



1     **Differences and influencing factors for underground water carbon**  
2             **uptake by karsts in Houzhai Basin, southwest China**

3             Junyi Zhang<sup>1,2</sup>, Zihao Bian<sup>1</sup>, Minghong Dai<sup>1</sup>, Lachun Wang<sup>1\*</sup>, Weici Su<sup>3</sup>

4     1.School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210023, China.

5     2.School of Tourism and Land Resources, Chongqing Technology and Business University,  
6     Chongqing 400067, China.

7     3.The Institute of Mountain Resources, Guizhou Academy of Sciences, Guiyang 550018, China.

8     Correspondence to: Lachun Wang (wang6312@263.net.cn)

9     **Abstract**

10         Karst geological carbon sink is an important part of the global carbon sink, so how to get the  
11         accurate carbon sink of karst ecosystem has become the core issue of the research. We used flow  
12         and carbon ion concentration data from three stations with different environmental background  
13         conditions in the Houzhai basin to analyze the differences in carbon uptake between stations and  
14         their impact factors. Results show that carbon sink discharge was mainly controlled by the flow of  
15         each site. The rapid increase in flow only has a partial dilution effect on ion concentrations,  
16         preliminary analysis considered due to the high speed and stability of chemical carbonate  
17         weathering. LUCC type has important effects on the bicarbonate ions concentrations, if runoff is  
18         stable, the influence of flow variation on ion concentration will be less than the effects of chemical  
19         carbonate weathering in different environmental conditions (comparison of Laoheitan and Liugu  
20         station results is 150%) on bicarbonate ion concentrations. However, if runoff increases  
21         significantly, the impact of runoff variation on bicarbonate ions will be greater than the effects of  
22         chemical carbonate weathering by different environmental conditions (comparison results of  
23         Laoheitan and Maoshuikeng station). This work provides a reference for the calculation of karst  
24         geological carbon sink.

25     **1. Introduction**

26         Global warming from emissions of greenhouse gases has become the core issue of global  
27         environmental change. One of the most pressing concerns in the science of global climate change  
28         is the effective accounting of the global budget for atmospheric CO<sub>2</sub> (Schindler,1999;Melnikov  
29         and Neill,2006;Liu et al.,2010;Kao et al.,2014), since in order to control global warming, it is  
30         necessary to control emissions of carbon dioxide through carbon capture and storage (CCS)  
31         technology. In addition to developing CCS technology, an understanding of a number of natural  
32         ecological and geological processes such as rock weathering, plant growth, and other physical,  
33         chemical, and biological processes can also improve CCS (Hoffmann et al.,2013). Carbonate  
34         weathering in rock weathering processes is considered to be both an important source and sink of  
35         CO<sub>2</sub> (Zeng et al.,2015;Lian et al.,2011;Liu and Zhao,2000;Serrano-Ortiz et al.,2010;James et



36 al.,2006). Carbonate rock dissolves more easily in water in which CO<sub>2</sub> is dissolved, and at a  
37 temperature of 15 °C and atmospheric CO<sub>2</sub> partial pressure of 380 ppmv, the equilibrium  
38 concentration of the dissolved inorganic carbon (DIC) in a water system of CaCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O can  
39 reach 1231 mol/L in the water with calcium carbonate (Dreybolt,1988). Moreover, karst is widely  
40 distributed around the world; it occupies about 11.2% of the Earth's surface, and about 15 million  
41 km<sup>2</sup> in the earth (Dür et al.,2005). Therefore, carbonate is closely associated with atmospheric  
42 CO<sub>2</sub> concentrations through carbonate weathering processes and becomes an important component  
43 of the global carbon cycle. As a result, carbon uptake from chemical weathering can significantly  
44 influence the evolution of atmospheric [CO<sub>2</sub>] in the Earth's long-term (over the past 100 million  
45 years) (Berner et al.,1983) and short-term climate (Liu,2012). Moreover, the previous research has  
46 shown that more carbon is sequestered from carbonate weathering than from silicate rock  
47 weathering (Liu,2012).

48 Consequently, it is very important to accurately estimate net carbon uptake from carbonate  
49 weathering processes. Currently, there are two main methods for calculating carbonate weathering  
50 carbon sinks. The first method uses the empirical relationship between carbon uptake rates and  
51 different lithology types and calculates the weathering by determining the different empirical  
52 dissolved constants such as 0.0294 (g C mm<sup>-1</sup>) or 0.0383g C mm<sup>-1</sup> estimated by Amiotte Suchet  
53 and Probst (1995) and Bluth and Kump (1994), respectively. The other method estimates carbon  
54 sinks using observations of river chemistry such as karst water flow and concentrations of  
55 bicarbonate. Nevertheless, there are always some differences between the results of the two  
56 calculation methods (Yan et al.,2011).

