



Concentrations and exports of solutes from surface runoff in Houzhai Karst Basin, southwest China

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ABSTRACT

Chemical concentrations and export rates from surface water were analyzed in Houzhai Karst Basin (HKB, area 80.65 km² in total), southwest China, for the past two decades from 1986 to 2007. Surface water chemistry was dominated by ions of calcium (Ca²⁺), magnesium (Mg²⁺), bicarbonate (HCO₃[−]) and sulfate (SO₄^{2−}), which together made up 96% (by weight) of the total dissolved solids measured in this study. Seasonal variability of chemical export rates was positively correlated with surface runoff discharge, with the concentrations generally diluting at high discharge. From 1986 to 2007, as a result of the responses of karst weathering to climatic factors, the concentrations of Ca²⁺, Mg²⁺, HCO₃[−], and SO₄^{2−} slowly increased in surface water. By contrast, changes in the concentrations of sodium (Na⁺), potassium (K⁺), and chloride (Cl[−]) showed a slowly decreasing pattern. We also found that the annual dissolved inorganic carbon (DIC) flux ranged from 10.1 to 34.1 g C m^{−2} yr^{−1}, with an average value of 24.2 g C m^{−2} yr^{−1}. Rainfall had the most important influence on DIC flux, although water pH may greatly affect the proportions of the three fractions (CO₂, HCO₃[−], CO₃^{2−}) of DIC. High water temperature in the wet season may reduce the solubility of CO₂ in water and consequently affect DIC export rate, but this effect is much smaller than that of rainfall. Based on the chemical mass balance in surface water, our results indicate that high concentrations of SO₄^{2−} by the large gypsum (CaSO₄·2H₂O) dissolution offset some anions such as HCO₃[−] in karst water, which can partly explain why carbon uptake is often overestimated by the empirical model using concentrations of HCO₃[−] in this karst water. It is concluded that the fluvial flux of DIC from karst water is important to the regional or national carbon budgets.

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1. Introduction

Chemical concentrations and export rates from runoff discharge are essential in the global cycle of many elements (Likens et al., 1981). The link between water chemistry and land cover has been used to understand how different sources and mechanisms could control the export rates of chemicals (Sabater et al., 1990; Ahearn et al., 2005; Petrone, 2010). Previous studies have been focused on small scale study of agriculture/forest catchments (Wu and Gibson, 1996; Binkley et al., 2004; Stutter et al., 2006; Lloret et al., 2011), or using the world largest rivers for a more global budget (Meybeck, 1987; Gaillardet et al., 1999; Amiotte-Suchet et al., 2003). However, there has been little work done in karst basins. Karst is a special type of landscape found on carbonate rocks, and is well known for fast chemical and hydrologic responses to changing earth surface conditions (Macpherson et al., 2008; Hartmann et al., 2009; Hartmann and

Moosdorf, 2011). Water flowing through carbonate rocks is enriched with chemical solutes and can potentially take up a significant amount of inorganic carbon (White, 1988; Katz et al., 1997; Liu et al., 2010a, 2010b). Hence, karst potentially plays an important role in the global cycle of carbon as a link between continents and oceans. However, chemical export rates by runoff discharge in karst basins are often neglected when discussing carbon budgets (Wallin et al., 2010).

In general, there are two parameters controlling the fluvial fluxes of chemicals from rivers or basins. The first one is water discharge. Although the concentrations of major cations/anions are diluted with increased discharge, the dilution factor in many watersheds is small, and the fluvial fluxes of chemicals increase at a higher discharge (Jarvie et al., 1997; Shanley et al., 2002; Raymond and Oh, 2007). A number of studies have shown that the watershed response to vegetation carbon dioxide (CO₂) fertilization led to increase of discharge, and the ratio of discharge over precipitation increased as evapotranspiration decreased (Gedney et al., 2006; Betts et al., 2007). The second parameter is the concentrations of chemicals. Recent studies demonstrated that the concentrations of many chemicals in watershed increased significantly by human activities, such as in Mississippi watershed (Raymond et al., 2008) and Ishigaki Island formed by

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carbonate rocks (Ushie et al., 2010). Karst systems are sensitive to change of many environmental factors, such as acid precipitation, global warming, and the increase of atmospheric CO_2 partial pressure (Cao et al., 2011). The highly variable interactions among chemical, physical and biological processes have a broad range of effects on water discharge and the concentrations of chemicals. Changes of these two parameters in large rivers or agriculture/forest catchments are well documented (Shanley et al., 2002; Stutter et al., 2006; Raymond and Oh, 2007; Lloret et al., 2011), but studies on responses of both water discharge and ion concentrations to climate change in karst basins are scarce (Liu et al., 2010a, 2010b; Christina, 2011).

Karst landscape occupies about 11.2% of the Earth's surface, an area of about 15 million km^2 (Dürr et al., 2005). A quarter of the world's population is supplied by karst water (White, 1988). Karstification process is a part of the global carbon cycle in which carbon is exchanged between atmosphere, surface and underground water and carbonate minerals (Liu and Zhao, 2000; Hartmann et al., 2009). Dissolution of carbonates, which is enhanced by the presence of acids in water, ties up carbon derived from the rock and from dissolved CO_2 as aqueous carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) (Gelbrecht et al., 1998; Wallin et al., 2010). A reliable assessment of the role of karst in the carbon cycle is still unclear and remains a topic of active research and discussion (Liu et al., 2010a, 2010b; Aufdenkampe et al., 2011; Christina, 2011). In terms of the global carbon budget, the chemical processes in karst basins are poorly understood. It is also a big challenge to measure concentrations of dissolved inorganic carbon (DIC) in surface water, because the fractions of different DIC speciations (CO_2 , HCO_3^- , CO_3^{2-}) in the bicarbonate buffer system are greatly affected by pH of water, and the equilibrium of different DIC is sensitive to degassing of CO_2 (Stumm and Morgan, 1996).

The karst surface covers 0.446 million km^2 of southwest China (Jiang and Yuan, 1999; Liu and Zhao, 2000), which has a typical sub-tropical monsoon climate with plenty of precipitation and large runoff discharge during the wet seasons (May to October). The objectives of this study are: (1) to provide the seasonal variability of chemical export rates and the long-term trends of ion concentration fluctuations in surface water of HKB in southwest China; (2) to estimate the export rates and influencing factors of the three fractions of DIC (CO_2 , HCO_3^- ,

CO_3^{2-}); (3) to reveal major chemical processes and the importance of DIC export in karst regions of southern China.

2. Materials and methods

2.1. Description of the field site

HKB is located in Guizhou Province, southwest China (latitudes: $26^\circ 13'$ to $26^\circ 15' \text{ N}$; longitude: $105^\circ 41'$ to $105^\circ 43' \text{ E}$). The total drainage area is 80.65 km^2 . Its topography is high in southeast and low in northwest where surface water exit (Fig. 1). The basin has a sub-tropical monsoon humid climate with an annual mean temperature of 15.2°C . The annual average precipitation is 1314.6 mm , and 85% of rain falls during the wet season (May to October). The bedrock type in the drainage area is primarily carbonate rocks of the Middle Triassic Guanling Formation, which can be divided into three members according to the combined characteristics of the lithology (Yang, 2001; Liu et al., 2010a, 2010b). The oldest member is approximately 200 m thick, occurs mainly in the upstream part of the basin, and composed mainly of shales, thin argillaceous dolomite layers, and inter-bedded argillaceous limestone. The middle member is approximately 240 m thick and occurs in the center of the basin. The lithologies are mainly charcoal gray thin limestone and medium thick limestone, marlite, dolomitic limestone, and thin argillaceous limestone. The youngest member occurs in the downstream part of the basin. The average thickness is about 100 m, and is made of thin to thick dolomite beds. The karst landform developed in this region mainly occurs in the form of bare karst, including peak-cluster depressions, funnels, and sinkholes (Chen and Chen, 2005; Liu et al., 2010a, 2010b). The Houzhai River is the only surface river with only one exit, and is fed by surface runoff only (Fig. 1).

