



## Effect of different land use/land cover on karst hydrogeochemistry: A paired catchment study of Chenqi and Dengzhanhe, Puding, Guizhou, SW China

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### SUMMARY

Rainfall, spring stage, water temperature, pH and conductivity in the paired karst spring catchments of Chenqi and Dengzhanhe, which shared the same climatic condition but different land use/land cover (LULC) at Puding, Guizhou Province, SW China, were monitored by two high-resolution multi-parameter auto-recordable instrument of CTD300 during the hydrological year of September 2007–September 2008. Other monthly hydrogeochemical and carbon isotopic ( $\delta^{13}\text{C}$ ) variations in the paired karst catchments during the same hydrological year were also investigated. A thermodynamic model was used to link the continuous data to monthly hydrogeochemical data allowing the calculation of  $\text{CO}_2$  partial pressure ( $p\text{CO}_2$ ) and calcite saturation index ( $\text{SI}_c$ ) on a continuous basis. The primary study objective was to understand how the karst processes and karst hydrogeochemistry respond to different LULC, which is essential to assessing the karst-related carbon cycle. Marked seasonal and storm-scale variations were found for pH, conductivity,  $p\text{CO}_2$ ,  $\text{SI}_c$  and  $\delta^{13}\text{C}$  of the two springs, indicating that both springs were dynamic and variable systems. However, there were differences in the magnitude and direction of the variations of these features between the two springs. The higher  $p\text{CO}_2$  and  $\text{HCO}_3^-$  concentration and lower pH,  $\text{SI}_c$  and  $\delta^{13}\text{C}$  in Chenqi spring than those in Dengzhanhe spring tend to be related to the difference in LULC between Chenqi and Dengzhanhe spring catchments: in the Chenqi spring catchment, there was larger soil cover and the paddy land was located in the discharge area, both of which produced and kept more  $\text{CO}_2$  (a major driving agent for the karst processes) and lower  $\delta^{13}\text{C}$  in the soil-aquifer system, while in the Dengzhanhe spring catchment area, there was larger bare carbonate rock occurrence and the paddy land was located mainly in the recharge area. Moreover, the pH increased and  $p\text{CO}_2$  decreased generally in Chenqi spring after rainfall, possibly due to more carbonate dissolution in the larger soil cover rich in limestone fragments in the spring catchment, while the pH decreased and  $p\text{CO}_2$  increased generally in Dengzhanhe spring after rainfall. All these differences show that soil cover and land use pattern played important roles in the karst processes. In other words, the karst hydrogeochemistry and the karst-related carbon cycle could be regulated effectively by different LULC. In addition, the higher concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and conductivity of Dengzhanhe spring were due to the dissolution of more gypsum and dolomite minerals in the strata of Dengzhanhe spring catchment. Therefore, the karst hydrogeochemical parameters, including pH, conductivity,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $p\text{CO}_2$ ,  $\text{SI}_c$ , and  $\delta^{13}\text{C}_{\text{DIC}}$ , could serve as good indicators of different LULC and the other environmental changes.

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### 1. Introduction

Land use and land cover change (LULCC) is the most important anthropogenic factor that shows the influence on the surface of the earth (Lambin et al., 2001). LULCC directly impacts biological diversities, contributes to the local and regional climate changes as well as to global warming, and may cause land degradation by altering

ecosystem services and livelihood support systems (Xu et al., 2005). LULCC has been designated as a core field of study by the International Geosphere–Biosphere Programme (IGBP) and the International Human Dimensions Programme on Global Environmental Change (IHDP), and has therefore received great attention from scholars worldwide (Turner et al., 1995; Xu et al., 2002). Since LULCC is closely related to human–nature interactions, it actually embodies the dynamic relations between human activities and the physical environment. The goal of the LULCC Plan, set by IGBP and IHDP, is 2-fold: first, to gain a clear understanding of the current state and the process of LULCC at various scales—local, regional