57 Karst is widely distributed in China, which has approximately 3.44 million km<sup>2</sup> of karst area,  
58 including buried, covered, and exposed carbonate rock areas (Jiang et al.,2014), and about 0.4  
59 million km<sup>2</sup> of karst is located in the southwest (Jiang and Yuan,1999). The most frequently used  
60 calculation methods for carbon sequestration are the forward method (Zhang,2011) and, in  
61 China's karst regions, the river chemistry method. But, there are some defects of the forward  
62 method because physical models cannot truly reflect the in situ karstification and carbon migration  
63 process (Zhiqiang et al.,2011), and for this reason the river chemistry method is more frequently  
64 adopted (Zhao et al.,2010;Yan et al.,2012;Zhang et al.,2015;Huang et al.,2015).

65 There are large discrepancies in the estimates of carbon sequestration in China, ranging from  
66 5 Tg Cyr<sup>-1</sup> (Jiang and Yuan,1999) to 12 Tg Cyr<sup>-1</sup> (Yan et al.,2011) and 18 Tg Cyr<sup>-1</sup> (Liu and  
67 Zhao,2000). These values are usually derived from the observed carbon discharge from a single  
68 water chemical observatory in a single basin in southwest China; however, there may be some  
69 deviations in the results of this single observation site because of the high heterogeneity of the  
70 karst system, the sensitivity of the response to external environment changes, and the interference  
71 of human activity which is usually intensified in karst regions. Studies have shown that, carbonate  
72 weathering is sensitive to ecosystem dynamics, which means that carbonate weathering and  
73 associated CO<sub>2</sub> consumption discharges quickly react to any global changes or land use

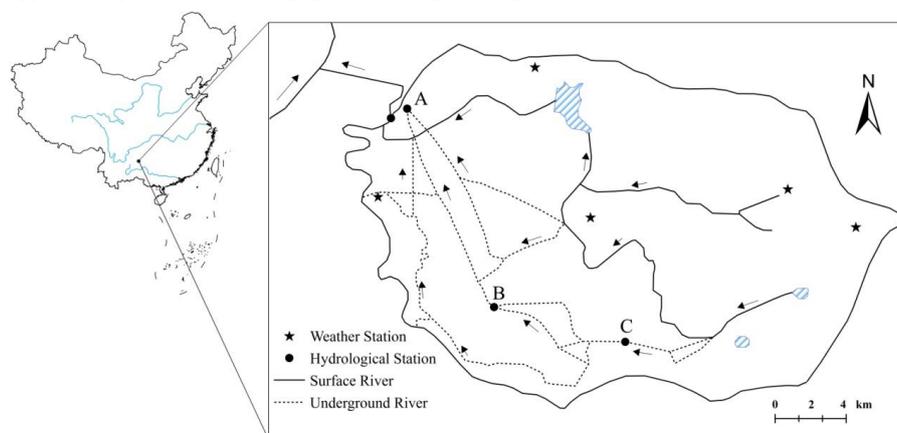


74 modifications (Calmels et al.,2014). Therefore, in this study we used flow and carbon ion  
75 concentration data from three observation stations with different environmental background  
76 conditions in the same karst groundwater basin in order to analyze the differences in carbon  
77 uptake between stations and their impact factors. This work also provides a reference for  
78 improving the calculation accuracy of karst geological carbon sink.

## 79 2. Materials and methods

### 80 2.1. Study Area

81 Houzhai basin is located in Puding county in the middle of Guizhou province ( $26^{\circ}13' - 26^{\circ}$   
82  $15' N$ ,  $105^{\circ}41' - 105^{\circ}43' E$ ). The total area of the basin is 80.65 km<sup>2</sup>, and the length of the main  
83 river is about 12 km (including the ground and underground river) (Figure 1). The southeastern  
84 portion of the basin is lower than the northwestern portion. The relative elevation of the basin is  
85 about 150 m, and its average altitude is 1250 m. A typical hoodoo depression physiognomy is  
86 distributed in the east of the basin where the main land-use type is forest vegetation, while karst is  
87 distributed in the west of the basin where the main land-use type is farmland. It has a subtropical  
88 humid climate; the average rainfall is 1316.8 mm and the average temperature is 15.5 °C. The  
89 rainy season occurs from May to October and the dry season from November to April.  
90 Precipitation during the rainy season accounts for more than 80% of annual rainfall. Bedrock in  
91 the basin is composed of mainly carbonate rock formed during the Triassic. As a result of  
92 lithology and geological structure, karstification is strong and karst formation is widely developed  
93 in the basin. Hydrological runoff processes are significantly influenced by karst underground  
94 space (gap and pipe) and its distribution characteristics. There is no obvious surface river valley  
95 upstream, and although there is a river valley midstream and downstream, seasonal runoff only  
96 appears temporarily, and leakage pits are arranged along the riverbed.