2.2. Field measurements and lab analysis

A permanent station was set up in 1976 for monitoring water discharge rate and providing chemical analysis of water samples collected at the exit (A) of HKB (Fig. 1). Five weather stations were installed in the 1980s. At each weather station, measurements of incoming

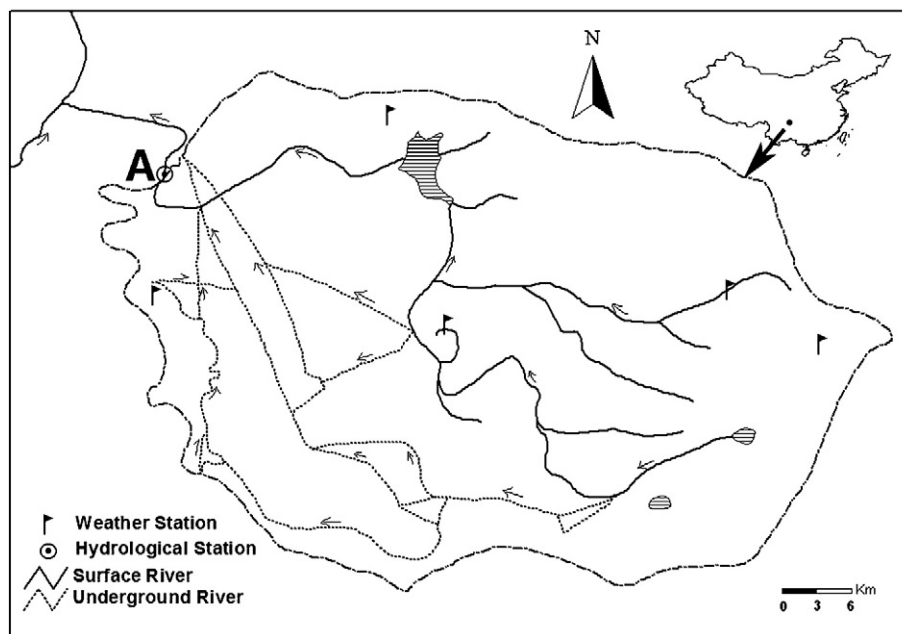


Fig. 1. Map of Houzhai Karst Basin and locations of surface (solid line) and underground rivers (dashed line). Flags showed the locations of Weather Stations. Arrows indicated the flow directions. All surface water samples were collected at exit A in a hydrological station. Houzhai River is the only surface river in this basin and A is the only exit of this surface river.

solar radiation, rainfall, wind speed and direction, relative humidity and air temperature were carried out at 2 m height. The annual rainfall was the average from the five weather stations. Missing data of one weather station were estimated by linear regression based on rainfall at one of the others when the correlation coefficient was greater than 0.95. The river stage was measured by an automatic fluvigraph since 1986. When the water table ($H < 0.85$ m) is low, water flows through the V-weir only, otherwise water passes through the V-weir and rectangle-weir together. The routine empirical equations in hydrological engineering were used to estimate surface water discharge rate (Q , m^3) for low and high river stage. The relative standard deviation (RSD) of the estimated discharge is estimated to be $< 5\%$. Further details of discharge data quality assessment can be found in Yan et al. (2011). Values of Q can be converted to surface runoff with unites of depth (mm) by $10^3 \times Q/A$, where A is the total basin area ($= 8.065 \times 10^7 \text{ m}^2$).

Six water samples were collected from the surface river at a water depth of 0.6 m at the exit site (A) in a month (usually at intervals of 5 days). Water pH was measured using a portable pH meter (Accuracy: ± 0.1 pH), the concentration of bicarbonate ($[\text{HCO}_3^-]$) determined by titration with standard hydrochloric acid (HCl) as well as water temperature (Accuracy: $\pm 0.1^\circ\text{C}$) were recorded immediately (< 2 h) after samples were taken. In the laboratory of this karst station, a relative standard deviation (RSD) of 5% in measurements of $[\text{HCO}_3^-]$ is required. Water samples were stored in a closed box and taken to the laboratory in the permanent station to determine ionic. Because of financial difficulties, measurements were temporarily suspended in 2003 and 2004, but resumed in 2005.

Concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+) were determined with the Jarrell Ash model 975 inductively coupled argon plasma spectrometer (RSD $< 1\%$). Sulfate (SO_4^{2-}) was estimated turbidimetrically as barium sulfate (BaSO_4) (RSD $< 3\%$) and chloride (Cl^-) was measured with specific ion electrodes (RSD $< 6\%$). Error bars of concentrations represent the one standard deviation of the six water samples taken from surface water in a month. All measured methods have not been changed since 1986.

2.3. Computation for concentration of dissolved inorganic carbon

The concentration of DIC ($[\text{DIC}]$) was calculated as a sum of the three fractions (Gelbrecht et al., 1998; Wallin et al., 2010), i.e:

$$[\text{DIC}] = [\text{HCO}_3^-] + [\text{CO}_2] + [\text{CO}_3^{2-}]. \quad (1)$$

$[\text{HCO}_3^-]$ in mg L^{-1} was measured in this study. $[\text{CO}_2]$ is the concentration of dissolved carbon dioxide assuming the concentration of free carbon acid, H_2CO_3 , negligible (Hutzing, 1980). $[\text{CO}_2]$ and $[\text{CO}_3^{2-}]$ were determined from the available data of water temperature (T , $^\circ\text{C}$) and pH, together with the measured $[\text{HCO}_3^-]$ according to the following equations (Stumm and Morgan, 1996):

$$[\text{CO}_2] = \frac{[\text{HCO}_3^-] \times 10^{-\text{pH}}}{K_1} \quad (2)$$

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-] \times K_2}{10^{-\text{pH}}} \quad (3)$$

where, K_1 and K_2 are the temperature dependent first and second equilibrium constants, respectively, which were derived from Eqs. (4) and (5) (Gelbrecht et al., 1998):

$$\log K_1 = \left(\frac{-3404.71}{T + 273.15} \right) + 14.844 - 0.033 \times (T + 273.15) \quad (4)$$

$$\log K_2 = \left(\frac{-2902.39}{T + 273.15} \right) + 6.498 - 0.0238 \times (T + 273.15). \quad (5)$$

2.4. Estimates of the monthly export rates and yearly flux

In this study, using the monthly concentration of ions or DIC and the estimated surface runoff, we calculated the monthly export rates (f , $\text{g m}^{-2} \text{ month}^{-1}$), and then the yearly flux of solutes (F , $\text{g m}^{-2} \text{ yr}^{-1}$). That is

$$\begin{cases} f_n = c_n Q_n / A \\ F = \sum_{n=1}^{12} f_n \end{cases} \quad (6)$$

where n represents month of year, varying from 1 to 12. Q is the monthly rate of water discharge (m^3), c is concentration of ions or DIC in water (mg L^{-1}), A is the total basin area ($= 8.065 \times 10^7 \text{ m}^2$).

Using the data of the concentrations or fluxes, we estimated the seasonal and interannual variations of the concentrations or fluxes (CV) by the following equation:

$$\begin{cases} CV_c = SD_c / \bar{c} \\ CV_F = SD_F / \bar{F} \end{cases} \quad (7)$$

where SD_c and SD_F are the standard deviation of the concentrations and fluxes during the period of timescale, respectively. $\bar{c}$ and $\bar{F}$ are the mean concentrations and fluxes at the same timescale, respectively.

The seasonal and inter-annual variations were examined by performing one-way analysis of variance, and multiple comparisons using the ANOVA procedure of SAS (Version 8.0). The linear regressions were plotted using the SigmaPlot (Version 10.0).

