature. Aquatic plants consume CO_2 and produce O_2 with photosynthesis as the dominant process. pH value, DO, and redox potential (Eh) tend to increase and the nitrification process is enhanced accordingly (ammonium nitrogen transform into nitrate nitrogen). During nighttime, air temperature drops and aquatic plants assimilate O_2 and release CO_2 as a result of respiration. pH value, DO, and Eh tend to decrease and the denitrification process is enhanced accordingly (that is, nitrate nitrogen converted into molecular nitrogen) (Brick & Moore 1996; Burns 1998; Gammons *et al.* 2011; Grimm 1987; Hayashi *et al.* 2012; Heffernan & Cohen 2010; Hessen *et al.* 1997; Johnson & Tank 2009; Manny & Wetzel 1973; Mulholland 1992; Roberts & Mulholland 2007; Rusjan & Mikoš 2010; Scholefield *et al.* 2005).

In Fig. 2, the diel variations in stream water temperature are mainly associated with the heat transfer over the water-gas interface. Water temperature rises with high air temperature in daytime. The pH value and

DO vary regularly on a daily basis, suggesting that the photosynthesis of aquatic plants and algae is indeed the controlling factor for the diel variations of the pH and DO of the stream at the Guancun Village.

The temperature of stream water changes on a daily basis as a result of higher air temperature and direct impact of solar radiation and other factors (Nimick *et al.* 2011). Generally speaking, the amplitudes of diel variations of water temperature tend to be larger during summer, during lower flows, and in streams that are wider and shallower (Nimick *et al.* 2005). Thus compared to surface streams in the usual sense, the hyporheic discharge commonly buffers the diel range in surface stream water temperature due to the relatively constant temperatures of shallow groundwater (Arrigoni *et al.* 2008).

The pH value influences not only carbonate geobiochemistry, but also broad variety of other abiotic processes. The diel variations in pH value thus lead to the diel variations in a series of hydrochemical parameters. At GCQ, the amplitude of diel pH variations was 0.4. The amplitudes of diel pH variations typically are less than 1 pH unit and increase as season warms, reported by Nimick *et al.* (2005). Whereas, during summer low-flow conditions in streams rich in aquatic plants, amplitudes of diel pH variations can be as much as 2 pH units (Jarvie *et al.* 2000).

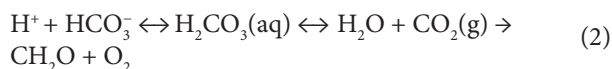
VARIATIONS IN DIC AND CARBON ISOTOPES

During the monitoring period, the DIC input (CK) was relatively stable of about 272.3 mg L^{-1} (4.46 mmol L^{-1}).

The concentrations of HCO₃⁻ and Ca²⁺ at GCQ and LY showed a diel cycle of daytime decrease and nighttime increase stagnation, with the amplitude of 22.4 % (Zhang *et al.* 2015). The minimum values were 222.6 mg L⁻¹ and 67.6 mg L⁻¹ respectively, observed during the period of 14:00 to 15:00. At night, the ion concentration levels corresponding to groundwater recharge recurred, and the values remained high (Fig. 3).

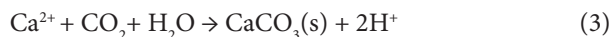
The DIC content in the karst river waters is mainly in the form of HCO₃⁻. The amplitude of DIC of the stream in Guancun Village was 22.4 %. This value is reasonable as it was found in the existing studies that the amplitude could reach as high as 30 % (Nagorski *et al.* 2003; Waldron *et al.* 2007; Poulson *et al.* 2010). The daytime decrease nadir and the nighttime wide stagnation of Ca²⁺ and HCO₃⁻ correspond to the daytime rise stagnation and the nighttime wide nadir of pH and DO, showing a remarkable inversed correlation. This indicates that when stream water temperature rises up, aquatic vegetation photosynthesis consumes HCO₃⁻, leading to decrease in DIC content and CaCO₃ precipitation. This is supported by the previous observations that when the dissolved CO₂ in waters is not available for carbon sequestration by aquatic plants (for photosynthesis), nearly half of aquatic plants would take carbon directly from the HCO₃⁻ in water for photosynthesis (Axelsson *et al.* 1999; Larsson *et al.* 1999).