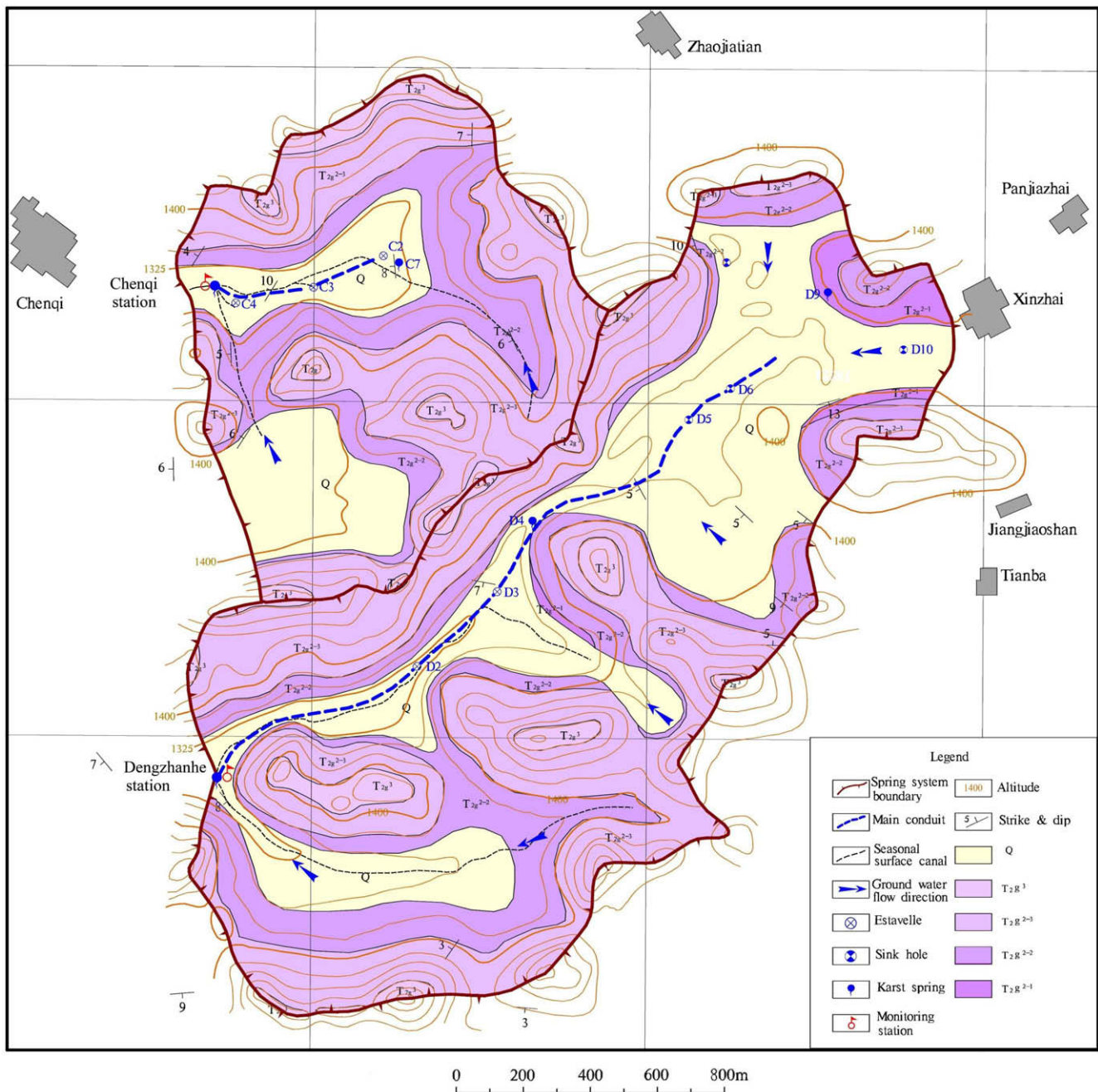
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and global; second, to understand the underlying forces—both natural and human—that drive the changes (Xu et al., 2002).

In recent years, significant progresses have been made in the study of LULCC. A variety of methods and new techniques have been developed and applied to analyze LULCC, including use of remote sensing, GIS, and statistical methods (Xu et al., 2002). Most of the existing studies focus on monitoring of quantitative changes in land use/land cover patterns. Some studies began to pay attention to land quality changes and the resultant environmental/ecological consequences (Keller et al., 1991; Bhaduri et al., 1997; Fohrer et al., 2001; Jiang et al., 2006; Bouma, 2002). The impact of agricultural activities on water quality gains more attention (Boyer and Pasquarell, 1996; Collins and Jenkins, 1996; Kolpin, 1997; Koh et al., 2007). Groundwater quality in a region is largely determined by both the

natural processes (lithology, groundwater velocity, quality of recharge waters, and interaction with other types of aquifers) and anthropogenic activities (agriculture, industry, urban development and increasing exploitation of water resources) (Helena et al., 2000; Bahara and Yamamuro, 2008). Land use is one of the most important factors determining water quality (Clinton and Vose, 2006). However, very few researches focus on the effect of LULCC on the karst hydrogeochemistry (Zhang et al., 2008), which is essential to understanding the karst process-related carbon cycle (Liu and Zhao, 2000; Gombert, 2002; Liu et al., 2008, 2010).

As a sensitive ecosystem, karst dynamic system is controlled by karst environment (Yuan, 1997, 2001). As a vulnerable factor of karst ecosystem, karst groundwater system is highly sensitive to LULCC (Zhang et al., 2005, 2008, Guo et al., 2007; Jiang et al.,



**Fig. 1.** Hydrogeological map of Chenqi and Dengzhanhe karst spring catchments. Q: Quaternary deposits; T<sub>2g</sub><sup>3</sup>: dolomite with gypsum of upper Guanling Formation of middle Triassic; T<sub>2g</sub><sup>2-3</sup>: limestone of upper part of middle Guanling Formation of middle Triassic; T<sub>2g</sub><sup>2-2</sup>: limestone intercalated with marl and shale of middle part of middle Guanling Formation of middle Triassic; T<sub>2g</sub><sup>2-1</sup>: marl intercalated with limestone and shale of lower part of middle Guanling Formation of middle Triassic.

