

Differences and influencing factors related to underground water carbon uptake by karsts in the Houzhai Basin, southwestern China

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Abstract

The karst geological carbon sink is an important part of the global carbon sink. Consequently, accurate determination of the carbon sink of karst ecosystems has become a core issue in research. We used flow and carbon ion concentration data from three stations with different environmental background conditions in the Houzhai basin to analyze the differences in carbon uptake between stations and to determine their impact factors. The results show that carbon sink discharge was mainly controlled by the flow at each site. Preliminary analysis indicated that the rapid increase in flow only had a partial dilution effect on the ion concentrations due to the high speed and stability of chemical carbonate weathering. The Land-Use and Land-Cover Change (LUCC) type had important effects on the bicarbonate ion concentrations; if runoff was stable, the influence of flow variation on the ion concentration was lower than the effects of chemical carbonate weathering on bicarbonate ion concentrations under different environmental conditions (a comparison of Laoheitan and Liugu stations showed a difference of 150%). However, if runoff increased significantly, the impact of runoff variation on bicarbonate ions was greater than the effects of chemical carbonate weathering caused by different environmental conditions (comparison results of Laoheitan and Maoshuikeng stations). This work provides a reference for the calculation of the karst geological carbon sink.

1. Introduction

Global warming from the emissions of greenhouse gases has become the core issue of global environmental change. One of the most pressing concerns in the science of global climate change is the effective accounting of atmospheric CO₂ in the global budget (Schindler, 1999; Melnikov and Neill, 2006; Liu et al., 2010; Kao et al., 2014) because in order to control global warming it is necessary to control emissions of carbon dioxide through carbon capture and storage (CCS) technology. In addition to developing CCS technology, an understanding of a number of natural ecological and geological processes such as rock weathering, plant growth, and other physical, chemical, and biological processes can also improve CCS (Hoffmann et al., 2013). Carbonate

36 weathering in rock weathering processes is considered to be both an important source and sink of
37 CO₂ (Zeng et al.,2015;Lian et al.,2011;Liu and Zhao,2000;Serrano-Ortiz et al.,2010;James et
38 al.,2006). Carbonate rock dissolves more easily in water in which CO₂ is dissolved, and at a
39 temperature of 15 °C and atmospheric CO₂ partial pressure of 380 ppmv, the equilibrium
40 concentration of dissolved inorganic carbon (DIC) in a water system of CaCO₃-CO₂-H₂O can
41 reach 1231 mol/L in water with calcium carbonate (Dreybolt,1988). Moreover, karst is widely
42 distributed around the world; it occupies approximately 11.2% of the Earth's surface and
43 approximately 15 million km² over the earth (Dürr et al.,2005).Therefore, carbonate is closely
44 associated with atmospheric CO₂ concentrations through carbonate weathering processes and has
45 become an important component of the global carbon cycle. As a result, carbon uptake from
46 chemical weathering can significantly influence the evolution of atmospheric [CO₂] in the Earth's
47 long-term (over the past 100 million years) (Berner et al.,1983) and short-term climate. Moreover,
48 previous research has shown that more carbon is sequestered from carbonate weathering than from
49 silicate rock weathering (Liu,2012). The problems associated with karst dissolved inorganic
50 carbon (DIC) re-precipitation occur in geological time scales. Existing studies have shown that
51 karst aquatic organisms can convert DIC into organic carbon (OC); consequently, carbonate
52 weathering has stable carbon sink effects on a long time scale (Chen et al.,2014;Liu,2012).
53 Moreover, the carbon sink intensity is 51 times higher than that of the ocean biological pump
54 (Passow and Carlson,2012;Chen et al.,2014). This shows that DIC used in photosynthesis of
55 aquatic organisms has important carbon sink effects in water. In addition, it also implies that DIC
56 can produce stable carbon sinks in karst areas.

57 Consequently, it is very important to accurately estimate net carbon uptake from carbonate
58 weathering processes. Currently, there are two main methods for calculating carbonate weathering
59 carbon sinks. The first method uses the empirical relationship between carbon uptake rates and
60 different lithology types and calculates weathering by determining different empirical dissolved
61 constants, such as 0.0294 g C mm⁻¹ and 0.0383 g C mm⁻¹ estimated by (Amiotte-Suchet and
62 Probst,1993) and (Bluth and Kump,1994), respectively. The other method estimates carbon sinks
63 using observations of river chemistry such as karst water flow and concentrations of bicarbonate.
64 Nevertheless, there are always some differences between the results of the two calculation
65 methods (Yan et al.,2011).