3. Results

3.1. Rainfall and surface runoff

The annual rainfall in HKB varied from 916 mm (2005) to 1805 mm (1996) with an average of 1363 mm during 1986–2007 (Fig. 2). The amount of rainfall in the wet season (May to October) was 4 times more than that in the dry season (November to April). June had the greatest rainfall during the year (304 mm on average). From 1986 to 2007, annual mean surface runoff was 382 mm, of which 72% occurred in the wet season and 28% in the dry season. The yearly surface runoff coefficient (annual surface runoff as percentage of annual rainfall) ranged from 17% (1989) to 38% (2001) with an average value of 29%. Within a year, the maximal surface runoff occurred in July, one month later than the maximal rainfall in June (Fig. 2).

Surface runoff is positively correlated with the rainfall (Fig. 2). About 55% ($y = 0.148x + 15.08$; $r^2 = 0.55$; $n = 228$; $P < 0.001$) of the monthly variation and 60% ($y = 0.265x + 15.40$; $r^2 = 0.60$; $n = 18$; $P < 0.001$) of the inter-annual variation in surface runoff could be explained by rainfall, and therefore rainfall scheme was a major driver of surface runoff in HKB. During the study period, although no significant temporal trend was found for the surface runoff because of the large variation of rainfall from one year to the other, the yearly surface runoff coefficient tended to increase over time (Table 1). In HKB, a small area of cropland has been converted to forested area since 1993 (Meng and Wang, 2009). Generally, surface runoff coefficient decreases with the forested area increasing (Jackson et al., 2005; Sun et al., 2006). Our observation was not consistent with this discipline. It was possibly resulted from the decreases of evapotranspiration with the increases in atmospheric CO_2 partial pressure or the variations of rainfall pattern derived by climate change.

3.2. Temperature and pH values in surface water

The mean monthly water temperature in HKB varied from the lowest in January or February (13.3°C) to the highest in September

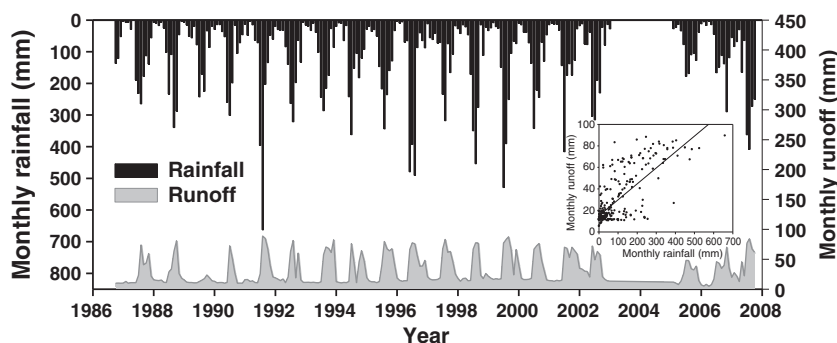


Fig. 2. Rainfall and surface runoff from 1986 to 2007 in Houzhai Karst Basin, Guizhou, China. Dark areas and gray areas for the monthly rainfall (mm month^{-1}) and the monthly surface runoff (mm month^{-1}), respectively. A scatter plot within Fig. 2 shows that the monthly surface runoff is positively correlated with the monthly rainfall ($y = 0.148x + 15.08$; $r^2 = 0.55$; $n = 228$; $P < 0.001$).

(20.2°C). From 1986 to 2007, the mean annual water temperature was 16.7°C and had no significant temporal trend (Fig. 3).

Values of pH in karst water were slightly alkaline in HKB. The yearly mean pH value in surface water was between 7.2 and 7.9, with an average of 7.5 (Fig. 3). Based on Le Chatelier's Principle, the pH in pure water falls as the temperature increases. Accordingly, we found that the monthly mean value of pH reached its lowest in summer but highest in winter at the seasonal scale (Fig. 3). However, it had a positive but non-significant relationship with water temperature at the annual scale, which indicated that the correlations between water pH and water temperature varied at different time scale. As a result, variation of water pH is strongly influenced by water temperature at the seasonal scale. At the inter-annual scale, internal system dynamics and their responses to environmental variables with a frequency longer than one year, such as rainfall can greatly affect water pH. A less annual rainfall was found in warmer years, which could result in the concentration of alkaline by small influx of water at the same time.

3.3. Exports of cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) from surface water

The highest and lowest monthly concentration was 81.2 and 43.5 mg L^{-1} for Ca^{2+} , 57.4 and 16.4 mg L^{-1} for Mg^{2+} , respectively

(Fig. 4). Higher concentrations of both Mg^{2+} and Ca^{2+} were found in the dry season and lower concentrations in the wet season. Although concentrations of Mg^{2+} ($\text{CV} = 21.0\%$) showed a stronger seasonal variability than those of Ca^{2+} ($\text{CV} = 10.7\%$), both of them showed roughly negative correlations with monthly surface runoff in HKB. It was also found that, from 1986 to 2007, concentrations of Mg^{2+} increased by 0.2 mg L^{-1} per year, while concentrations of Ca^{2+} showed an increase of 0.8 mg L^{-1} per year (Fig. 4). In karst water, concentrations of Na^+ or K^+ are usually much lower than those of Ca^{2+} or Mg^{2+} . The monthly concentration of total Na^+ and K^+ in HKB changed from 1.2 to 8.9 mg L^{-1} . There was no difference between the wet season and the dry season, but a decreasing trend of 0.1 mg L^{-1} per year was found from 1986 to 2007.

The variations of the monthly export rates were largely caused by the variations of seasonal surface runoff for either Ca^{2+} or Mg^{2+} (Fig. 6), because the monthly runoff had relatively greater variations than concentrations of Ca^{2+} or Mg^{2+} . The mean annual flux was $24.7 \pm 6.7 \text{ g m}^{-2} \text{ yr}^{-1}$ and $13.0 \pm 2.6 \text{ g m}^{-2} \text{ yr}^{-1}$ for Ca^{2+} and Mg^{2+} , respectively (Table 1). The inter-annual variations of Ca^{2+} and Mg^{2+} fluxes were also similar to the variations of annual surface runoff (Table 1). Hence, runoff pattern caused by rainfall scheme is the major driver of the seasonal and inter-annual variations of export rates.

Table 1
Annual rainfall (mm), annual surface runoff (mm) and annual surface runoff coefficient in Houzhai Karst Basin from 1987 to 2006. The mean annual concentration (Mg L^{-1}) and annual sums of flux ($\text{g m}^{-2} \text{ yr}^{-1}$) of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} in surface water in Houzhai Karst Basin from 1987 to 2006.