2008). Different karst areas possess different hydrochemical and isotopic characteristics. Even in the same area, the hydrochemical compositions will have great changes at different times (Liu et al., 2004, 2007). Several studies of the hydrochemical characteristics of karst groundwater under different LULCCs at different time scales have been made in China (Zhang et al., 2005, 2008; Guo et al., 2007; Jiang et al., 2008). However, most of the study conclusions were drawn by using the existing occasional hydrochemical data combined with remote-sensing data to the comparative study

of the water chemistry before and after the LULCC. So, it is very difficult to understand the detailed dynamic hydrochemical variations in the karst system caused by different LULC though some general hydrochemical changes with LULCCs in karst systems have been investigated (Zhang et al., 2005, 2008; Guo et al., 2007; Jiang et al., 2008). Recently, with the achievement in technology, the high-resolution multi-parameter data logger has been available to monitor the continuous hydrochemical variations. In this paper, the detailed karst hydrochemical changes obtained by this new

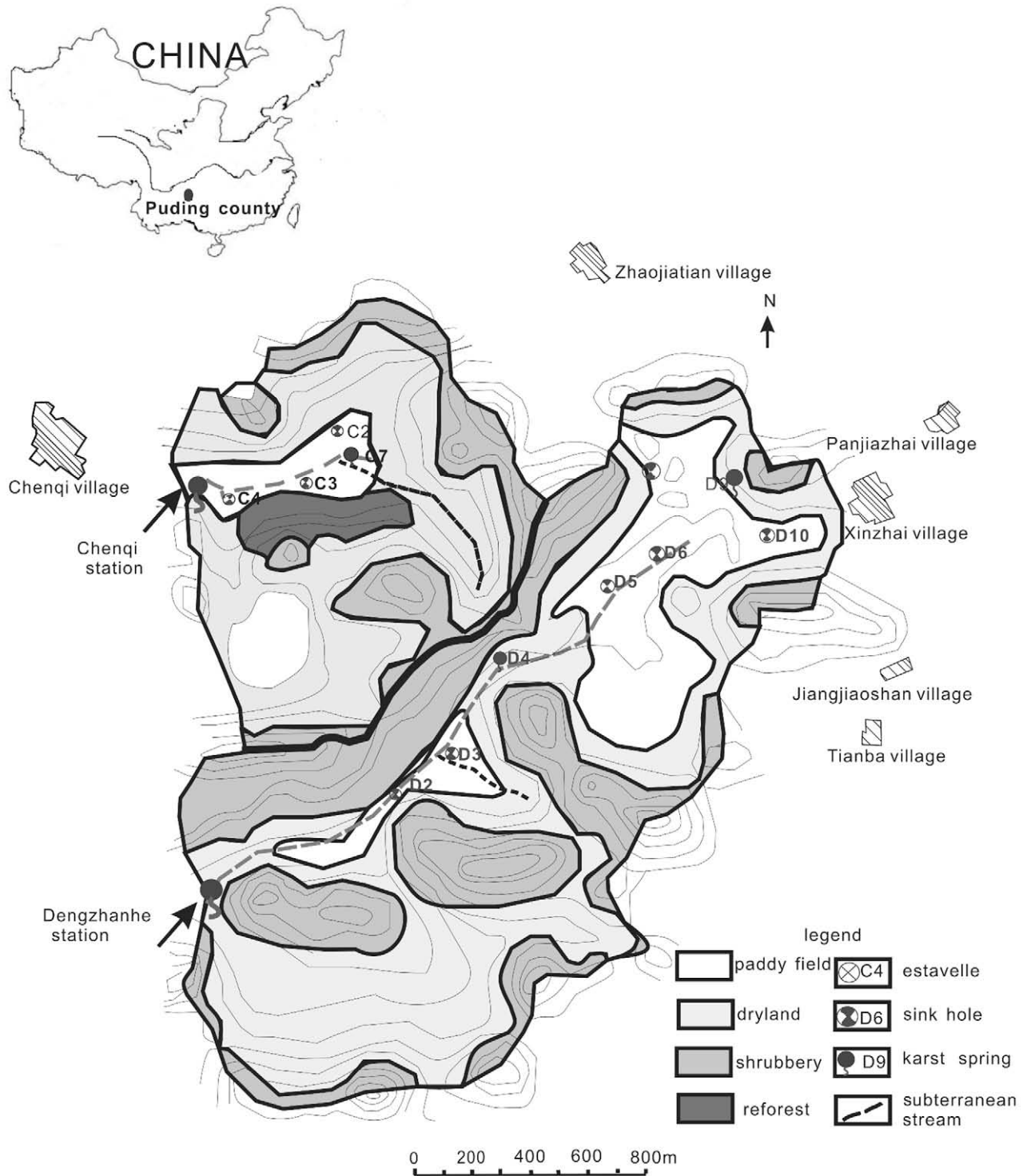


Fig. 2. Comparison of distribution of various land use types between Chenqi and Dengzhanhe spring catchments.

technology and the difference of these changes under different LULC will be discussed based on paired catchments of Chenqi and Dengzhanhe, Puding, Guizhou, SW China.