66 The karst carbon sink is influenced by different factors, such as vegetation type, temperature
67 and aquatic microorganisms (Hagedorn and Cartwright,2009). Existing studies show that the
68 carbon sink can differ by more than 14% under different land cover types (Table 1) (Qin et
69 al.,2011). There was a significant correlation between temperature and the CO₂ concentration in
70 20- and 50-cm deep soil layers in the Wangpai mountain of the Maolan conservation area
71 (Wan,1995), and the mechanism and intensity of soil CO₂ were closely related to the habitat of the
72 soil. However, there was no significant correlation between temperature change and carbon sink
73 flux (Yu et al.,2015). This may have occurred because the temporal resolution effects did not

74 match those of the temperature and carbon sink changes or changes in the "biological pump" of
 75 aquatic organisms caused by changes in light and temperature. There was a significant correlation
 76 between the biomass of aquatic organisms and their DIC utilization, and the change in $\delta^{13}\text{C}$ in
 77 a few submerged plant environments was much smaller than the large number of submerged plant
 78 growth environments. However, the change in $\delta^{13}\text{C}$ was mainly influenced by changes in the
 79 metabolism of aquatic plants during the day and at night (Chen et al.,2014).

80 Karst is widely distributed in China, which has approximately 3.44 million km^2 of karst area,
 81 including buried, covered, and exposed carbonate rock areas (Jiang et al.,2014), and about 0.4
 82 million km^2 of karst is located in southwestern China (Jiang and Yuan,1999).The most frequently
 83 used calculation method for carbon sequestration is the forward method (Zhang,2011) and in
 84 China's karst regions, the river chemistry method. However, there are some defects in the forward
 85 method because physical models cannot truly reflect the in situ karstification and carbon migration
 86 process (Kang et al.,2011); consequently, the river chemistry method is more frequently adopted
 87 (Zhao et al.,2010;Yan et al.,2012;Zhang et al.,2015;Huang et al.,2015). There are large
 88 discrepancies in the estimates of carbon sequestration in China, ranging from 5 Tg Cyr^{-1} (Jiang and
 89 Yuan,1999) to 12 Tg Cyr^{-1} (Yan et al.,2011) and 18 Tg Cyr^{-1} (Liu and Zhao,2000). These values
 90 are usually derived from the observed carbon discharge from a single water chemical observatory
 91 in a single basin in southwestern China; however, there may be some deviations in the results of
 92 this single observation site because of the high heterogeneity of the karst system, the sensitivity of
 93 the response to external environment changes, and the interference of human activity, which is
 94 usually intensified in karst regions. Studies have shown that carbonate weathering is sensitive to
 95 ecosystem dynamics, which means that carbonate weathering and associated CO_2 consumption
 96 discharges quickly react to any global changes or land use modifications (Calmels et
 97 al.,2014).Therefore, in this study, we used flow and carbon ion concentration data from three
 98 observation stations with different environmental background conditions in the same karst
 99 groundwater basin in order to analyze the differences in carbon uptake between stations and their
 100 impact factors. This work also provides a reference for improving the calculation accuracy of the
 101 karst geological carbon sink.

102 Table 1 The proportion of different land cover types and characteristics of underground river chemicals in the
 103 Dagou River

Region	Forest land (%)	Arable land (%)	Bare Rock (%)	Barren land (%)	HCO_3^- (mg/L)	PCO_2 (Pa)	Carbon sink ($t \text{ C/km}^2 a$)
The west bank of Dagou River	56.13	15.15	14.1	10.98	233.71	909.46	45.67
The east bank of Dagou River	20.8	12.95	29.57	25.95	177.26	257.37	40.12

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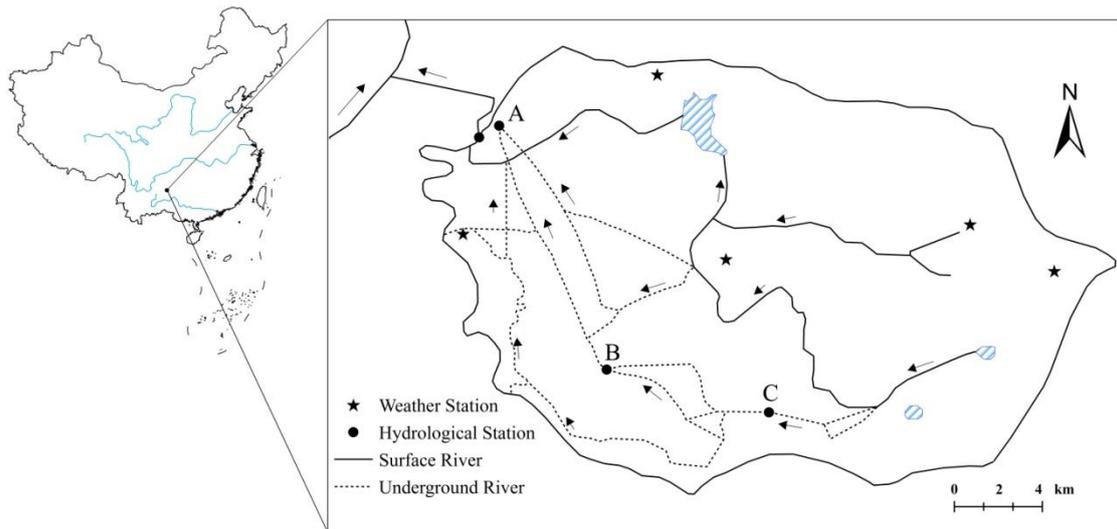


Figure 1. The distribution of drainage systems and weather hydrological stations.