97

98 Figure 1. The distribution of drainage systems and weather hydrological stations.

### 99 2.2. Data Sources and Methods

#### 100 2.2.1. Data Sources

101 The main data are derived from three groundwater hydrology and water quality monitoring



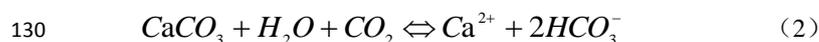
102 stations: A (Maoshuikeng MSK), B (Liugu LG), and C (Laoheitan LHT) (Figure1). The three  
 103 stations are located in the upstream, midstream and downstream reaches of the basin, respectively.  
 104 The LHT station is located on the edge of the peak cluster depression, the LG station is located in  
 105 the region of the peak cluster basin, and the control areas of the two stations are 24.06 km<sup>2</sup> and  
 106 15.81 km<sup>2</sup>, respectively (Wang et al.,2010). MSK station is located at the outlet of the  
 107 underground river, and its control area is 80.56 km<sup>2</sup> (Figure1). We selected continuous and  
 108 complete data, which contain the average daily flow data and  $HCO_3^-$  concentration data from  
 109 MSK station (1996-2001), LG station (1992-1996), and LHT station (1988-2002). Average annual  
 110 temperatures from 1988-2002 were provided by Puding station, which was located at the boundary  
 111 of the basin. Concentration data were measured directly by the water samples station. Water  
 112 samples were collected from the underground rivers at a water depth of 0.6 m at exit, 6 times per  
 113 month in the rainy season (May to October) and 3 times a month in the dry season (November to  
 114 April of the following year) sampling, and water samples were measured for pH using a portable  
 115 meter. Water temperature and the concentration of bicarbonate ( $[HCO_3^-]$ ) were determined by  
 116 titration with standard hydrochloric acid (HCl) immediately after samples were taken at the  
 117 sampling site.

### 118 2.2.2. Determination of Water Samples and DIC Method

119 Bicarbonate concentration was measured using a neutralization titration method. The steps of  
 120 the method are as follows: (1) Add a sample to a 100 ml beaker and drip 4 drops of phenol red  
 121 indicator and then shake the sample well; (2) Titrate the sample using standard HCl (0.025 mol/L)  
 122 until the red disappears at a pH of 8.4 and record the standard HCL usage quantity  $V_1$ ; (3) Drip  
 123 three drops of methyl orange indicator into the sample and shake well, then titrate using standard  
 124 HCl until the color of the sample changes to orange at a pH of 4.4, and record the HCl usage  
 125 quantity ( $V_2$ ); and (4) Finally, measure the concentration of carbonate ions in the water samples  
 126 by using formula (1):

$$127 \quad \rho = \frac{(V_2 - V_1) \times c \times 61.017 \times 1000}{V} \quad (1)$$

128 In a karst environment, carbon dioxide dissolves in water and undergoes a reversible chemical  
 129 process (2) with calcium carbonate:



131 Under a steady state, the quantity of carbon dioxide dissolved in karst water is equal to the  
 132 discharge of CO<sub>2</sub> from the atmosphere. That discharge in g C m<sup>-2</sup> time step<sup>-1</sup> is calculated  
 133 according to the following formula (3) (Yan et al.,2011;Amiotte-Suchet and Probst,1993).

$$134 \quad F = \frac{1}{2} c q \frac{M_c}{M_{HCO_3}} \quad (3)$$



135 where  $c$  is the concentration of bicarbonate ions ( $\text{g/m}^3$ );  $q$  is the production flow ( $\text{m}^3/\text{time}$   
 136 step);  $M_C$  and  $M_{\text{HCO}_3^-}$  are the molecular weights of C and  $\text{HCO}_3^-$ , respectively, and  $1/2$  means that  
 137 1 mol of bicarbonate needs only half a mole of  $\text{CO}_2$  from the soil or atmosphere. Additionally,  
 138 karst water is generally alkaline. The content of  $\text{CO}_3^{2-}$ -C in dissolved inorganic C is very small, so  
 139 we did not need to consider it in the DIC calculation (Gelbrecht et al., 1998; Yan et al., 2011). In  
 140 this study, we used the formula  $F_1$  below to calculate net carbon uptake by karst, using the  
 141 estimates of year mean  $[\text{HCO}_3^-]$ , ion concentration during the dry-wet season, and the mean daily  
 142 underground flow discharge.