In this study, the maximum diel amplitude of the isotope was about 3.10 ‰. This value is not only less than 4.5 ‰, the maximum diel amplitude of the δ¹³C_{DIC} in surface water according to the study by Parker *et al.* (2010), but also less than 5 ‰, the amplitude of δ¹³C_{DIC} variation as a result of CO₂ degassing in karst springs reported by Michaelis *et al.* (1985) and surface streams fed by karst water (Doctor *et al.* 2008). As shown in Fig. 5, a significantly positive correlation exists between the reciprocal of DIC and the carbon isotope δ¹³C_{DIC}, indicating that the carbon loss from streams during daytime is prominently controlled by biological processes, i.e. aquatic vegetation photosynthesis and calcification. Photosynthesis consumes dissolved CO₂ or (HCO₃⁻+H⁺) and shifts the following chemical equilibrium (Eq.(2)) to the right (Hayashi *et al.* 2012; McConnaughey 1998). As a result, the activity of H⁺ decreases and pH increases, accompanied by synchronous increases in DO concentration.

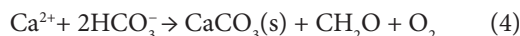


Aquatic plants use bicarbonate for photosynthesis by conversion of HCO₃⁻ into CO₂ with H⁺ depletion. H⁺ can be generated through extracellular or intracellular

acid secretion, or ATPase powered calcification (McConnaughey 1998) (reaction 3).



Adding reaction 2 and 3 yields the following result:



Accordingly, in mildly alkaline karst water, where HCO₃⁻ is the dominant species of DIC, calcification might protonate HCO₃⁻ to CO₂. The two H⁺ derived from calcification protonate 2 HCO₃⁻ to produce 2 CO₂. One CO₂ is used for calcification, leaving one for photosynthesis (McConnaughey 1998), thus resulting in-stream diel variations of concentrations of Ca²⁺ and HCO₃⁻.

The studies on the characteristics of the temporal and spatial variations of δ¹³C_{DIC} value can help evaluate degassing, biological processes, carbonate dissolution and precipitation processes with respect to ecosystems (De Montety *et al.* 2011; Finlay 2003; Gammons *et al.* 2011; Jiang *et al.* 2013; Parker *et al.* 2005, 2007, 2010; Poulson & Sullivan 2010; Smith *et al.* 2011; Spiro & Pentecost 1991; Waldron *et al.* 2007). Jiang *et al.* (2013) stated that aquatic plants raise δ¹³C_{DIC} by using DIC, the same as the effect of degassing. But degassing usually leads to only a small increase in δ¹³C_{DIC}. As a result, respiration is the dominant factor causing the decrease of δ¹³C_{DIC}.

CO₂ FLUXES AT THE WATER-GAS INTERFACE

The values of pCO₂ of the waters at the outlet of the underground stream were high, with the average daily value of 8,494 μatm (Tab. 3). After the underground stream rising up and discharging into downstream of spring, the calculated pCO₂ gradually decreased with flow distances (Arrow I in Fig. 6). At 880 m away from the outlet, the pCO₂ dropped to 2,565 μatm, with the decreasing amplitude of 67.4 μatm every 10 m. At 1,350 m, it dropped to only 1,844 μatm, with the decreasing amplitude of 15.3 μatm every 10 m, indicating that the decreasing rate of pCO₂ reduces with distance. The pCO₂ value exhibits a significant inversed correlation with DO at both GCQ and LY. The sharp rise of DO during daytime leads to the significant drop of pCO₂, indicating that the diel variations are in fact dominated by aquatic vegetation photosynthesis (Arrow II in Fig. 6).

As shown in Tab. 3, the calculated pCO₂ value of water at the outlet of the underground stream was much larger than the atmospheric pCO₂ concentration (390 ppm), suggesting the high water-gas exchange flux (FCO₂). According to the calculation using Equation 1 (k=0.8), the value of FCO₂ through the water-gas interface at the outlet of the underground