Year	Rainfall (mm)	Surface runoff (mm)	Surface runoff coefficient	Ca^{2+}		Mg^{2+}		HCO_3^-		SO_4^{2-}	
				Concentration (Mg L^{-1})	Flux ($\text{g m}^{-2} \text{ yr}^{-1}$)	Concentration (Mg L^{-1})	Flux ($\text{g m}^{-2} \text{ yr}^{-1}$)	Concentration (Mg L^{-1})	Flux ($\text{g m}^{-2} \text{ yr}^{-1}$)	Concentration (Mg L^{-1})	Flux ($\text{g m}^{-2} \text{ yr}^{-1}$)
1987	1224.3	334.3	0.27	56.2 ± 5.4	18.7	33.7 ± 4.6	11.1	256.6 ± 24.5	82.4	62.3 ± 19.7	19.7
1988	1187.6	333.3	0.28	57.0 ± 4.4	18.9	36.3 ± 5.4	11.5	294.5 ± 13.5	100.0	72.7 ± 24.7	18.4
1989	1029.8	170.0	0.17	61.6 ± 4.9	10.3	40.5 ± 5.9	6.8	282.7 ± 15.5	47.7	75.1 ± 20.9	12.3
1990	1129.6	251.3	0.22	62.8 ± 3.5	15.1	39.1 ± 6.5	9.6	273.0 ± 12.9	67.1	67.8 ± 18.6	15.4
1991	1726.9	409.0	0.24	54.2 ± 2.5	21.9	35.6 ± 4.8	13.8	280.8 ± 18.2	116.6	61.3 ± 17.8	20.1
1992	1320.7	340.7	0.26	59.4 ± 3.8	19.9	35.9 ± 7.6	11.5	287.9 ± 20.3	96.5	50.8 ± 25.1	15.3
1993	1254.7	420.3	0.33	63.9 ± 5.9	26.2	32.6 ± 7.8	12.7	278.0 ± 23.1	115.4	58.4 ± 14.4	23.8
1994	1386.8	366.5	0.26	65.0 ± 6.9	24.2	36.4 ± 8.4	12.6	299.7 ± 19.8	109.6	57.3 ± 24.6	17.9
1995	1406.2	440.2	0.31	67.4 ± 6.5	29.0	34.0 ± 7.9	14.0	299.0 ± 14.4	131.8	54.6 ± 16.7	20.7
1996	1805.2	477.5	0.26	69.9 ± 3.7	33.1	37.7 ± 8.9	16.4	286.7 ± 22.9	133.9	52.9 ± 20.2	23.4
1997	1248.4	447.5	0.36	68.7 ± 2.8	30.6	30.6 ± 7.8	12.8	287.5 ± 16.8	130.5	49.6 ± 11.4	20.6
1998	1559.7	387.5	0.25	69.3 ± 3.1	26.2	35.8 ± 6.4	13.3	296.6 ± 14.9	112.0	56.3 ± 11.0	21.0
1999	1655.9	531.0	0.32	67.9 ± 3.0	35.4	30.6 ± 4.8	14.9	294.5 ± 16.6	154.8	55.4 ± 20.5	25.1
2000	1371.2	410.7	0.30	69.9 ± 2.9	29.1	39.6 ± 4.0	16.1	291.3 ± 16.7	121.4	84.0 ± 19.8	34.4
2001	1285.4	490.4	0.38	69.4 ± 4.9	33.3	36.8 ± 7.5	17.4	300.9 ± 6.8	147.1	70.7 ± 24.7	30.4
2002	1385.9	419.2	0.30	69.9 ± 2.5	29.0	41.8 ± 8.9	15.8	301.0 ± 13.5	126.3	73.3 ± 20.7	29.7
2005	916.2	290.8	0.32	70.7 ± 2.1	20.2	37.9 ± 4.6	10.5	302.9 ± 8.9	88.4	65.0 ± 6.8	18.2
2006	1114.8	331.0	0.30	71.4 ± 2.1	23.3	41.3 ± 7.5	12.5	305.0 ± 8.6	101.7	70.2 ± 11.3	21.5
Average	1333.9	380.6	0.29	65.3	24.7	36.5	13.0	289.9	110.2	63.2	21.6

$\pm$ means the one standard error of the monthly values in a year. The yearly flux is the sum of the monthly exports of ions. The seasonal variations of surface runoff and ions concentrations are accounted for.

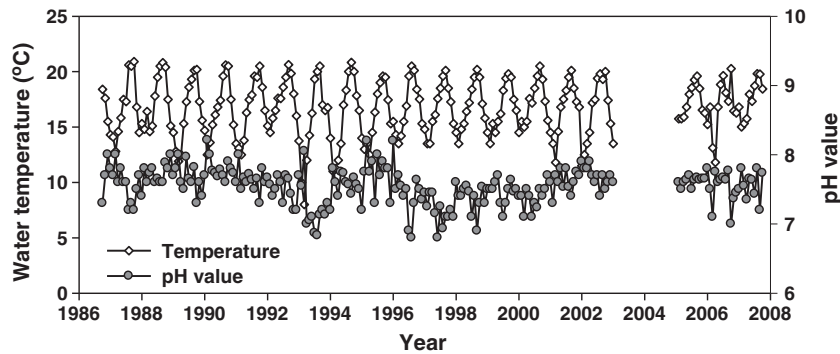


Fig. 3. The mean monthly water temperature (°C) and the mean monthly pH value in surface water from 1986 to 2007 in Houzhai Karst Basin, southwest China.

3.4. Exports of anions (HCO_3^- , SO_4^{2-} , and Cl^-) from surface water

The three major anions in the order of decreasing importance were HCO_3^- , SO_4^{2-} and Cl^- (Fig. 5). Concentrations of three anions showed a similar seasonal pattern, with lower concentrations during the wet season and higher during the dry season. Concentrations of SO_4^{2-} ($\text{CV}=32.8\%$) showed the largest seasonal variation among the three anions (HCO_3^- : $\text{CV}=6.9\%$; Cl^- : $\text{CV}=24.0\%$). From 1986 to 2007, concentrations of HCO_3^- increased significantly by 1.6 mg L^{-1} per year in surface water. It was also found that concentrations of SO_4^{2-} had a slow increase by 0.2 mg L^{-1} per year. By contrast, concentrations of Cl^- decreased by 0.1 mg L^{-1} per year (Fig. 5).

The variations of seasonal export rates were largely explained by the variations of seasonal surface runoff for both HCO_3^{2-} and SO_4^{2-} (Fig. 6). The annual flux by surface runoff was the lowest in 1989 ($47.7 \text{ g m}^{-2} \text{ yr}^{-1}$) and highest in 1999 ($154.8 \text{ g m}^{-2} \text{ yr}^{-1}$) for HCO_3^- , and was the lowest in 1989 ($12.3 \text{ g m}^{-2} \text{ yr}^{-1}$) and highest in 2000 ($34.4 \text{ g m}^{-2} \text{ yr}^{-1}$) for SO_4^{2-} (Table 1). The large variations of inter-annual fluxes for both HCO_3^- and SO_4^{2-} could be due to the significant differences of surface runoff between years. The inter-annual variation of yearly SO_4^{2-} export rate had a similar pattern as that of HCO_3^- (Table 1).

3.5. Export of dissolved inorganic carbon

The monthly DIC concentration in surface water was calculated using Eqs. (1)–(5) from 1986 to 2007. Annual flux of DIC with surface runoff discharge was estimated as the sum of the monthly DIC export

(Eq. (6)). The monthly proportions of the three fractions of DIC were surveyed over the observation period in HKB (Fig. 7). It was found that the highest proportion was carbon in the form of HCO_3^- , which ranged from 82% to 95%. The proportion of carbon in the form of CO_2 ranged from 5% to 18%. The increase of carbon in the form of CO_2 could be caused by the decline of pH in water. The proportion of carbon in the form of CO_3^{2-} was usually smaller than 1% in the total DIC, which could be due to the alkaline in karst water.

Within a year, about 70% of total annual DIC flux occurred in the wet season, in spite of the slightly lower DIC concentration caused by larger discharge at the same time. Fig. 7 showed the annual DIC flux ranged from 10.1 to $34.1 \text{ g C m}^{-2} \text{ yr}^{-1}$, with an average value of $24.2 \text{ g C m}^{-2} \text{ yr}^{-1}$. The three fractions of DIC were positively related to surface runoff at both the seasonal and annual scales (Fig. 8). The wet season and the rainy years had a larger surface runoff and therefore were the important periods for atmospheric carbon sequestration in karst water.