$$143 \quad F_1 = \frac{1}{2} \cdot \frac{M_C}{M_{\text{HCO}_3^-}} \cdot \bar{c} \cdot \sum_{n=1}^{12} q_n \quad (4)$$

144 where  $\bar{c}$  is either the annual average bicarbonate density or the ion concentration in the dry-wet  
 145 season ( $\text{mg/L}$ ), and  $q$  is the average daily excretion ( $\text{m}^3/\text{s}$ ,  $n=365$  day).

### 146 3. Results

#### 147 3.1. Dry -Wet Seasonal and Inter-annual Variations of Ion Concentration and Discharge

148 For each site during the study period, the ion concentration in the wet season was slightly  
 149 smaller than in the dry season. LHT station, which had the longest study period, exhibited the  
 150 highest and lowest values for bicarbonate ion concentration, which were  $240.5 \text{ mg/L}$  (1994) and  
 151  $201.7 \text{ mg/L}$  (1999) in the rainy season,  $259.6 \text{ mg/L}$  (2002) and  $234.7 \text{ mg/L}$  (1991) in the dry  
 152 season, and  $248.3 \text{ mg/L}$  (1994) and  $218.8 \text{ mg/L}$  (1999) for the whole year, respectively. Moreover,  
 153 there was a negative correlation between ion concentration and discharge (Figures 2, 3, and 4).  
 154 From 1992-1996, the annual average concentration of bicarbonate ions in the rainy season, dry  
 155 season, and whole year were  $228.8 \text{ mg/L}$ ,  $249.3 \text{ mg/L}$ ,  $239.1 \text{ mg/L}$ , respectively for LHT station  
 156 and  $222.0 \text{ mg/L}$ ,  $253.5 \text{ mg/L}$ ,  $237.8 \text{ mg/L}$ , respectively at LG station. Although there is little  
 157 difference in ion concentration between the two stations, when considering the stability of ion  
 158 concentration changes (Table 1), LG station was more stable than LHT station. During the same  
 159 period, from 1996-2001, the annual average ion concentrations in the rainy season, dry season,  
 160 and whole year were  $217.8 \text{ mg/L}$ ,  $247.4 \text{ mg/L}$ , and  $232.6 \text{ mg/L}$ , respectively for LHT station, and  
 161  $209.9 \text{ mg/L}$ ,  $226.4 \text{ mg/L}$ ,  $218.2 \text{ mg/L}$ , respectively for MSK station. Table 1 shows that MSK  
 162 station was more stable than LHT station with respect to the standard deviation of ion  
 163 concentration variation. Although, the difference in ion concentrations between LHT and LG was  
 164 smaller than that between LHT and MSK, differences in the site as a whole were small.

165 The discharge from MSK station, which is located at the outlet of the underground river basin,  
 166 was larger than the discharge from LG and LHT. From 1996-2001, the annual average flow values  
 167 of MSK in the rainy season, dry season, and whole year were  $282.5 \text{ m}^3$ ,  $121.3 \text{ m}^3$ ,  $403.9 \text{ m}^3$ ,  
 168 respectively, and the flow in the rainy season was significantly greater than in the dry season. The  
 169 flow of LG and LHT in the rainy and dry seasons exhibited the same trend (Figure 2, 3, and 4).

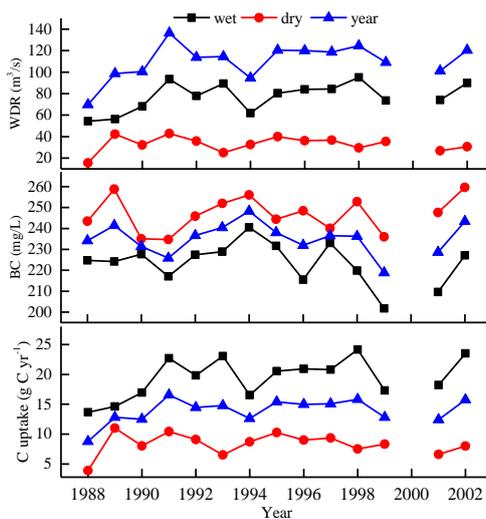


170 From Table 1, we can determine the stability of flow as follows: MSK>LG>LHT.

171 Table 1. Standard deviation of production flow, ion concentration, and carbon sink for each station in the dry  
 172 and wet seasons and over the whole year