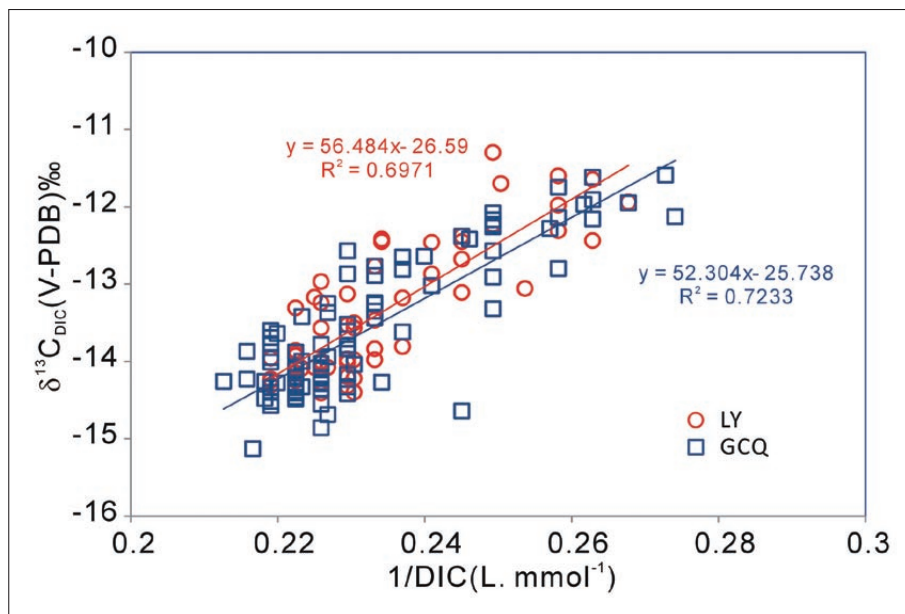


Fig. 5: Relation between $\delta^{13}C_{DIC}$ and $1/DIC$.

stream was as high as $289.43 \text{ mmol m}^{-2} \text{ d}^{-1}$, while those at GCQ and LY dropped to $77.71 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $51.94 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively, with the decreasing amplitudes of $2.41 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $0.55 \text{ mmol m}^{-2} \text{ d}^{-1}$ every 10 m respectively. This shows that the CO_2 degassing of the surface stream fed by karst groundwater mainly occurred in the upper reaches of the surface stream right after groundwater exposed to the surface. The values (at GCQ and LY) of FCO_2 at the water-gas interface of a low order stream is similar to the average value in tropics ($79.5 \text{ mmol m}^{-2} \text{ d}^{-1}$), but higher than the average value in a temperate climate ($31.8 \text{ mmol m}^{-2} \text{ d}^{-1}$) (St. Louis *et al.* 2000), and much higher than the values in Loch Ness in Scotland ($12.3 \text{ mmol m}^{-2} \text{ d}^{-1}$, Jones *et al.* (2001)), and the Hongfeng Lake in Guizhou Province of China ($13.2 \text{ mmol m}^{-2} \text{ d}^{-1}$, Wang *et al.* (2012)) as well as the global average value ($\sim 16.2 \text{ mmol m}^{-2} \text{ d}^{-1}$, Cole *et al.* (1994)).

According to Equation 1 and the above two decreasing rates with flow distance, the FCO_2 at the water-gas interface of the stream section per 10 m could also be calculated (if the average river width is assumed to be 3.5 m). From this, the total CO_2 exchange flux of the en-

tire monitoring stream section (from CK to LY) was calculated to be 29.83 kg d^{-1} ($677.95 \text{ mol d}^{-1}$). Considering the fact that the degassing mainly occurred around the outlet of underground streams, this exchange flux calculated on the basis of the equivalent pCO_2 decreasing amplitudes could be possibly larger than the actual value.

CARBON FLUXES AND CO_2 DEGASSING

The groundwater (at CK) originating from karst areas was saturated with respect to calcite (Fig. 6). It remained saturated with respect to calcite and has high partial CO_2 pressure so it can lead to calcium carbonate precipitation and CO_2 escape (pH rise) (Arrow I in Fig. 7). The average daily Ca^{2+} declined from 4.24 mmol L^{-1} (at CK) to 4.04 mmol L^{-1} (at GCQ) and 3.89 mmol L^{-1} (at LY), an average decrease of $0.023\text{--}0.032 \text{ mmol L}^{-1}$ every 100 m.