2. Materials and methods

2.1. Study Area

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

2.2. Data Sources and Methods

2.2.1. Data Sources

The main data were derived from three groundwater hydrology and water quality monitoring stations: A (Maoshuikeng MSK), B (Liugu LG), and C (Laoheitan LHT) (figure 1). The three stations are located in the upstream, midstream and downstream reaches of the basin, respectively.

133 The LHT station is located on the edge of the peak cluster depression, the LG station is located in
 134 the region of the peak cluster basin, and the control areas of the two stations are 24.06 km² and
 135 15.81 km², respectively (Wang et al.,2010). The MSK station is located at the outlet of the
 136 underground river, and its control area is 80.56 km² (Figure1). We selected continuous and
 137 complete data, which contain average daily flow data and HCO_3^- concentration data from the
 138 MSK station (1996-2001), LG station (1992-1996), and LHT station (1988-2002). The average
 139 annual temperatures from 1988-2002 were provided by the Puding station, which is located at the
 140 boundary of the basin. Concentration data were measured directly by the water sampling station.
 141 Water samples were collected from the underground rivers at a water depth of 0.6 m at the exit, 6
 142 times per month in the wet season (May to October) and 3 times per month in the dry season
 143 (November to April of the following year), and water samples were measured for pH using a
 144 portable meter. The water temperature and concentration of bicarbonate ($[HCO_3^-]$) were
 145 determined by titration with standard hydrochloric acid (HCl) immediately after samples were
 146 collected at the sampling site.

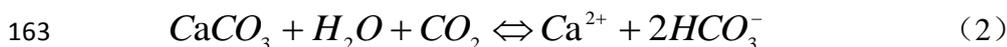
147 **2.2.2. Determination of Water Samples and DIC Method**

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

$$156 \quad \rho = \frac{(V_2 - V_1) \times c \times 61.017 \times 1000}{V} \quad (1)$$

157 The flow discharge data of each station were converted from the water level using a
 158 stage-discharge curve. The discharge monitoring frequency was twice a day, with eight points in
 159 the AM and eight points in the PM, and the average value of the two time periods was calculated
 160 as the discharge data for one day.

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



164 Under a steady state, the quantity of carbon dioxide dissolved in karst water is equal to the
 165 discharge of CO₂ from the atmosphere. That discharge in a g C m⁻² time step⁻¹ is calculated
 166 according to the following formula (3) (Yan et al.,2011;Amiotte-Suchet and Probst,1993):

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

where c is the concentration of bicarbonate ions (g/m^3); q is the production flow ($\text{m}^3/\text{time step}$); M_C and $M_{HCO_3^-}$ are the molecular weights of C and HCO_3^- , respectively, and $1/2$ indicates that 1 mol of bicarbonate needs only half a mole of CO_2 from the soil or atmosphere. Additionally, karst water is generally alkaline. The content of CO_3^{2-} C in dissolved inorganic C is very small, so we did not need to consider it in the DIC calculation (Yan et al.,2011;Gelbrecht et al.,1998). In this study, we used the formula F_1 below to calculate net carbon uptake by karst, using the estimates of mean annual $[HCO_3^-]$, ion concentration during the dry-wet season, and the mean daily underground flow discharge.

$$F_1 = \frac{1}{2} \cdot \frac{M_c}{M_{HCO_3}} \cdot \bar{c} \cdot \sum_{n=1}^{12} q_n \quad (4)$$

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

3. Results

3.1. Dry -Wet Seasonal and Inter-annual Variations in Ion Concentration and Discharge

There was a negative correlation between ion concentration and discharge (figures 2, 3, and 4). For each site during the study period, the ion concentration in the wet season was slightly lower than in the dry season. The LHT station, which had the longest study period, exhibited the highest and lowest values for bicarbonate ion concentration (Table 2), and the difference in the ion concentration between wet season and dry season was not significant. The flow, ion concentration and carbon flux data of 2001 from LHT were lacking, and we therefore replaced them with the 2002 data in the paper.

Table 2 The highest and lowest ion concentration in the wet season, dry season and throughout the whole year for the LHT station 1988-2002

	LHT ion concentration (mg/L)							
	highest	lowest	highest	lowest	highest	lowest		
wet season	240.5	201.7	dry season	259.6	234.7	whole year	248.3	218.8
	(1994)	(1999)		(2002)	(1991)		(1994)	(1999)

The annual average ion concentrations recorded at the LG station were more stable than those from the LHT station. From 1992-1996, the annual average concentration of bicarbonate ions in the wet season, dry season, and whole year were 222.0 mg/L, 253.5 mg/L, and 237.8 mg/L, respectively at the LG station and 228.8 mg/L, 249.3 mg/L, and 239.1 mg/L, respectively at the LHT station. However, there was little difference in ion concentration between the two stations when considering the stability of ion concentration changes (Table 3).