4. Discussion

4.1. Major chemical processes in HKB

Karst areas are essentially made of carbonate compositions, such as limestone (CaCO_3), dolomite ($\text{MgCa}(\text{CO}_3)_2$), and others (e.g. gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)). Water chemistry therefore was dominated by Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} , which together make up 96% (by weight) of the total dissolved solids measured in HKB. The conceptual model of a karst dynamic system can be simplified by the following equation

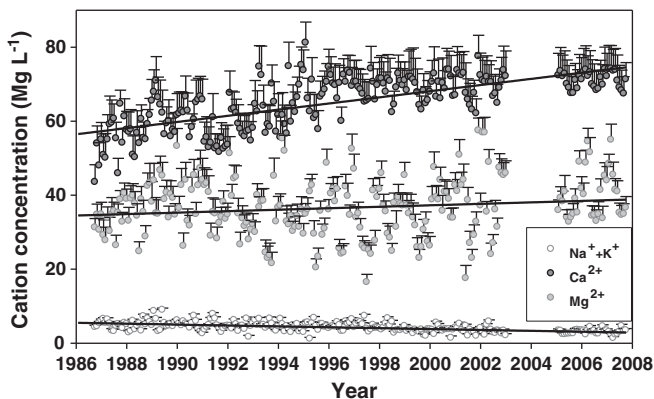


Fig. 4. The measured monthly concentrations of cations (Mg L^{-1}) in surface water in Houzhai Karst Basin from 1987 to 2008. The error bars represent the one standard error of six water samples taken from surface water. For clarity, we only plot the upper error bars in this figure. The line trend of the concentrations of cations as shown by the black line is 0.8 , 0.2 and $-0.1 \text{ g m}^{-2} \text{ yr}^{-1}$ for Ca^{2+} , Mg^{2+} and the sum of Na^+ and K^+ , respectively.

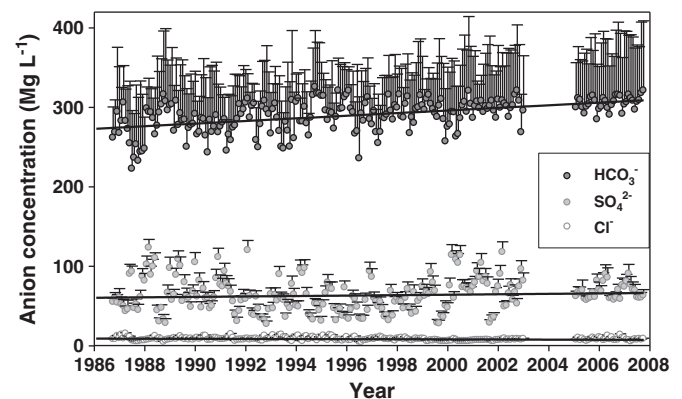


Fig. 5. The measured monthly concentrations of anions (Mg L^{-1}) in surface water in Houzhai Karst Basin from 1987 to 2008. The error bars represent the one standard error of six water samples taken from surface water. For clarity, we only plot the upper error bars in this figure. The line trend of the concentrations of cations as shown by the black line is 1.6 , 0.2 and $-0.1 \text{ g m}^{-2} \text{ yr}^{-1}$ for HCO_3^- , SO_4^{2-} and Cl^- , respectively.

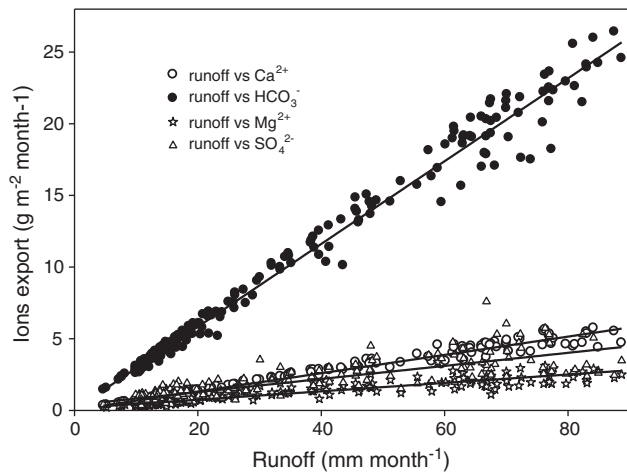


Fig. 6. Linear relationships between export rates of ions ($\text{g m}^{-2} \text{ month}^{-1}$) and the monthly surface runoff (mm month^{-1}) derived from Houzhai Karst Basin during the study period. The monthly surface runoff can explain of 97%, 98%, 87% and 71% of the monthly variations of export rates for Ca^{2+} , HCO_3^- , Mg^{2+} and SO_4^{2-} , respectively.

if there were no other carbonate compositions (e.g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dissolved (Jiang and Yuan, 1999):



where, MeCO_3 represents CaCO_3 and $\text{MgCa}(\text{CO}_3)_2$. In principal, plots of HCO_3^- concentration (in $\mu\text{mol L}^{-1}$) against the sum concentration (in $\mu\text{mol L}^{-1}$) of Ca^{2+} and Mg^{2+} should fit the line of $y = 2x$, because of the following equation:

$$m[\text{HCO}_3^-] = 2m([\text{Ca}^{2+}] + [\text{Mg}^{2+}]). \quad (9)$$

However, our results showed that plots between concentrations (in $\mu\text{mol L}^{-1}$) of anions (HCO_3^-) and cations (Ca^{2+} and Mg^{2+}) did not fit the line of $y = 2x$ (Fig. 9a). Comparison with concentrations (in $\mu\text{mol L}^{-1}$) of HCO_3^- , the total concentrations (in $\mu\text{mol L}^{-1}$) of Ca^{2+} and Mg^{2+} tended to be supersaturated and to be plotted on the right side of the line ($y = 2x$). In general, the ratio between total concentrations (in $\mu\text{mol L}^{-1}$) of cations and anions in water is close to unity. In other words, the plot between concentrations (in $\mu\text{mol L}^{-1}$) of anions and cations should fit into the line of $y = x$. To

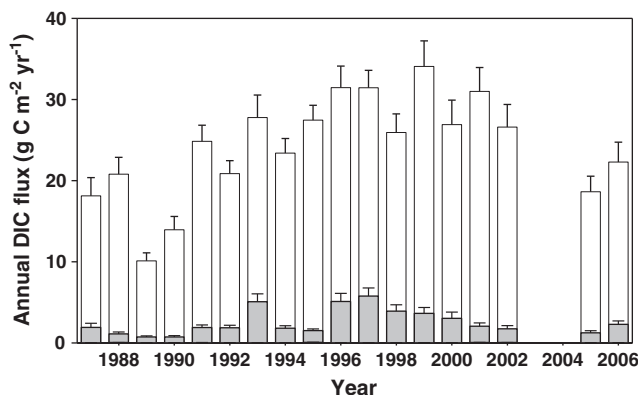


Fig. 7. One standard deviation of the estimated annual dissolved inorganic carbon (DIC) export rate ($\text{g C m}^{-2} \text{ yr}^{-1}$) (three fractions) in the surface water from 1987 to 2006 in Houzhai Basin. Open bar for carbon export rate ($\text{g C m}^{-2} \text{ yr}^{-1}$) in the form of HCO_3^- ; gray bar for carbon export rate ($\text{g C m}^{-2} \text{ yr}^{-1}$) in the form of CO_2 ; and carbon export rate ($\text{g C m}^{-2} \text{ yr}^{-1}$) in the form of CO_3^{2-} is very small and is hardly showed with dark bar.

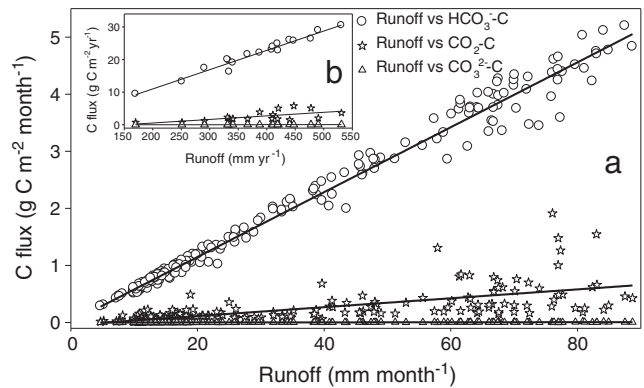
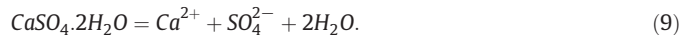


Fig. 8. Linear relationships between carbon export rates (g C m^{-2}) of the three fractions of dissolved inorganic carbon (DIC) and surface runoff (mm) at both the seasonal (a) and annual (b) scales derived from Houzhai Karst Basin during the study period. The monthly surface runoff can explain of 98%, 48% and 46% of the monthly variations of carbon export rates in the form of HCO_3^- , CO_2 and CO_3^{2-} , respectively. The annual surface runoff can explain of 96%, 39% and 30% of the annual variations of carbon fluxes in the form of HCO_3^- , CO_2 and CO_3^{2-} , respectively.