The $\text{pH}\text{--}\text{HCO}_3^-$ values of the stream waters at both GCQ and LY had their projection points all above the dolomite saturation curve, indicating that the water was supersaturated regarding to calcite and dolomite (Fig. 7). The pH and HCO_3^- values at both GCQ and LY showed significant diel variations. Influenced by aquatic vegetation photosynthesis, the pH increased while the HCO_3^-

Tab. 3: The partial CO_2 pressures in water and CO_2 fluxes at the water-gas interface at the monitoring sites.

Monitoring site	Flow distance (m)	pCO_2 (μatm)	ΔpCO_2 ($\mu\text{atm}/10\text{m}$)	FCO_2 ($\text{mmol}/\text{m}^2.\text{d}$)	ΔFCO_2 ($\text{mmol}/\text{m}^2.\text{d}.10\text{m}$)
CK	0	8494	67.4	289.43	2.41
GCQ	880	2565			
LY	1350	1844	15.3	51.94	0.55

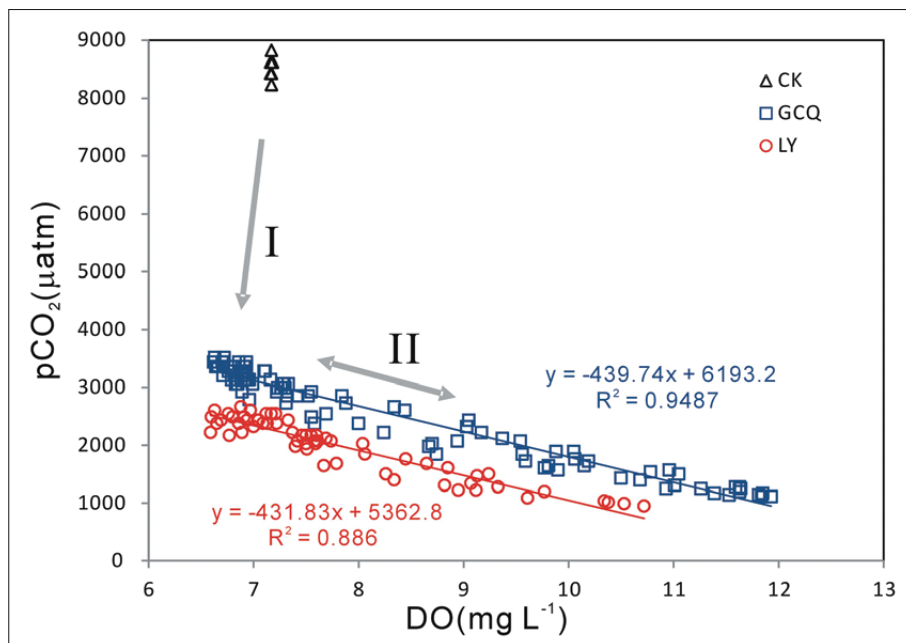


Fig. 6: Relation between dissolved oxygen and CO₂ partial pressure. The arrow I shows the drop of partial CO₂ pressure due to the CO₂ degassing and the two-headed arrow II indicates the diel variations in pCO₂ and DO due to biotic processes.

decreased during daytime. Influenced by both the CO₂ produced by respiration and the recharge of groundwater rich in HCO₃⁻, the pH decreased while HCO₃⁻ increased during nighttime (Arrow II in Fig. 7). The HCO₃⁻ content of the groundwater at CK was 4.46 mmol L⁻¹. Along the flow path, it dropped to 4.25 mmol L⁻¹ (at GCQ) and 4.18 mmol L⁻¹ (at LY) as a result of CO₂ degassing, an average decrease of 0.015–0.024 mmol/L every 100 m. During daytime, the HCO₃⁻ decrease reached 0.83–0.93 mmol/L at both GCQ and LY. In addition, as shown in Fig. 7 the HCO₃⁻ variations caused by the process II were much greater than those by the process I, suggesting that the HCO₃⁻ consumption of rivers is mainly influenced by

aquatic vegetation photosynthesis (Equation 4) and to less extent by degassing. The positive correlation between the partial CO₂ pressure and the DO in the lower reaches is in agreement with this (Fig. 6).

Based on the calculation of the bicarbonate fluxes at CK (input) and LY (output), the reduction of bicarbonate in water influenced by biological processes can be described in mass balance terms (in unit of kg d⁻¹). During the monitoring period, the average discharge was 152.9 L s⁻¹ (Wang *et al.* 2012). Calculated by the HCO₃⁻ content of water samples and the average discharge, the input amount of dissolved inorganic carbon by the underground stream was 3,597.5 kg HCO₃⁻ d⁻¹ (Tab. 4). The

Tab. 4: The C mass balance of the monitoring stream profile.