Station	Water Discharge Rate			Bicarbonate Concentration			Carbon Uptake		
	wet	dry	year	wet	dry	year	wet	dry	year
MSK	19.59	19.87	21.83	6.46	6.64	5.26	1.12	0.84	0.43
LG	19.78	2.67	18.55	10.64	4.81	4.99	2.93	0.45	1.54
LHT	13.28	7.33	16.37	10.04	8.41	7.55	3.34	1.84	2.05

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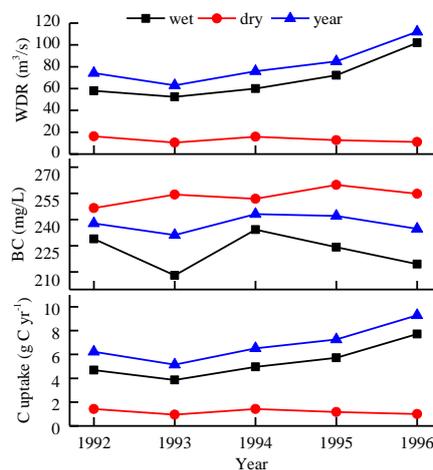


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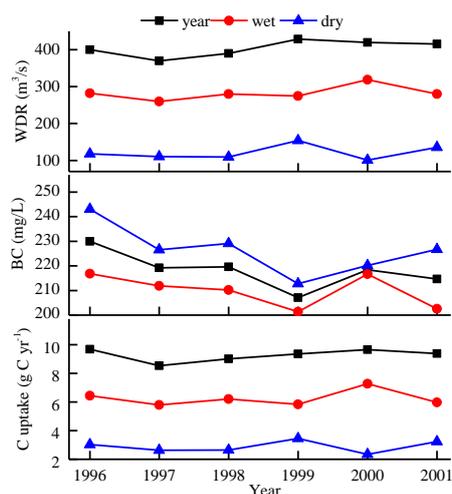
Figure 2. Variation in runoff, ion, and carbon sink for LHT station (1988-2002).



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178

Figure 3. Variation in runoff, ion, and carbon sink for LG station (1992-1996).



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 180

Figure 4. Variation in runoff, ion, and carbon sink for MSK station (1996-2001).

181 **3.2. Dry and Wet Seasonal and Inter-annual Variations in Carbon Uptake Rate**

182 From 1996-2001 at MSK station, the annual average carbon sink discharges of underground  
 183 water in the rainy season, dry season, and whole year was 12.51, 5.78, and 9.28g/m<sup>2</sup>, respectively,  
 184 with a significantly greater net discharge in the rainy season compared to the dry season. From  
 185 1992-1996 at LHT station, the annual average carbon sink discharges in the rainy season, dry  
 186 season, and whole year was 10.78g/m<sup>2</sup>, 2.38g/m<sup>2</sup>, and 6.89g/m<sup>2</sup>, respectively. From 1988-2002  
 187 (data from 2000 is missing) at LHT station, the annual average carbon sink discharges in the rainy  
 188 season, dry season, and whole year were 19.48, 8.34, and 13.91g/m<sup>2</sup>, respectively, greater than  
 189 both LG and MSK stations (Figure 6). From 1996-2002 at LHT station, the annual average net  
 190 carbon sink discharges in the rainy season, dry season, and whole year were 20.82 g/m<sup>2</sup>, 8.14 g/m<sup>2</sup>,  
 191 and 14.48 g/m<sup>2</sup>, respectively while from 1992-2002 the respective values were 20.18 g/m<sup>2</sup>, 8.72  
 192 g/m<sup>2</sup>, and 14.45 g/m<sup>2</sup>. Comparing the results for the same period, we found that the annual carbon  
 193 sink discharge in the rainy season, dry season, and whole year for LHT station were greater than  
 194 those for MSK and LG stations. However, with respect to the stability of carbon discharge (Table  
 195 1), MSK was the most stable in the rainy season while LG was the most stable in the dry season.