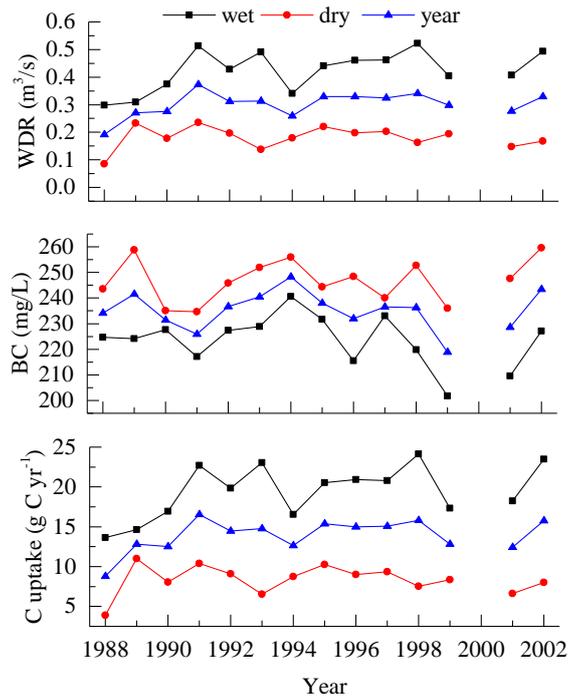
197 The differences in ion concentrations across the site as a whole were small. The annual
 198 average ion concentrations measured at the MSK station were more stable than those at the LHT
 199 station with respect to the standard deviation of the ion concentration (Table 3). During the same
 200 period, i.e., from 1996-2001, the annual average ion concentrations in the wet season, dry season,
 201 and whole year were 217.8 mg/L, 247.4 mg/L, and 232.6 mg/L, respectively, for the LHT station,
 202 and 209.9 mg/L, 226.4 mg/L, and 218.2 mg/L, respectively, for the MSK station. The difference
 203 in ion concentrations between LHT and LG was smaller than that between LHT and
 204 MSK ~~differences in the site as a whole were small.~~

205 The flow in the wet season was significantly greater than in the dry season. The discharge
 206 from the MSK station, which is located at the outlet of the underground river basin, was larger
 207 than the discharge from LG and LHT. From 1996-2001, the annual average flow values of MSK
 208 in the wet season, dry season, and whole year were 1.55 m³/s, 0.67 m³/s, and 1.11 m³/s,
 209 respectively, ~~and the flow in the wet season was significantly greater than in the dry season.~~ The
 210 LG and LHT flows in the rainy and dry seasons exhibited the same trend (figure 2, 3, and 4). From
 211 Table 3, we can determine the stability of flow as follows: MSK>LG>LHT.

212 Table 3. Standard deviation of production flow, ion concentration, and carbon sink for each station in the dry
 213 and wet seasons and over the whole year

Station	Water Discharge Rate (m ³ /s)			Bicarbonate Concentration (mg/L)			Carbon uptake (g C yr ⁻¹)		
	wet	dry	year	wet	dry	year	wet	dry	year
Maoshuikeng	0.108	0.109	0.060	6.46	6.64	5.26	1.12	0.84	0.43
Liugu	0.109	0.015	0.051	10.64	4.81	4.99	2.93	0.45	1.54
Laoheitan	0.073	0.061	0.045	10.04	8.41	7.55	3.34	1.84	2.05

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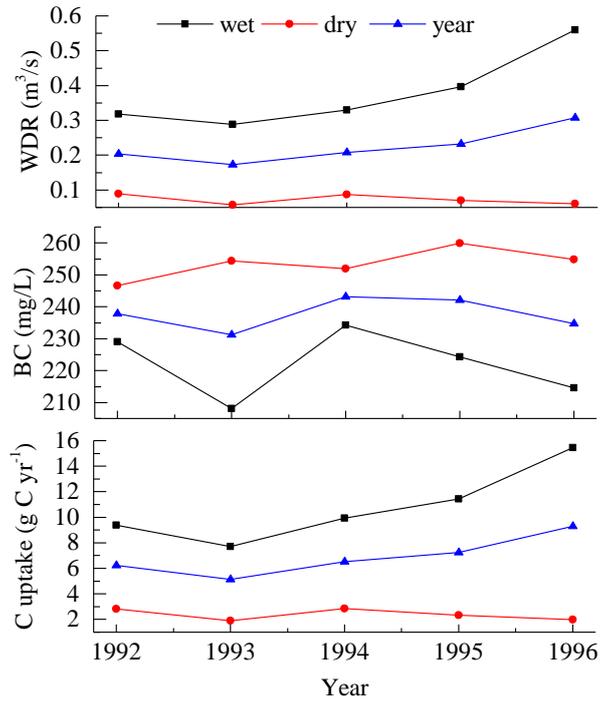


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Figure 2. Variation in runoff, ion concentration, and carbon sink for the LHT station (1988-2002).