		Ca ²⁺	HCO ₃ ⁻	degassing	bio uptake	
mg L ⁻¹	CK	84.8	272.3			
	GCQ	80.7	259.1			
	LY	77.8	254.7			
kg d ⁻¹	CK	1120.1	3597.5			
	GCQ	1066.4	3423.3			
	LY	1027.7	3365.2			
kmoles d ⁻¹	CK	28.0	59.0			
	GCQ	26.7	56.1			
	LY	25.7	55.2			
mg L ⁻¹	CK-LY	7.0	17.6			
kg d ⁻¹	CK-LY	92.3	232.3			
kmoles d ⁻¹	CK-LY	2.3	3.8			
kgC d ⁻¹	CK-LY	27.7	45.7	8.1	9.9	
% respect to DIC loss		60.6		17.8	21.6	100.0
% respect to initial DIC		3.9		1.1	1.4	6.5
		precipitation		degassing	bio-uptake	Total

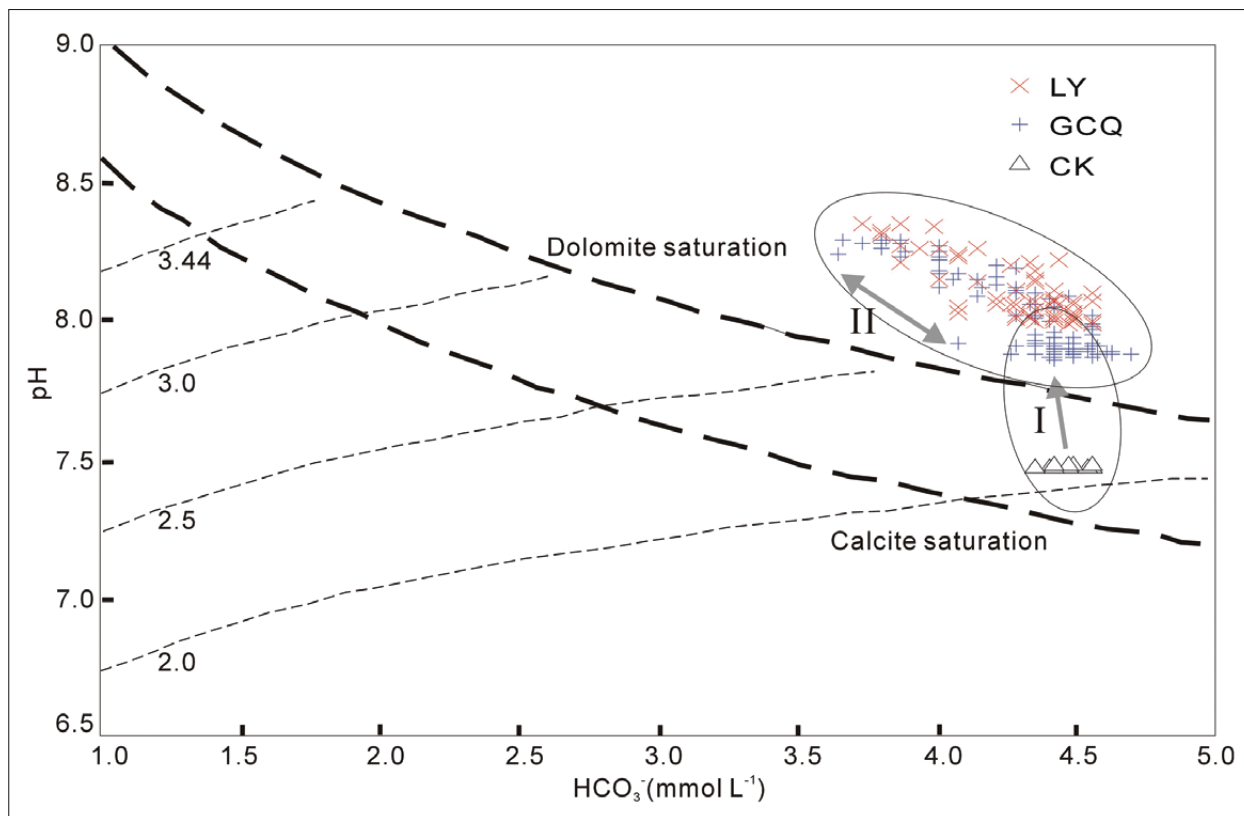


Fig. 7: Relation between pH and HCO_3^- concentrations in stream water. The two bold dashed lines indicate the saturating curves of calcite and dolomite respectively. The fine dashed line represents the equilibrium line of CO_2 ($-\log \text{pCO}_2$), and the arrow I and the two-headed arrow II indicate the variations of pH and HCO_3^- along the flow path and daily respectively.

output amount of dissolved inorganic carbon at LY was $3,365.2 \text{ kg HCO}_3^- \text{ d}^{-1}$. Along the flow path and downstream from CK to LY, the loss of dissolved inorganic carbon was $232.3 \text{ kg HCO}_3^- \text{ d}^{-1}$, namely $172.1 \text{ g HCO}_3^- \text{ m}^{-1} \text{ d}^{-1}$, about 45.7 kg C d^{-1} . This shows that, dominated by photosynthesis and calcification (McConnaughey 1998), inorganic carbon was indeed converted partly to organic carbon downstream along the flow path, which should be considered as a natural carbon sink as a part of the carbon flux of water.

The CO_2 exchange flux at the water-gas interface of the monitoring stream section from CK to LY was $677.95 \text{ mol d}^{-1}$, equivalent to 8.14 kg C d^{-1} , accounting for 17.8 % of the DIC loss. This indicates that the variation of inorganic carbon in the stream is mainly caused by ecosystem activity, namely aquatic vegetation photosynthesis and calcification, accounting for 21.6 % and 60.6 % of the loss amount, respectively (Tab. 4). Thus approximately 4/5 of the loss was converted into organic

carbon and inorganic carbon in form of Ca precipitation. Eventually they would be stored in streambed sediments and form karst carbon sink.