## 2. Description of the paired catchments of Chenqi and Dengzhanhe

Paired catchment studies are originally used for determining changes in water yield resulting from alterations in vegetation. They involve the use of two catchments with similar characteristics in terms of slope, aspect, soils, area, climate and vegetation located adjacent or in close proximity to each other (Brown et al., 2005). One of the advantages of paired catchment studies is that they remove climate variability through the comparison of two catchments subject to the same climatic conditions under different LULC. The separation of climatic variability effects from the water yield and hydrochemical changes as a result of vegetation and/or soil alterations is a key problem for time trend studies. In cases where paired catchments are available, the separation of LULC impacts from climatic factors can be achieved through the comparison of the two catchments (Brown et al., 2005).

### 2.1. Geology, climate and hydrogeology

Chenqi (1.31 km<sup>2</sup>) and Dengzhanhe (2.82 km<sup>2</sup>) karst spring catchments (105°42'–105°43'E, 26°14'–26°15'N) are close to each other and both locate in Puding County, Guizhou Province, SW China (Fig. 1). The main lithology is limestone and dolomite of the Guanling Formation of middle Triassic. However, there is larger distribution of gypsum and dolomite in Dengzhanhe catchment than in Chenqi catchment ( $T_{2g}^3$ , Fig. 1). Both catchments are characterized by a humid subtropical monsoon climate, with >80% of annual precipitation occurring during the rainy season from May to October, an annual average precipitation of about 1314.6 mm, and mean air temperature of 15.1 °C.

Chenqi and Dengzhanhe spring catchments are higher in the east and lower in the west in general. The lowest altitude is 1310 m. The highest altitude in the Chenqi spring catchment is 1524 m, while in the Dengzhanhe spring catchment is 1559 m. Thus, the relative elevation difference in the two catchments is larger than 200 m. The main geomorphology of both catchments is karst valley. Most part of the valleys is covered with loose Quaternary deposits and has been reclaimed for paddy land and dry land (Fig. 1, Fig. 2). The two karst springs locate at the west of the valleys. Their flow is variable, but perennial.

### 2.2. Land use/land cover changes and the difference between the paired catchments

Chenqi and Dengzhanhe spring catchments both have been changed to farmlands, including dry land, paddy land, shrubbery

land, and fruit tree land, where the paddy land and dry land are rich in soil with limestone fragments, while bare carbonate rock with little soil cover locates in the shrubbery land and fruit tree land (Figs. 2 and 3). However, there are large differences in the distribution and area proportion of land use types between the paired catchments. In Chenqi catchment, the paddy land (14.39%) located in the discharge area, while it (18.76%) located mainly in the recharge area of the Dengzhanhe catchment (Fig. 2). In addition, the area proportion of dry land in the Chenqi catchment (55.65%) was remarkably higher than that (44.2%) in the Dengzhanhe catchment, and the Dengzhanhe catchment had shrubbery land cover of 37.04%, which is higher than that of Chenqi catchment (23.35%). In addition, there was a patch of fruit tree land in the Chenqi catchment (6.61%). Therefore, the Chenqi spring catchment was characterized by higher (>10%) soil cover than Dengzhanhe catchment, while Dengzhanhe spring catchment has more shrubbery land cover with bare carbonate rock occurrence.

## 3. Methods

The study methods include hydrochemical data logging, in situ titrating, sample analysis in the laboratory, and hydrochemical model calculation.

### 3.1. Hydrochemical data logging

To obtain detailed hydrochemical processes in the paired catchments with different LULC, a CTD300 multi-parameter data logger (made by Greenspan in Australia) was used in Chenqi and Dengzhanhe springs to record water stage, water temperature, pH, electrical conductivity (EC), and rainfall, with resolutions of 0.01 cm, 0.01 °C, 0.01 pH, 0.01 μs/cm and 0.05 mm at a time interval of fifteen minutes during the hydraulic year of September 2007–September 2008 (Liu et al., 2007). The logger was calibrated prior to deployment using pH (4, 7 and 10) and conductivity (1412 μs/cm) standards. Hand-held water quality meter (WTW MultiLine P3 pH/LF-SET, made in Germany) measurements were undertaken to check the reliability of data logger measurements (water temperature, pH, EC) at monthly interval, when retrieving data from data logger was conducted in each month. It was found that the hand held meter and logger measurements are identical within 5% error.

### 3.2. In situ-titrating and laboratory sample analysis of hydrochemistry

In situ titrating was used to measure the [HCO<sub>3</sub><sup>-</sup>] and [Ca<sup>2+</sup>] of water with the Aquamerck Alkalinity Test and Hardness Test monthly. The resolutions are 6 and 1 mg/L respectively (Liu et al., 2007). Two sets of 60 ml samples were transferred in acid-washed hydroplastic bottles for chemical analysis of cations and anions after filtering through 0.45 μm Millipore filters. The samples for cation analysis were acidified to pH < 2.0 using concentrated nitric acid. Unstable parameters (temperature, pH and EC) were measured in situ by the WTW MultiLine P3 pH/LF-SET hand-held water quality meter as stated above.