keep concentrations (in $\mu\text{mol L}^{-1}$) of anions and cations in balance, there should be other sources except CaCO_3 and $\text{MgCa}(\text{CO}_3)_2$ that were dissolved in the surface water in HKB. Interestingly, we found that surface water of HKB had a high concentration of SO_4^{2-} . Taken SO_4^{2-} into account, the plot between concentrations (in $\mu\text{mol L}^{-1}$) of cations ($[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$) and anions ($[\text{HCO}_3^-]/2$ and $[\text{SO}_4^{2-}]$) was a good approximate fit to the line of $y = x$. The dots distribution near the line ($y = x$) were expected (Fig. 9b). The source of SO_4^{2-} could be from the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) into the surface water of HKB:



Dissolution of SO_4^{2-} in surface water plays an important role in HKB for the balance of ion concentrations and offset some anions such as HCO_3^- . In our previous research, we found that one of the empirical models as used in global modeling overestimated the net carbon uptake at the same study site by 29%, but the cause was not clear (Yan et al., 2011). The parameters in this model were derived from the standard rock of karst. In fact, besides carbonate rocks, karst areas are usually made of other compositions (e.g. gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)). Hence, high concentrations of SO_4^{2-} could partly explain why carbon uptake is often overestimated by the empirical model using the concentration of HCO_3^- in this karst water.

It should be noted that the concentrations of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} in surface water of HKB were extremely high as compared to other major rivers in the world (Holland, 1978; Gaillardet et al., 1999), indicating that carbonate rock–water reactions have occurred extensively in karst areas. It is likely that high concentration of DIC in surface water is mainly from the dissolution of carbonate minerals within karst basins (Szramek et al., 2007; Ushie et al., 2010; Cao et al., 2011). Influences of other drivers on DIC export rates will be discussed in the following section.

4.2. DIC export related to rainfall, water temperature and pH

On average, 1952 tons ($24.2 \pm 6.4 \text{ g C m}^{-2} \text{ yr}^{-1}$) of carbon were fluvially exported as DIC per year from the entire HKB (80.65 km^2). The rate of DIC export depends on DIC concentration and runoff discharge, which is affected by rainfall, water temperature and pH (Back and Hanshaw, 1970; Oh and Raymond, 2006; Åberg et al., 2010).

It is well known that an increase in rainfall causes the increase of runoff discharge, which in turn, increases DIC export rate. The correlation between the monthly rainfall and DIC export rate in HKB is

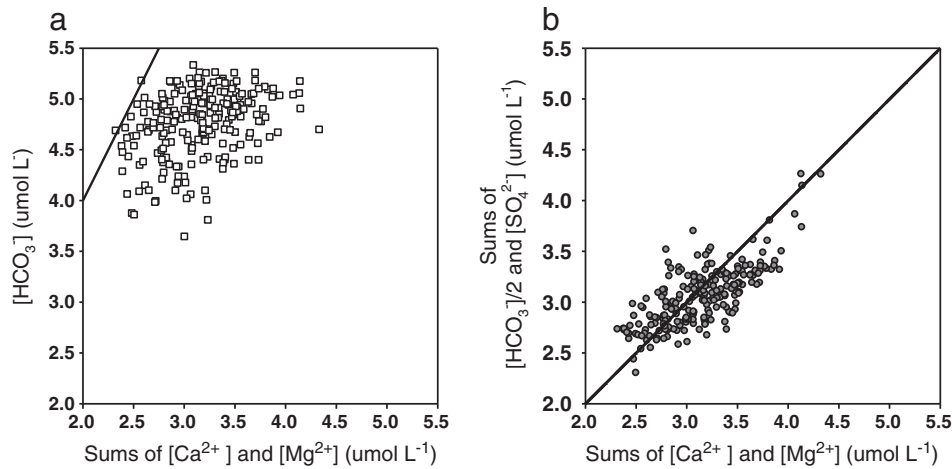


Fig. 9. Empty squares in panel (a) for the variations of the monthly mean bicarbonate concentration ($[\text{HCO}_3^-]$, $\mu\text{mol L}^{-1}$) with the total concentrations of the monthly mean calcium and magnesium ($[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$, $\mu\text{mol L}^{-1}$); gray circles in panel (b) for the variations of the total concentrations of $[\text{HCO}_3^-]/2 + [\text{SO}_4^{2-}]$, $\mu\text{mol L}^{-1}$ with the total concentrations of the monthly mean calcium and magnesium ($[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$, $\mu\text{mol L}^{-1}$) in the surface water in Houzhai Karst Basin from 1987 to 2008. The solid line for the line of $y = 2x$; the dash line for the line of $y = x$.

positive and statistically significant ($R^2 = 0.54$, $n = 229$, $P < 0.001$). Within a year, about 70% of total annual DIC flux occurred in the wet season. At the inter-annual scale, DIC flux also showed the large variation with a range of $10.1\text{--}34.1 \text{ g C m}^{-2} \text{ yr}^{-1}$. The greatest value of DIC flux was found in the driest year and the lowest value was presented in the wettest year during the study period. A significant correlation was also found between rainfall and annual carbon export in three major U.S. watersheds (Raymond and Oh, 2007). It is concluded that water discharge is the most important factor to control DIC flux. The correlation between DIC flux and water temperature was unclear in previous studies. There are only a few field studies in which effects of water temperature on DIC export rate were successfully analyzed, through comparing different regions characterized by large annual temperature differences (Dessert et al., 2003). The study site is strongly influenced by the Asian monsoon. At the seasonal scale, water temperature and rainfall showed a positive relationship across seasons, with warmer in wet seasons (May to October) and cooler in dry seasons (November to April). A caution is therefore required in deriving the relationship between DIC flux and water temperature in the study site. Because of a co-variation between runoff discharge and water temperature, the monthly DIC export rate significantly increased with water temperature ($R^2 = 0.37$, $n = 229$, $P < 0.001$). Positive correlation ($R^2 > 0.30$) was also found between DIC concentration and water temperature at three of the headwater sites of a boreal stream network, but negative correlation at two sites of the stream network (Wallin et al., 2010).

The other main factor that affects DIC export rate is pH value in surface water. In HKB, surface water was always alkaline and yearly mean pH value ranged from 7.2 to 7.9. Higher pH in karst water may shift the bicarbonate equilibrium towards a much higher proportion of HCO_3^- (Wallin et al., 2010). A high proportion of carbon in the form of CO_2 was consistently associated with low pH value in water, whereas a high proportion of carbon in the form of CO_3^{2-} was estimated at a high value of water pH. For most rivers or basins, the majority of DIC is in the form of HCO_3^- (Raymond et al., 2008). In HKB, the proportion of carbon in the form of HCO_3^- was the greatest with a range of 82–95%. A previous study estimated that the mean carbon uptake by the form of HCO_3^- in surface water was $10.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the same site (Yan et al., 2011) and 90% of the total carbon uptake estimated in the present study ($12.1 \text{ g C m}^{-2} \text{ yr}^{-1}$). There was only 10% carbon uptake by the forms of CO_2 and CO_3^{2-} . Previous studies have focused mainly on carbon uptake by the form of HCO_3^- in karst areas (Jiang and Yuan, 1999; Liu and Zhao, 2000; Yan et al., 2011). Here, we

show that there is an important but previously underestimated carbon sink by dissolution process of carbonate rocks. If the forms of CO_2 and CO_3^{2-} are not accounted for, estimates of carbon uptake by karst can be biased by about 10%.