Compared with the total carbon input by the underground stream, this carbon loss only accounts for 6.5 % of the total carbon amount (1.4 % of which was converted into organic carbon and 1.1 % of which was degassed to the atmosphere), indicating that the DIC of the karst groundwater in low order surface streams is stable in general, with roughly 1% being lost to the atmosphere. This finding is similar to the results from the karst spring fed surface rivers in Florida (De Montety *et al.* 2011). The impact of CO_2 degassing on DIC variations can be negligible on a daily scale as the loss induced by degassing in this study is much lower than the carbon flux on a catchment scale. This suggests that carbon loss in the form of CO_2 of low-order Guangcun karst stream is not significant on a daily timescale (Zavadlav *et al.* 2013).

CONCLUSION

Results from high-resolution data logger monitoring and high frequency sampling indicated that the changes in aqueous chemistry of spring-fed stream in Guancun are closely associated with biogeochemical processes. pH, SpC, DO, HCO_3^- and $\delta^{13}\text{C}_{\text{DIC}}$ all showed diel variations, reflecting strong influence of photosynthesis and calcite precipitation. The concentrations of HCO_3^- and Ca^{2+} at downstream showed a diel cycle of daytime decrease and nighttime increase, with an amplitude of 22.4 %. Diel DIC change indicate that the stream is losing inorganic carbon along its flow path, the daily loss of Ca^{2+} and DIC are estimated to be about 92.3 kg d^{-1} and 232.3 kg d^{-1} (namely 45.7 kg C d^{-1}), respectively along the 1350 m of the Guancun River. The total CO_2 exchange flux of the

entire monitoring stream profile was calculated to be 8.14 kg C d^{-1} , accounting for 17.8 % of the DIC loss. This indicates that the variation of inorganic carbon in the stream is mainly caused by ecosystem activity, namely aquatic vegetation photosynthesis and calcification, accounting for 21.6 % and 60.6 % of the loss amount, respectively. Compared with the total carbon input by the underground stream, this carbon loss only accounts for 6.5 % of the total carbon amount (1.4 % of which was converted into organic carbon and 1.1 % of which was degassed to the atmosphere), suggesting that carbon loss in the form of CO_2 of low-order Guancun karst stream is not significant on a daily timescale.

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