196 **4. Discussion**

197 **4.1. Flow and Ion Concentration Change and its Effects on Carbon Sink**

198 According to the flow trend of each station, we can see that the flow in the rainy season is  
 199 consistent with the flow trend for the whole year, suggesting that the runoff from precipitation in  
 200 the rainy season accounts for the majority of the annual runoff. This is mainly a result of the  
 201 monsoon climate where summer (May-September) precipitation levels are significantly higher  
 202 than in the winter (December-February); however, the flow trend in the dry season was smooth  
 203 (figure 5) because of less rainfall in the dry season when the runoff was mainly supplied by soil



204 water and fissure/pore water. It also suggests that the composition of underground karst aquifer  
205 medium structures have important effects on the dry season flow. However, due to the difference  
206 between the control area and the surface to underground diversion ratio, the flows between sites  
207 cannot be compared.

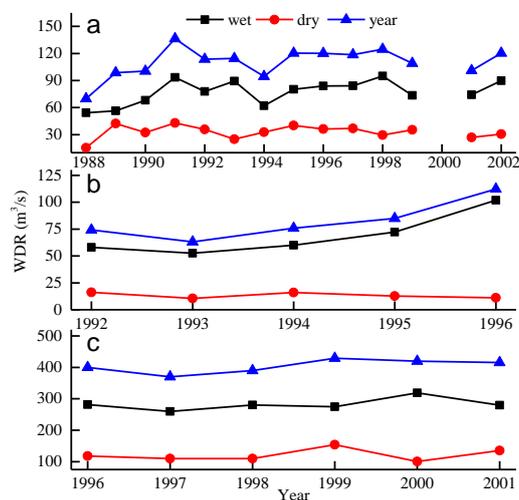
208 The trends in annual runoff among sites are consistent with carbon sink discharge but differ  
209 from the trends for bicarbonate ions (figure 2, 3, 4). This suggests that the effect of flow change on  
210 carbon sink is greater than on ion concentration. According to changes in ion concentrations in the  
211 rainy season, dry season, and whole year (figure 2, 3, and 4), flow correlated negatively with  
212 carbon ion concentration, but if there was a significant difference between flow in the rainy season  
213 and in the dry season, bicarbonate ion concentrations would not decrease when the flow increased  
214 rapidly. Although we found differences between bicarbonate ion concentrations in the dry and wet  
215 seasons (ion concentrations in the dry season are greater than in the rainy season), they were  
216 small.

217 We then contrasted the results of each site. From 1992-1996, the annual average carbon ion  
218 concentration was 237.8 mg/L for LG station and 239.1 mg/L for LHT station. The annual average  
219 flow of LHT station was 1.37 times that of LG station, but the ion concentration did not decline  
220 significantly due to the increase in flow. The basin area controlled by LHT station is characterized  
221 by peaks and valleys, which have good vegetation cover that recovers rapidly. Previous studies  
222 have shown that the concentration of  $\text{HCO}_3^-$  is vulnerable to LUCC (land cover and land use  
223 change) and other environmental changes (Zhao et al.,2010;Lan et al.,2015). In particular, the fast  
224 recovery of vegetation can significantly promote the dissolution of carbonate and thus increase  
225 bicarbonate ion concentration in karst groundwater (Liu et al.,2010;Berner,1997). This suggests  
226 that when there is little change in flow, the effect of flow increase on ion concentration dilution is  
227 smaller than the environmental effects of chemical carbonate weathering.

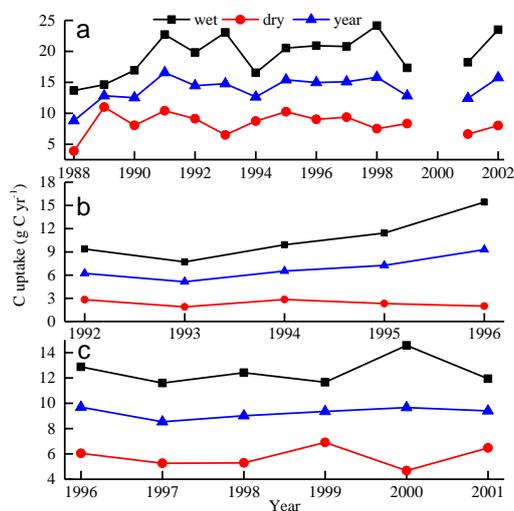
228 From 1996-2001, annual average carbon ion concentrations at LHT and MSK stations were  
229 232.6 mg/L and 218.2 mg/L, respectively, but the average annual flow for LHT was only 115.6 m<sup>3</sup>,  
230 while MSK exhibited an annual flow of 3.49 times that value. Similarly, ion concentration did not  
231 decline significantly as a result of the increase in flow. MSK station is located at the edge of a  
232 paddy field, which has thicker soil coverage, and the underground rivers have more biological  
233 carbon sources that could produce more  $\text{HCO}_3^-$  in the ground water compared to LHT. Therefore,  
234 the flow only has a partial dilution effect on ion concentration. Meanwhile, the effect of flow  
235 increase on ion concentration dilution exceeded the environmental effects of carbonate weathering.  
236 This shows that the dilution effects of the flow change on ion concentrations were not  
237 multiplicative. That is to say, the flow was just a part of the dilution effect on ion concentrations,  
238 and thus carbonate weathering was significantly affected by factors other than flow. Bicarbonate  
239 ion concentrations of karst underground water may have a relatively stable extremum when