In the laboratory, cation concentrations of Na, K, Ca, and Mg were determined by inductively coupled plasma optical emission spectrometer (ICP-OES). The anion concentrations of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> were analyzed by ion chromatography (Dionex ICS-90).

### 3.3. Measurements of stable carbon isotopic compositions of dissolved inorganic carbon ( $\delta^{13}C_{DIC}$ )

Water samples for  $\delta^{13}C_{DIC}$  analysis were collected in 600 ml hydroplastic bottles. The pH values of the water samples were in-

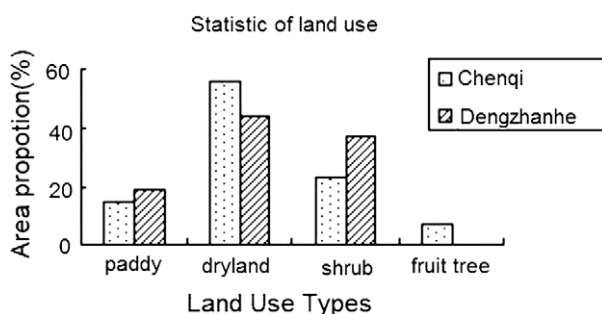


Fig. 3. Comparison in area proportion of land uses between Chenqi and Dengzhanhe spring catchments.

creased to above 12.00 by using NaOH (2 N), and all dissolved inorganic carbon was precipitated as BaCO<sub>3</sub> with a saturated BaCl<sub>2</sub> solution (Liu et al., 2003) in situ. During the processes, the bottles were filled completely (without any air left) to avoid exchanges with CO<sub>2</sub> in the ambient air, and then stored at refrigerator until further analysis. The precipitate was filtered and heated. The BaCO<sub>3</sub> was analyzed in the laboratory with GV IsoPrim IRMS. The carbon isotope data refers to the composition of the dissolved inorganic carbon and are given as per mil (‰) deviations from the PDB standard in the data notation and the standard deviation (1σ) is 0.15‰.

#### 3.4. Calculating CO<sub>2</sub> partial pressure and calcite saturation index from continuous records of temperature, pH and EC

The CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) and calcite/dolomite saturation index (SI<sub>c</sub>/SI<sub>d</sub>) of spring water are related to its Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations, pH and temperature as described in an earlier study (Liu et al., 2007). However, while the continuous monitors directly measure pH and temperature, continuous Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations have to be estimated indirectly. In the case of the paired catchments, the spring composition is dominated by calcite, dolomite and gypsum dissolution. Thus, Ca<sup>2+</sup> and Mg<sup>2+</sup> are the major cations and HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the major counterbalancing anions. Consequently, these ions dominate the EC and their concentrations are directly proportional to the EC. As the EC is directly measured continuously, this feature is used to estimate Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations from the continuous EC data. For this purpose, the linkages between concentrations of these ions and EC need to be established from the spot-sampled monthly data.

In the Chenqi spring catchment, these concentrations were linearly related to EC by the relationships:

$$[\text{Ca}^{2+}] = 0.20\text{EC} - 4.12, \quad r^2 = 0.85 \quad (1)$$

$$[\text{Mg}^{2+}] = 0.02\text{EC} + 1.12, \quad r^2 = 0.83 \quad (2)$$

$$[\text{HCO}_3^-] = 0.29\text{EC} + 68.83, \quad r^2 = 0.62 \quad (3)$$

$$[\text{SO}_4^{2-}] = 0.31\text{EC} - 68.59, \quad r^2 = 0.58 \quad (4)$$

and for the Dengzhanhe spring catchment, the relationships are:

$$[\text{Ca}^{2+}] = 0.19\text{EC} - 8.88, \quad r^2 = 0.89 \quad (5)$$

$$[\text{Mg}^{2+}] = 0.05\text{EC} - 5.12, \quad r^2 = 0.83 \quad (6)$$

$$[\text{HCO}_3^-] = 0.1\text{EC} - 137.44, \quad r^2 = 0.57 \quad (7)$$

$$[\text{SO}_4^{2-}] = 0.63\text{EC} - 183.78, \quad r^2 = 0.93 \quad (8)$$

where brackets denote species concentrations in mg/L and EC is specific conductivity in μS/cm at 25 °C.

This information was used with the EC data to determine continuous changes in pCO<sub>2</sub> and SI<sub>c</sub>.