4.3. Estimation of karst carbon uptake from atmosphere in southern China

DIC in water and accumulated organic carbon in plants were considered as the two major sinks of the atmospheric carbon (Gaillardet et al., 1999). The amount of atmospheric/soil CO_2 consumed by chemical weathering can be estimated from DIC flux at the exit of karst basins. For the weathering of carbonate minerals, only half of carbon flux originated from atmospheric/soil CO_2 . The other half was supplied by the dissolved carbonate minerals (Amiotte-Suchet and Probst, 1993; Jiang and Yuan, 1999). Because of the estimated uncertainty in carbon sink by karst water (Liu et al., 2007, 2010a, 2010b; Cao et al., 2011; Yan et al., 2011), the study of carbon uptake by dissolution process has therefore received wide attention with the global change. In the present study, we estimated that the carbon uptake from atmosphere and soil using the concentrations of DIC was $12.1 \text{ g C m}^{-2} \text{ yr}^{-1}$. Interestingly, this is comparable to the estimated rate of carbon uptake in the Pearl River Basin (It contains about 17% of China's surface karst), which absorbs about $1.85 \text{ Tg C yr}^{-1}$ ($11.7 \text{ g C m}^{-2} \text{ yr}^{-1}$) (Cao et al., 2011). The total area of karsts in southern China is $44.6 \times 10^{10} \text{ m}^2$ (Li, 1992), and most karst areas in south China have similar rainfall as our study field. Using the result of DIC export rate by surface runoff, we could estimate that the yearly carbon uptake by dissolution process in southern China was 5.4 Tg C yr^{-1} . It is higher than 3.7 Tg C yr^{-1} estimated by the corrosion rate of carbonate rock (Jiang and Yuan, 1999). Difference between these two estimates can be largely explained by hydrodynamics and hydrochemical processes. The estimation method by Jiang and Yuan (1999) had neglected hydrodynamics. In southwest China, the average slope gradient of the river is larger than 1.23‰ (Cao et al., 2011). Such dramatic hydrodynamic conditions should promote the corrosion rate and intensity of carbonate rocks. Hydrochemical processes were not accounted for in their calculation. Allogenic water has stronger solution capacity than autogenic water (Cheng et al., 2005), which can enhance the corrosion rate of carbonate rocks. The worldwide distribution of carbonate rocks makes karst terrain an important component of the Earth Surface System. The dissolution process of carbonate rocks causes rapid uptake of CO_2 from atmosphere and soil. Runoff discharge from karst area may

act as an important transporter to move atmospheric carbon to rivers, lakes, and oceans, where they could be buried by biological processes in fluvial, lake and marine sediments as a relatively long-term carbon sink (Einsle et al., 2001; Lerman and Mackenzie, 2005).

5. Conclusions

The long-term field measurements of hydro-chemical characteristics in HKB, southwest China, allowed estimating the chemical concentration and DIC export rate of solutes from surface runoff discharge. The main findings of the present study are:

1. The yearly surface runoff coefficient (annual runoff as the percentage of annual rainfall) ranged from 18% to 38% with an average value of 28% in HKB. Within a year, the maximal surface runoff occurred in July, and lagged the maximal rainfall in June by one month.
2. From 1986 to 2007, there was no significant difference in water temperature (mean annual value 16.7°C). Surface water pH was alkaline in HKB ranging from 7.2 to 7.9, with an average value of 7.5.
3. Surface water chemistry was dominated by ions Ca^{2+} , Mg^{2+} , HCO_3^- , and SO_4^{2-} , which were exported by surface runoff discharge with average rate of 24.7, 13.0, 110.2, and 21.6 $\text{g m}^{-2} \text{yr}^{-1}$, respectively.
4. Seasonal variability of chemical export rate was positively correlated with surface runoff discharge, with the concentration generally diluted at high discharge. From 1986 to 2007, the concentrations of Ca^{2+} , Mg^{2+} , HCO_3^- , and SO_4^{2-} showed a slowly increasing trend in surface water, while concentration changes of Na^+ , K^+ , and Cl^- exhibited an opposite pattern.
5. Annual DIC flux ranged from 10.1 to 34.1 $\text{g C m}^{-2} \text{yr}^{-1}$, with an average value of 24.2 $\text{g C m}^{-2} \text{yr}^{-1}$. Rainfall had the most important influence on DIC export rate, but the proportions of three fractions of DIC was controlled by water pH. High water temperature in the wet season could reduce the solubility of CO_2 in water, but its effect on DIC export rate was much smaller than that of rainfall.
6. Using the concentrations of DIC, we estimated that carbon uptake by karstification was 12.1 $\text{g C m}^{-2} \text{yr}^{-1}$ and was similar to 11.7 $\text{g C m}^{-2} \text{yr}^{-1}$ estimated in Pearl River Basin (It contains about 17% of China's surface karst). The yearly carbon uptake by karstification in southern China was 5.4 Tg C yr^{-1} and it was higher than 3.7 Tg C yr^{-1} estimated by the corrosion rates of carbonate rocks.

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References

Aberg, J., Jansson, M., Jonsson, A., 2010. Importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO_2 in a boreal lake. *Journal of Geophysical Research* 115, G02024. doi:10.1029/2009JG001085.

Ahearn, D.S., Sheibley, R.W., Dahlgren, R.A., Anderson, M., Johnson, J., Tate, K.W., 2005. Land use and land cover influence on water quality in the last free-flowing river draining the western Sierra Nevada, California. *Journal of Hydrology* 313, 234–247.

Amiotte-Suchet, P., Probst, J.L., 1993. CO_2 flux consumed by chemical-weathering of continents – influences of drainage and lithology. *Comptes Rendus de l'Académie des Sciences Serie II* 317 (5), 615–622.

Amiotte-Suchet, P., Probst, J.L., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochemical Cycles* 17 (2), 1038. doi:10.1029/2002GB001891.

Aufdenkampe, A.K., Mayoga, E., Raymond, P.A., Melack, J.M., Doney, S.C., Alin, S.R., Aalto, R.E., Yoo, K., 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment* 9 (1), 53–60.

Back, W., Hanshaw, B.B., 1970. Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. *Journal of Hydrology* 10, 330–368.

Betts, R.A., Boucher, O., Collins, M., Cox, P.M., Falloon, P.D., Gedney, N., Hemming, D.L., Huntingford, C., Jones, C.D., Sexton, D.M.H., Webb, M.J., 2007. Projected increase in continental runoff due to plant responses to increasing carbon dioxide. *Nature* 448, 1037–1041.

Binkley, D., Ice, G.G., Kaye, J., Williams, C.A., 2004. Nitrogen and phosphorus concentration in forest streams of the United States. *Journal of the American Water Resources Association* 40, 1277–1291.

Cao, J.H., Yang, H., Kang, Z.Q., 2011. Preliminary regional estimation of carbon sink flux by carbonate rock corrosion: a case study of the Pearl River Basin. *Chinese Science Bulletin* 56, 3766–3773.

Chen, H.Y., Chen, B.Y., 2005. Lithologic characteristics of Houzhai karst small valley, Puding Guizhou province. *Guizhou Geology* 22, 284–288 (in Chinese with English summary).

Cheng, X., Shi, Z., Li, C., 2005. Mechanism of Karstic Development and Hydrogeochemical Characteristics of Tumen in Yiyuan County. *Shandong Land and Resources* 21, 37–39 (in Chinese with English summary).

Christina, L., 2011. An unsung carbon sink. *Science* 334, 886–887.

Dessert, C., Dupré, B., Gaillardet, J., François, L.M., Allègre, C.J., 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chemical Geology* 202, 257–273.

Dürr, H.H., Meybeck, M., Dürr, S.H., 2005. Lithologic composition of the Earth's continental surfaces derived from a new digital map emphasizing riverine material transfer. *Global Biogeochemical Cycles* 19, GB4510. doi:10.1029/2005GB002515.

Einsle, G., Yan, J., Hinderer, M., 2001. Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. *Global and Planetary Change* 30, 167–195.

Gaillardet, J., Dupré, B., Louvat, P., Alle'gre, C.J., 1999. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chemical Geology* 159, 3–30.