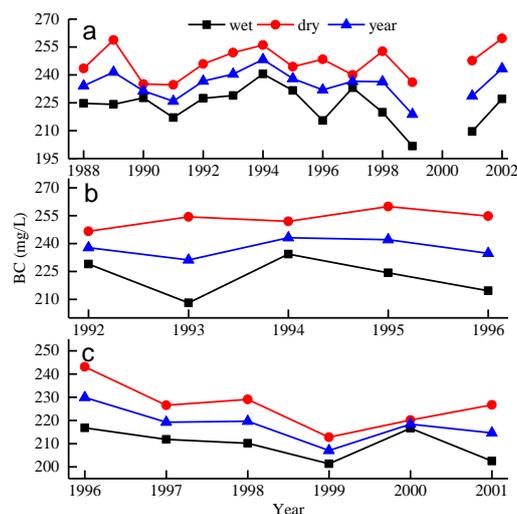
240 environmental conditions are stable. In addition, although studies have shown that under the  
 241 conditions of a stable LUCC, the strength of the carbon sink from rock weathering will depend on  
 242 the climate (e.g. temperature T, precipitation P) (Hagedorn and Cartwright,2009;Gislason et  
 243 al.,2009;Tipper et al.,2006), the annual average carbon sink trend for LHT station, which had the  
 244 longest study period (1988-2002), differed significantly from the annual average temperature trend.  
 245 However, this may be a result of time resolution limitations of the monitoring data.



246  
 247 Figure 5. Variation in flow among sites in the rainy season, dry season, and whole year during the study period (a.  
 248 LHT; b. LG; c. MSK).



249  
 250 Figure 6. Variation in net carbon discharge among sites in the rainy season, dry season, and whole year during the  
 251 study period.  
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253

254

Figure 7. Variation in bicarbonate ion concentrations among sites in in the rainy season, dry season, and whole

255

year during the study period.

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#### 4.2. Variation in Carbon Sink Discharge for Each Site

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The carbon sink discharge for each site in the rainy season was greater than for that of the dry season and the annual average, while the carbon sink discharge in the dry season was less than the annual average (figure 6). This shows that the karst carbon sink (karstification's absorption of atmospheric CO<sub>2</sub> and soil CO<sub>2</sub>) changes significantly with the seasons and exhibits striking seasonal patterns. The reason for this is that the considerable summer rainfall runoff significantly increases the amount of carbon sink discharge in the rainy season. The annual average carbon sink discharge of all the stations during study period shows that LHT>MSK>LG; however, comparisons cannot be made due to the different study periods.

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During the same period, the carbon sink values for LHT station in the rainy season, dry season, and whole year were greater than both LG and MSK stations. From 1992-1996, the flow for LG in the rainy season and dry season were both significantly less than for LHT (figure 6). The annual average concentration for LG in the rainy season and dry season were 239.1 mg/L and 237.8 mg/L, respectively, and are slightly less than LHT (figure 6). The difference in carbon sink discharge between the two stations results from differences in flow. Furthermore, the LHT control basin station is surrounded mainly by forest vegetation while the LG control basin is surrounded mainly by dry farmland, and the different LUCC types may further increase differences in carbon sink discharge between the two stations.

274

From 1996-2001, the carbon sink discharge for LHT station in the dry and wet seasons and whole year were greater than for MSK station. The annual average concentration for LHT (230.4 mg/L) was greater than for MSK (218.2 mg/L), while the runoff was significantly greater for