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

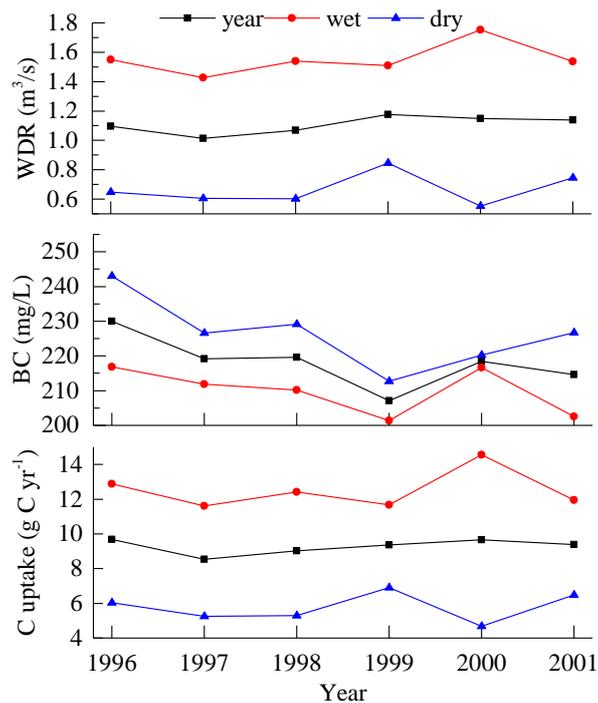


Figure 4. Variation in runoff, ion concentration, and carbon sink for the MSK station (1996-2001).

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

There was a significantly greater discharge in the wet season compared to the dry season. From 1996-2001 at the MSK station, the annual average carbon sink discharges of underground water in the wet season, dry season, and whole year were 12.51, 5.78, and 9.28 $\text{g C/m}^2 \cdot \text{yr}^{-1}$, respectively ~~with a significantly greater net discharge in the wet season compared to the dry season~~. From 1992-1996 at the LG station, the annual average carbon sink discharges in the wet season, dry season, and whole year were 10.78, 2.38, and 6.89 $\text{g C/m}^2 \cdot \text{yr}^{-1}$, respectively. From 1988-2002 at the LHT station, the annual average carbon sink discharges in the wet season, dry season, and whole year were 19.48, 8.34, and 13.91 $\text{g C/m}^2 \cdot \text{yr}^{-1}$, respectively, i.e., greater than both the LG and MSK stations (figure 6). From 1996-2002 at the LHT station, the annual average net carbon sink discharges in the wet season, dry season, and whole year were 20.82, 8.14, and 14.48 $\text{g C/m}^2 \cdot \text{yr}^{-1}$, respectively, while from 1992-1996 the respective values were 20.18, 8.72, and 14.45 $\text{g C/m}^2 \cdot \text{yr}^{-1}$. Comparing the results for the same period, the annual carbon sink discharge in the wet season, dry season, and whole year for the LHT station was greater than that for the MSK and LG stations. However, with respect to the stability of the carbon discharge (Table 3), MSK was the most stable in the wet season while LG was the most stable in the dry season.

4. Discussion

4.1. Flow and Ion Concentration Change and their Effects on Carbon Sink

The trends in annual runoff among sites are consistent with the carbon sink discharge but differ from the trends of the bicarbonate ions (figure 2, 3, 4). This suggests that the effect of flow change on the carbon sink was greater than on the ion concentration. ~~According to the flow trend~~

243 ~~of each station, we can see that~~The flow in the wet season was consistent with the flow trend for
244 the whole year. ~~, suggesting that the runoff from precipitation in the wet season accounts for the~~
245 ~~majority of the annual runoff.~~This is a result of the monsoon climate where wet season
246 precipitation levels are significantly higher than in the dry season, ~~winter (December-February);~~
247 ~~however, the flow trend in the dry season was smooth (figure 5)~~due to less rainfall in the dry
248 season when the runoff is mainly supplied by soil water and fissure/pore water. Therefore, the
249 composition of underground karst aquifer medium structures has important effects on the dry
250 season flow. ~~But due to the difference between the control area and the surface-to-underground~~
251 ~~diversion ratio, the flows between sites cannot be compared.~~According to changes in ion
252 concentrations in the wet season, dry season, and whole year (figure 2, 3, and 4), flow correlated
253 negatively with the carbon ion concentration, but if there was a significant difference between the
254 flow in the wet season and in the dry season, the bicarbonate ion concentrations would not
255 decrease when the flow increased rapidly.