The full hydrochemical data sets, including recorded temperature and pH, calculated Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> through the regression equations above, mean monthly values of K<sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> were processed through the program WATSPEC (Wigley, 1977), which calculates pCO<sub>2</sub>, SI<sub>c</sub> and SI<sub>d</sub>. pCO<sub>2</sub> assumed to be in equilibrium with the sampled waters is calculated by the following equation:

$$\text{pCO}_2 = \frac{(\text{HCO}_3^-)(\text{H}^+)}{K_1 K_{\text{CO}_2}}$$

where K<sub>1</sub> and K<sub>CO<sub>2</sub></sub> are the equilibrium constants for carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and CO<sub>2</sub> respectively.

SI<sub>c</sub> is calculated from:

$$\text{SI}_c = \left( \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_c} \right)$$

where K<sub>c</sub> is the equilibrium constant of calcite dissolution.

If SI<sub>c</sub> = 0, the equilibrium is reached; if SI<sub>c</sub> > 0, water is supersaturated with respect to calcite and if SI<sub>c</sub> < 0, water is aggressive to the mineral.

## 4. Results and discussion

The results of this work are extensive and summarizing the findings is difficult without reference to the full data set. Statistical analysis (Table 1) simply does not convey the detail of the record and the data is therefore presented graphically in time series to allow visual assessment alongside the summary text. Time series for the full data set are presented in Fig. 4 for both Chenqi spring and Dengzhanhe spring, which shows the seasonal variability superimposed on the fine detail of storm-scale fluctuations. Fig. 5 shows further the storm-scale variations on June 6–14, 2008 for the detail to show the difference in the dilution effect between the paired catchments under different rainfall intensity.

In this case of the paired catchments, the groundwater composition is dominated mainly by limestone dissolution. Therefore, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> are the major cation and anion in the springs (Table 1). The higher SO<sub>4</sub><sup>2-</sup> and Mg<sup>2+</sup> concentrations in Dengzhanhe spring than Chenqi spring (Table 1) were related to the dissolution of more gypsum and dolomite in the formation of Dengzhanhe catchment (Fig. 1). Therefore, the groundwater chemical type of

**Table 1**

Minimum, maximum and annual mean values of chemical concentrations in Chenqi and Dengzhanhe springs.

Item	Unit	Chenqi spring			Dengzhanhe spring		
		Min.	Max.	Mean (n = 12)	Min.	Max.	Mean (n = 12)
Temp.	°C	11.4	18.3	16.14	14.9	17.8	17.01
pH	–	6.94	7.36	7.15	7.25	7.92	7.48
K <sup>+</sup>	mg/l	0.71	1.89	1.19	0.95	1.87	1.54
Na <sup>+</sup>	mg/l	0.92	4.71	1.72	1	3.04	1.83
Ca <sup>2+</sup>	mg/l	84	140	105.91	74	210	148.33
Mg <sup>2+</sup>	mg/l	11.76	26.01	15.89	15.93	56.3	31.85
Cl <sup>-</sup>	mg/l	3.83	9.39	6.42	3.61	9.03	5.79
SO <sub>4</sub> <sup>2-</sup>	mg/l	37.98	211.42	96.49	117.52	585.65	321.21
HCO <sub>3</sub> <sup>-</sup>	mg/l	176.9	280.6	229.97	158.6	256.2	209.16
NO <sub>3</sub> <sup>-</sup>	mg/l	0.01	26.88	16.33	12.44	35.95	19.52
EC	μS/cm	457	677	570.82	452	1124	794.17
δ <sup>13</sup> C <sub>DIC</sub>	‰, PDB	–12.75	–9.85	–11.21	–11.56	–8.05	–10.01
SI <sub>c</sub>	–	–0.272	0.159	–0.05	–0.15	0.79	0.24
pCO <sub>2</sub>	Pa	706.32	2799	1508.16	206.06	1193.99	630.37