276



277 MSK than for LHT. On the one hand, the fact that the carbon sink discharge for MSK was less  
278 than LHT might be linked to the water conveying distance and LUCC type of the control area. The  
279 carbon sink for MSK, which is the groundwater outlet for the whole basin, was influenced by the  
280 landform and LUCC type of the entire river basin (Figure 1). Previous research has shown that  
281 karst erosion rates under soil vary significantly for different LUCC types in karst watersheds, and  
282 the averages for cultivated land, thickets, secondary forests, grassland, and forest were found to be  
283 4.02, 7.0, 40.0, 20.0 and 63.5 t km<sup>2</sup> a<sup>-1</sup>, respectively (Zhang,2011), with the erosion rate of  
284 carbonate karst under the cover of cultivated land being the lowest (Yan et al.,2014). Previous  
285 research has also shown that vegetation can increase the speed of weathering by 3-10 times  
286 (Berner,1997). According to monitoring data from Guilin province in China vegetation restoration  
287 can significantly increase the average annual concentration of soil CO<sub>2</sub> (increased by 266% in 10  
288 years). The increase in CO<sub>2</sub> promotes the dissolution of carbonate rock and greatly increases  
289 HCO<sub>3</sub> concentrations in groundwater (Liu,2012;Waterson and Canuel,2008). Research in the  
290 Houzhai valley has shown that forest recovery causes more carbon dioxide (CO<sub>2</sub>) to be dissolved  
291 in karst water, which in turn allows for carbon uptake by forests (Yan et al.,2014). This research  
292 also suggested that karst hydro-geochemistry and the karst-related carbon cycle could be regulated  
293 effectively by different LUCC types (Zhao et al.,2010). On the other hand, in the process of runoff  
294 converging at the outlet, much of the water flows into the surface river and flows across the thick  
295 soil of paddy fields, but our calculation method only considers carbonate weathering carbon sinks  
296 (water - rock - gas interaction) and not the organic processes, which may affect calculation results.  
297 Research has shown that aquatic photosynthesis uses dissolved inorganic carbon to synthesize  
298 organic carbon (Waterson and Canuel,2008;Tao et al.,2009), and this is also one of the factors  
299 affecting the results. In addition, differences in basin surface water and groundwater proportions  
300 controlled by geological landform could also affect the calculation results.

301 To sum up, the calculation results for carbon sink discharge from karstification using  
302 watershed monitoring data in areas limited to a dominant single LUCC type may differ in a small  
303 watershed where geomorphology, hydrology, and land use cover are different. This is one of the  
304 reasons why there is such a large deviation in China's total carbon sink discharge estimated by  
305 using carbon sink data from a single watershed in a karst region. Therefore, considering the  
306 diversity of landform types and surface covers in the southwestern karst area, it is important to  
307 develop a monitoring network in different topographical and surface cover regions, using a variety  
308 of monitoring technologies to improve the accuracy of karst carbon sink estimates.

## 309 5. Conclusion

310 It is important basic significance to determine the main factors that affect the karst  
311 geological carbon sink and understand the mechanism of their effects on the karst geological  
312 carbon sink. Through the contrast analysis of flow, bicarbonate ion concentrations and carbon sink



313 discharge between the different sites in three stations located upstream, midstream and  
314 downstream of Houzhai basin, respectively, we analyzed the reasons for the difference of flow,  
315 bicarbonate ion concentrations and carbon sink discharge. The preliminary conclusions are as  
316 follows: (1) The carbon sink discharge was mainly controlled by the flow of each site, and LUCC  
317 type has important effects on the bicarbonate ions concentrations in each site. (2) The large  
318 difference in flow among sites did not lead to significant differences in bicarbonate ion  
319 concentrations in the sites, showing that the rapid increase in flow only has a partial dilution effect  
320 on ion concentrations. Due to the high speed and stability of chemical carbonate weathering,  
321 bicarbonate ion concentrations did not change significantly, and thus did not affect carbon sink  
322 discharge. (3) For different LUCC conditions, if runoff is stable, the influence of flow variation on  
323 ion concentration will be less than the effects of chemical carbonate weathering by different  
324 environmental conditions (comparison of LHT and LG results is 150%) on bicarbonate ion  
325 concentrations. However, if runoff increases significantly, the impact of runoff variation on  
326 bicarbonate ions will be greater than the effects of chemical carbonate weathering by different  
327 environmental conditions (comparison results of LHT and MSK).

328 In addition, this study without considering the proportional distribution problem of the  
329 surface and underground runoff in catchment area of each monitoring sites, which may have  
330 influence on the results. Therefore, it is necessary to monitor runoff and bicarbonate ions of the  
331 surface and underground simultaneously, but unfortunately the monitoring data we used  
332 did not achieve it.

333

### 334 **Acknowledgements**

335 This work was partially supported by the National Natural Science Foundation of China  
336 (No.41371045) and the National Key Technology R&D Program of the Ministry of Science and  
337 Technology of China(No.2014BAB03B001).

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