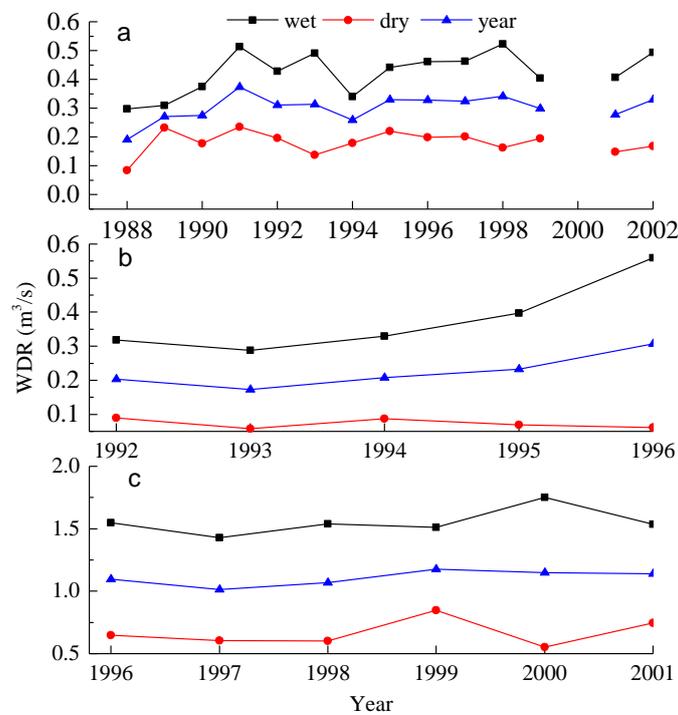
256 Although the ion concentrations were higher in the dry season than in the wet season, the
257 differences were small. When there was little change in flow, the effect of flow increase on the ion
258 concentration dilution was smaller than the environmental effects of chemical carbonate
259 weathering. Contrasts were made between each site: from 1992-1996, the annual average carbon
260 ion concentration was 237.8 mg/L for the LG station and 239.1 mg/L for the LHT station. The
261 annual average flow of the LHT station was 1.37 times that of the LG station, but the ion
262 concentration did not decline significantly due to the increase in flow. The basin area controlled by
263 the LHT station is characterized by peaks and valleys, which have good vegetation cover that
264 recovers rapidly. Previous studies have shown that the concentration of HCO_3^- is vulnerable to
265 LUCC and other environmental changes (Zhao et al.,2010;Lan et al.,2015). In particular, the rapid
266 recovery of vegetation can significantly promote the dissolution of carbonate and thus increase the
267 bicarbonate ion concentration in karst groundwater (Berner,1997;Liu et al.,2010).

268 The flow only had a partial dilution effect on the ion concentration, and the results were not
269 multiplicative. That is to say, carbonate weathering was significantly affected by factors other than
270 flow. This also implies that the bicarbonate ion concentrations in the karst underground water may
271 have a relatively stable extremum under stable environmental conditions. ~~This shows that the~~
272 ~~dilution effects of the flow change on ion concentrations were not multiplicative. That is to say,~~
273 ~~the flow was just a part of the dilution effect on ion concentrations, and thus carbonate weathering~~
274 ~~was significantly affected by factors other than flow. Bicarbonate ion concentrations of karst~~
275 ~~underground water may have a relatively stable extremum when environmental conditions are~~
276 ~~stable.~~From 1996-2001, the annual average carbon ion concentrations at the LHT and MSK
277 stations were 232.6 mg/L and 218.2 mg/L, respectively, but the average annual flow at LHT was
278 only $0.32 \text{ m}^3/\text{s}$, while MSK exhibited an annual flow of $1.11 \text{ m}^3/\text{s}$, i.e., 3.47-fold higher. Similarly,

279 the ion concentration did not decline significantly as a result of the increase in flow. The MSK
 280 station is located at the edge of a paddy field, which has thicker soil coverage, and the
 281 underground rivers have more biological carbon sources that could produce more HCO_3^- in the
 282 ground water compared to LHT. The effect of the flow increase on the ion concentration dilution
 283 exceeded the environmental effects of carbonate weathering at the LHT and MSK stations.

284 In addition, although studies have shown that under stable LUCC conditions, the strength of
 285 the carbon sink from rock weathering will depend on the climate (e.g. temperature,) (Hagedorn
 286 and Cartwright,2009;Gislason et al.,2009;Tipper et al.,2006), the annual average carbon sink trend
 287 for the LHT station, which had the longest study period (1988-2002), differed significantly from
 288 the annual average temperature trend. However, this may be a result of time resolution limitations
 289 of the data.