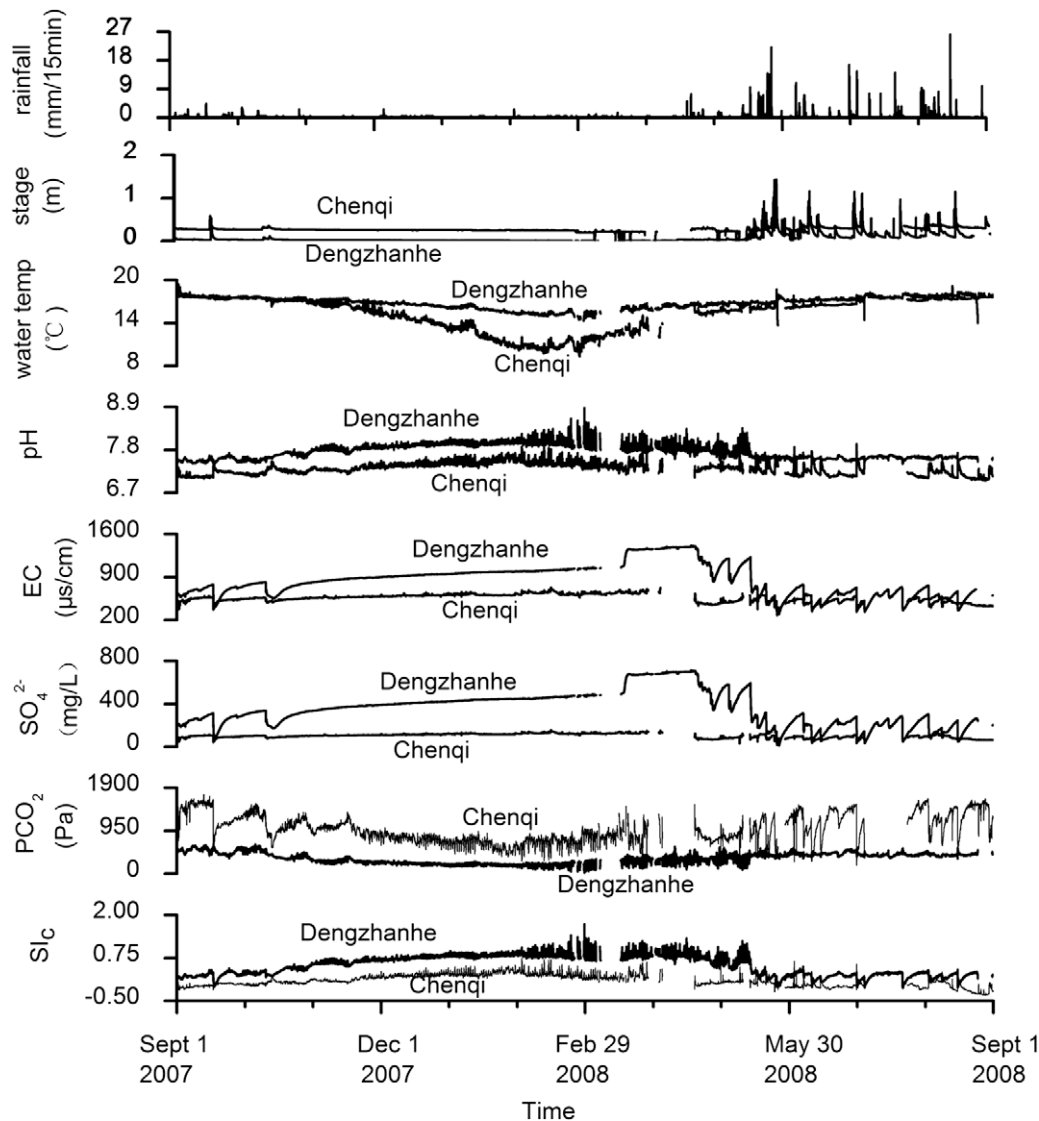


Fig. 4. Comparison of continuous hydrochemical variations between Chenqi spring and Dengzhanhe spring in relation with rainfall (The discontinuities in the curves are due to human disturbance).

Dengzhanhe spring was of  $\text{HCO}_3\text{SO}_4\text{—Ca}\cdot\text{Mg}$  or  $\text{SO}_4\text{HCO}_3\text{—Ca}\cdot\text{Mg}$  type, compared to the  $\text{HCO}_3\text{—Ca}$  type of Chenqi spring. The dominant types of water chemistry in the groundwater can be further illustrated by the Piper diagrams (Fig. 6).

#### 4.1. Hydrochemical variations

##### 4.1.1. Major ions hydrochemistry and monthly variations

Major ions of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and also agricultural pollution indicative ion  $\text{NO}_3^-$  were shown in Fig. 7. It can be seen that  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions showed higher concentrations in the dry season, while lower concentrations in the rainy season, indicating that the dilution effect was the main reason for the change. However, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and conductivity of Dengzhanhe spring were remarkably higher than those of Chenqi spring with factors of 1.4, 3.3, 2.0 and 1.4 respectively (Table 1), which is possibly due to the dissolution of more gypsum and dolomite minerals in the strata of Dengzhanhe spring catchment as stated above. Contrasting with the change of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and conductivity,  $\text{NO}_3^-$  showed higher concentration in the rainy season, while lower concentration in the dry season, indicating that

the agricultural pollution from nitrogenous fertilizer use mainly in summer rainy growing season was the main reason for the change.

##### 4.1.2. Continuous hydrochemical variations

Continuous data of water temperature, pH, EC, calculated  $\text{CO}_2$  partial pressure ( $\text{pCO}_2$ ) and calcite saturation index ( $\text{SI}_c$ ) have been obtained from the paired catchments at a 15-min interval from September 1, 2007 to September 1, 2008. Remarkable seasonal changes were found, where  $\text{pCO}_2$  showed in-phase change with temperature, while pH and  $\text{SI}_c$  show inverse change with temperature at Chenqi and Dengzhanhe karst springs (Fig. 4).