Gedney, N., Cox, P.M., Betts, R.A., Boucher, O., Huntingford, C., Stott, P.A., 2006. Detection of a direct carbon dioxide effect in continental river runoff records. *Nature* 439, 835–838.

Gelbrecht, J., Fait, M., Dittrich, M., Steinberg, C., 1998. Use of GC and equilibrium calculations of CO_2 saturation index to indicate whether freshwater bodies in north-eastern Germany are net sources or sinks for atmospheric CO_2 . *Fresenius' Journal of Analytical Chemistry* 361 (1), 47–53. doi:10.1007/s002160050832.

Hartmann, J., Jansen, N., Dürr, H.H., Kempe, S., Köhler, P., 2009. Global CO_2 -consumption by chemical weathering: what is the contribution of highly active weathering regions? *Global and Planetary Change* 59, 185–194.

Hartmann, J., Moosdorf, N., 2011. Chemical weathering rates of silicate-dominated lithological classes and associated liberation rates of phosphorus on the Japanese Archipelago—implications for global scale analysis. *Chemical Geology* 287, 125–157.

Holland, H.D., 1978. *The Chemistry of the Atmosphere and Oceans*. John Wiley, New York.

Hutzing, O., 1980. *Environmental Chemistry*, Vol. 1, part A. Springer, New York.

Jackson, R.B., Jobbágy, E.G., Avissar, R., Roy, S.B., Barrett, D.J., Cook, C.W., Farley, K.A., Maitre, D.C.L., McCar, B.A., Murray, B.C., 2005. Trading water for carbon with biological carbon sequestration. *Science* 310, 1944–1947.

Jarvie, H.P., Neal, C., Leach, D.V., Ryland, G.P., House, W.A., Robson, A.J., 1997. Major ion concentrations and the inorganic carbon chemistry of the Humber rivers. *Science of the Total Environment* 194, 285–302.

Jiang, Z., Yuan, D., 1999. CO_2 source-sink in karst processes in karst areas of China. *Episodes* 22 (1), 33–35.

Katz, B.G., Coplen, T.B., Bullen, T.D., Davis, J.H., 1997. Use of chemical and isotopic tracers to characterize the interactions between ground water and surface water in mantled Karst. *Ground Water* 35, 1014–1028.

Lerman, A., Mackenzie, F.T., 2005. CO_2 air-sea exchange due to calcium carbonate and organic matter storage, and its implications for the global carbon cycle. *Aquatic Geochemistry* 11, 345–390.

Li, G., 1992. 1:4000,000 karst hydrogeological map of China, China Cartographic Publishing House, Beijing.

Likens, G.E., Bormann, F.H., Johnson, N.M., 1981. Interactions between major biogeochemical cycles in terrestrial ecosystems. In: Likens, G.E. (Ed.), *Some Perspectives of the Major Biogeochemical Cycles*. Scientific Committee on Problems of the Environment, pp. 93–112.

Liu, L., Shu, L., Chen, X., Oromo, T., 2010a. The hydrologic function and behavior of the Houzhai underground river basin, Guizhou Province, southwestern China. *Hydrogeology Journal* 18, 509–518.

Liu, Z., Dreybrodt, W., Wang, H., 2010b. A new direction in effective accounting for the atmospheric CO_2 budget: considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. *Earth-Science Reviews* 99, 162–172.

Liu, Z., Li, Q., Sun, H., Wang, J., 2007. Seasonal, diurnal and storm-scale hydrochemical variations of typical epikarst springs in subtropical karst areas of SW China: soil CO_2 and dilution effects. *Journal of Hydrology* 337, 207–223.

Liu, Z., Zhao, J., 2000. Contribution of carbonate rock weathering to the atmospheric CO_2 sink. *Environmental Geology* 39 (9), 1053–1058.

Lloret, E., Dessert, C., Gaillardet, J., Albéric, P., Crispi, O., Chaduteau, C., Benedetti, M.F., 2011. Comparison of dissolved inorganic and organic carbon yields and fluxes in the watersheds of tropical volcanic islands, examples from Guadeloupe (French West Indies). *Chemical Geology* 280, 65–78.

Macpherson, G.L., Roberts, J.A., Blair, J.M., Townsend, M.A., Fowle, D.A., Beisner, K.R., 2008. Increasing shallow groundwater CO_2 and limestone weathering, Konza Prairie, USA. *Geochimica et Cosmochimica Acta* 72, 5581–5599.

Meng, H.H., Wang, L.C., 2009. Hydrological responses to land-use changes in karst area—a case study in Houzhai river, Guizhou province. *Carsologica Sinica* 28, 227–234 (in Chinese with English summary).

- Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. *American Journal of Science* 287, 401–428.
- Oh, N.H., Raymond, P.A., 2006. Contribution of agricultural liming to riverine bicarbonate export and CO₂ sequestration in the Ohio River basin. *Global Biogeochemical Cycles* 20, GB3012. doi:10.1029/2005GB002565.
- Petrone, K.C., 2010. Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan-Canning River system, southwestern Australia. *Journal of Geophysical Research* 115, G01016. doi:10.1029/2009JG001051.
- Raymond, P.A., Oh, N.H., 2007. An empirical study of climatic controls on riverine C export from three major U.S. watersheds. *Global Biogeochemical Cycles* 21, GB2022. doi:10.1029/2006GB002783.
- Raymond, P.A., Oh, N.H., Turner, R.E., Broussard, W., 2008. Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. *Nature* 451, 449–452.
- Sabater, F., Sabater, S., Armengol, J., 1990. Chemical characteristics of a Mediterranean river as influenced by land uses in the watershed. *Water Research* 24, 143–155.
- Shanley, J.B., Kendall, C., Smith, T.E., Wolock, D.M., McDonnell, J.J., 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes* 16, 589–609.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*, 3rd ed. John Wiley, New York.
- Stutter, M.I., Deeks, L.K., Low, D., Billett, M.F., 2006. Impact of soil and groundwater heterogeneity on surface water chemistry in an upland watershed. *Journal of Hydrology* 318, 103–120.
- Sun, G., Zhou, G.Y., Zhang, Z.Q., Wei, X.H., McNulty, S.G., Vose, J.M., 2006. Potential water yield reduction due to forestation across China. *Journal of Hydrology* 328, 548–558.
- Szramek, K., McIntosh, J.C., Williams, E.L., Kanduc, T., Ogrinc, N., Walter, L.M., 2007. Relative weathering intensity of calcite vs. dolomite in carbonate-bearing temperate zone watersheds: carbonate geochemistry and fluxes from catchments within the St. Lawrence and Danube River Basin. *Geochemistry, Geophysics, Geosystems* 8, 1–28.
- Ushie, H., Kawahata, H., Suzuki, A., Murayama, S., Inoue, M., 2010. Enhanced riverine carbon flux from carbonate catchment to the ocean: a comparative hydrogeochemical study on Ishigaki and Iriomote islands, southwestern Japan. *Journal of Geophysical Research* 115, G02017. doi:10.1029/2009JG001039.
- Wallin, M., Buffam, I., Öquist, M., Laudon, H., Bishop, K., 2010. Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: concentrations and downstream fluxes. *Journal of Geophysical Research* 115, G02014. doi:10.1029/2009JG001100.
- White, W.B., 1988. *Geomorphology and Hydrology of Karst Terrains*. Oxford University Press, Oxford.
- Wu, Y., Gibson, C.E., 1996. Mechanisms controlling the water chemistry of small lakes in Northern Ireland. *Water Research* 30, 178–182.
- Yan, J.H., Wang, Y.P., Zhou, G.Y., Li, S.G., Yu, G.R., Li, K., 2011. Carbon uptake by karsts in the Houzhai Basin, Southwest China. *Journal of Geophysical Research*. doi:10.1029/2011JG001686.
- Yang, Y., 2001. A study on the structure of karst aquifer medium and the groundwater flow in Houzhai underground river basin. *Carsologica Sinica* 20, 17–20.