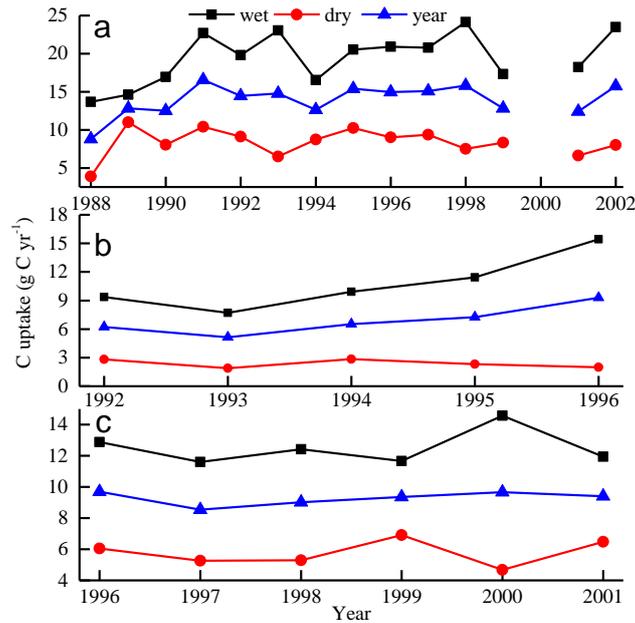
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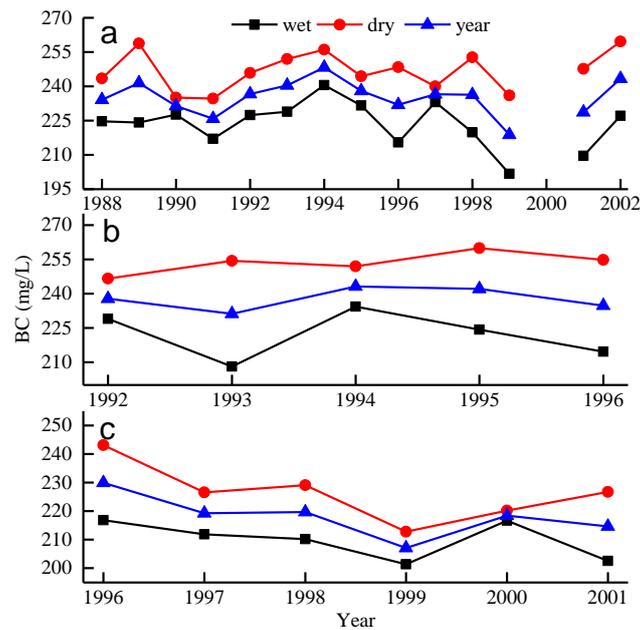
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293 Figure 5. Variation in flow among sites in the wet season, dry season, and whole year during the study period (a.
 294 LHT; b. LG; c. MSK).



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Figure 6. Variation in net carbon discharge among sites in the wet season, dry season, and whole year during the study period.



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Figure 7. Variation in bicarbonate ion concentrations among sites in the wet season, dry season, and whole year during the study period.

302 4.2. Variation in Carbon Sink Discharge for Each Site

303 The karst carbon sink changed significantly with the seasons, exhibiting striking seasonal
304 patterns. The carbon sink discharge for each site in the wet season was greater than the dry season
305 and the annual average, while the carbon sink discharge in the dry season was lower than the
306 annual average (figure 6). This shows that the karst carbon sink (karstification's absorption of
307 atmospheric CO₂ and soil CO₂) changes significantly with the seasons and exhibits striking

308 ~~seasonal patterns.~~ The reason for this is that the considerable summer rainfall runoff significantly
309 increased the amount of carbon sink discharge in the wet season. ~~The annual average carbon sink~~
310 ~~discharge of all the stations during study period shows that LHT>MSK>LG; however,~~
311 ~~comparisons cannot be made due to the different study periods.~~

312 The difference in carbon sink discharges between the LHT and LG stations resulted from
313 differences in flow. ~~Furthermore, the different LUCC types may further increase differences in~~
314 ~~carbon sink discharge between the two stations.~~ During the same period, the carbon sink values
315 for the LHT station (wet season, dry season, and whole year) were greater than those for LG
316 stations (figure 6). From 1992-1996, the flow for LG in the wet and dry seasons was lower than
317 for LHT (figure 5), but the annual average bicarbonate concentration of LG was 237.8 mg/L,
318 slightly less than LHT (239.1 mg/L) (figure 7). ~~Different LUCC types may further increase~~
319 ~~differences in carbon sink discharge between two stations.~~ The LHT control basin station is
320 surrounded mainly by forest vegetation while the LG control basin is surrounded mainly by dry
321 farmland.

322 From 1996-2001, the carbon sink for the LHT station in the dry and wet seasons and whole
323 year was greater than for the MSK station (figure 6). The annual average concentration for LHT
324 (232.6 mg/L) was greater than for MSK (218.2 mg/L), while the runoff was significantly greater
325 for MSK than for LHT (figure 7). ~~We hypothesize the above results are caused by two main~~
326 ~~reasons as follows:~~ On the one hand, the fact that the carbon sink for MSK was less than that for
327 LHT might be linked to the water conveyance distance and LUCC type of the control area. The
328 carbon sink for MSK, which is the groundwater outlet for the whole basin, was influenced by the
329 landform and LUCC type of the entire river basin. Existing research has shown that karst erosion
330 rates under soil vary significantly for different LUCC types in karst watersheds, and the averages
331 for cultivated land, thickets, secondary forests, grassland, and forest were found to be 4.02, 7.0,
332 40.0, 20.0 and 63.5 t km² a⁻¹, respectively (Zhang,2011), among which the cultivated land value
333 was the lowest (Yan et al.,2014).Vegetation can increase the speed of rock weathering by
334 3–10-fold (Berner,1997). According to monitoring data from Guilin province in China, vegetation
335 restoration resulted in a 266% increase in the average annual concentration of soil CO₂ over 10
336 years. ~~The increase in CO₂ promotes the dissolution of carbonate rock and greatly increases HCO₃~~
337 ~~concentrations in groundwater~~ Research in the Houzhai valley has shown that forest recovery
338 causes more carbon dioxide (CO₂) to be dissolved in karst water (Yan et al.,2014), and karst
339 hydro-geochemistry and the karst-related carbon cycle could be regulated effectively by different
340 LUCC types (Zhao et al.,2010).

341 On the other hand, in the process of underground runoff converging at the outlet (MSK
342 station), much of the water flows into the surface river and across the thick soil of paddy fields,
343 but our calculation only considered carbonate weathering carbon sinks (water - rock - gas

344 interaction), which may have affected the results. Research has shown that dissolved inorganic
345 carbon is used in aquatic photosynthesis for the synthesis of organic carbon (Waterson and
346 Canuel,2008;Tao et al.,2009). In addition, the precipitation recharge coefficients of MSK, LG and
347 LHT were 0.485 and 0.503, respectively (Chen et al.,2014). The difference in the precipitation
348 recharge coefficient for the basin determines the groundwater quantity, under the same rainfall
349 conditions, and the development degree of the underground pipe network also influences the
350 water-rock contact time. Differences in surface and ground water proportions controlled by
351 geological landforms could also affect the calculation results.

352 ~~To sum up, the calculation results for carbon sink discharge from karstification using~~
353 ~~watershed monitoring data in areas limited to a dominant single LUCC type may differ in a small~~
354 ~~watershed where geomorphology, hydrology, and land use cover are different. This is one of the~~
355 ~~reasons why there is such a large deviation in China's total carbon sink discharge estimated by~~
356 ~~using carbon sink data from a single watershed in a karst region.~~

357 **5. Conclusion and Suggestions**

358 ~~It is important basic significance to determine the main factors that affect the karst~~
359 ~~geological carbon sink and understand the mechanism of their effects on the karst geological~~
360 ~~carbon sink.~~Through contrast analysis based on three stations located upstream, midstream and
361 downstream of the Houzhai basin, we analyzed the reasons for the differences in flow, bicarbonate
362 ion concentrations and carbon sink discharge. The preliminary conclusions are as follows: (1) The
363 carbon sink discharge was mainly controlled by the flow of each site, and LUCC type had
364 important effects on the bicarbonate ion concentrations at each site. (2) The large difference in
365 flow among sites did not lead to significant differences in bicarbonate ion concentrations between
366 the sites, showing that the rapid increase in flow only had a partial dilution effect on the ion
367 concentrations. Due to the high speed and stability of chemical carbonate weathering, the
368 bicarbonate ion concentrations did not change significantly, and thus did not affect the carbon sink
369 discharge. (3) For different LUCC conditions, if the runoff is stable, the influence of flow
370 variation on ion concentration will be less than the effects of chemical carbonate weathering on
371 bicarbonate ion concentrations caused by different environmental conditions (a comparison of
372 LHT and LG showed a difference of 150%). However, if runoff increases significantly, the impact
373 of runoff variation on bicarbonate ions will be greater than the effects of chemical carbonate
374 weathering caused by different environmental conditions (comparison results of LHT and MSK).

375 In summary, the calculation results for carbon sink discharge from karstification using
376 watershed monitoring data in areas restricted to a dominant single LUCC type may differ in a
377 small watershed where geomorphology, hydrology, and land use cover are different. This is one of
378 the reasons why there is such a large deviation in China's total carbon sink discharge estimated
379 using carbon sink data from a single watershed in a karst region. In future research, considering

380 the diversity of landform types and surface covers in the southwestern karst area, it is important to
381 develop a monitoring network in different topographical and surface cover regions, using a variety
382 of monitoring technologies to improve the accuracy of karst carbon sink estimates.

383 In addition, we cannot properly quantify the impact of vegetation and other factors on the
384 karst carbon sink in the research basin because the data used in the study do not have a high
385 temporal resolution. At the same time, the data failed to provide a quantitative conclusion.
386 However, based on the purpose of this paper, the existing data can meet the needs of the analysis,
387 so as to draw a qualitative research conclusion. From the point of view of research and
388 development in the future, high temporal resolution monitoring using automatic monitoring
389 equipment should be the basis for quantitative studies on vegetation and other factors that impact
390 the karst carbon sink; this may help to reduce uncertainty error and is our main research direction
391 for the future.

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