All these indicate the influence of seasonal climate change on the vegetation growth and biological activity in soil, which controls the production of soil  $\text{CO}_2$  and the intensity of karst processes (Liu et al., 2004, 2007). However, the remarkable difference between Chenqi and Dengzhanhe springs was the magnitude in  $\text{pCO}_2$ , pH,  $\text{SI}_c$  (Figs. 4 and 5) and  $\text{HCO}_3^-$  concentration. The higher  $\text{pCO}_2$  (2.39-fold) and  $\text{HCO}_3^-$  concentration (1.1-fold) and lower pH (0.33 lower) and  $\text{SI}_c$  (0.29 lower) in Chenqi karst spring than those in Dengzhanhe spring (Table 1) tend to be related to the difference

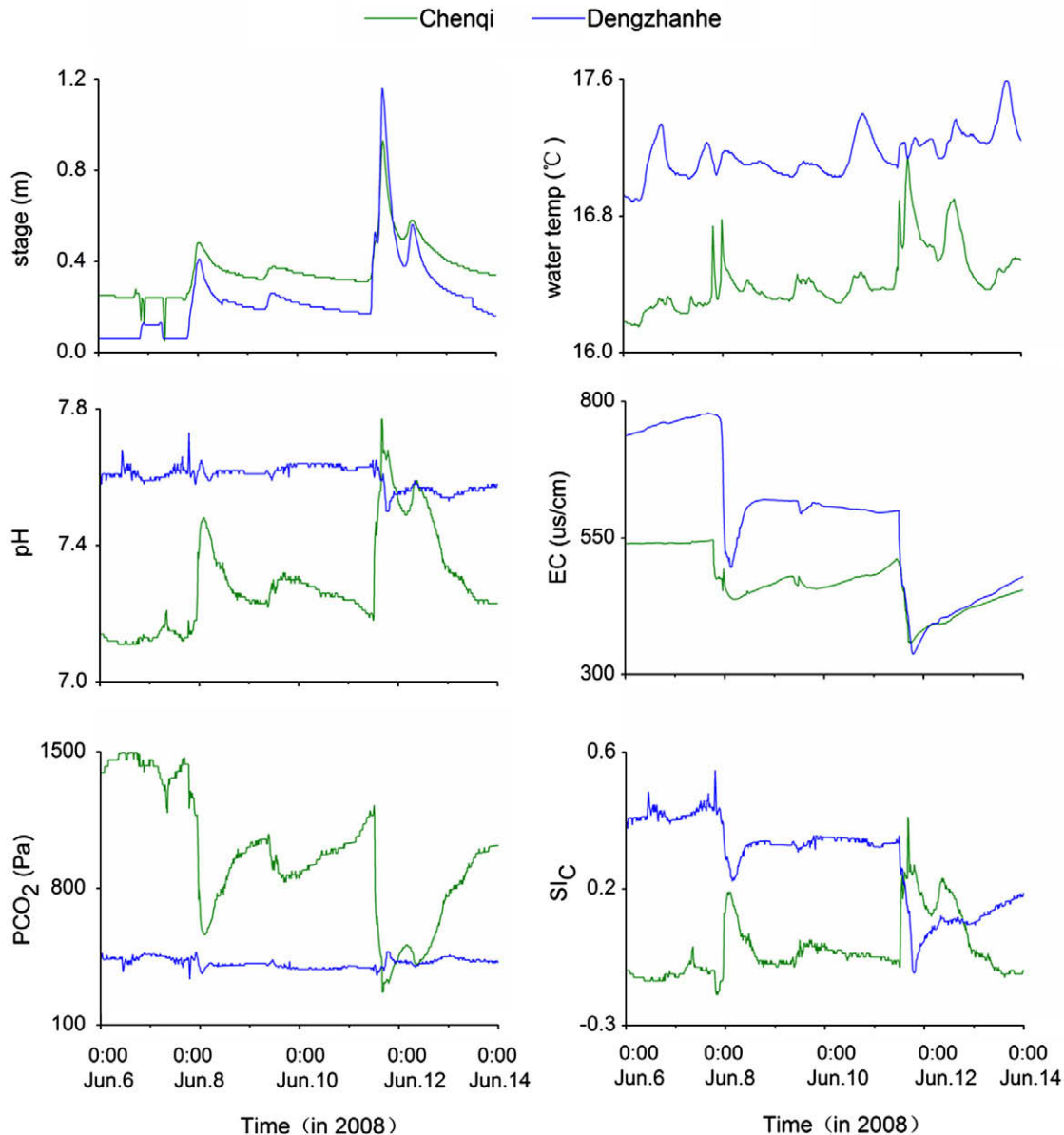


Fig. 5. Comparison of storm-scale hydrochemical variations during June 6–14, 2008 between Chenqi spring and Dengzhanhe spring.

in LULC between Chenqi and Dengzhanhe spring catchments: in the Chenqi spring catchment, there was larger (>10%) soil cover and the paddy land was located in the discharge area, both of which produced and kept more  $\text{CO}_2$  (a major driving agent for the karst processes) in the soil-aquifer system, while in the Dengzhanhe spring catchment area, there was less soil cover/larger bare carbonate rock occurrence and the paddy land was located mainly in the recharge area, the latter contributing to the  $\text{CO}_2$  release from water.

On the other hand, Figs. 4 and 5 also suggested that dilution effect on conductivity happened after rainfall (Liu et al., 2004, 2007). However, the pH increased and  $\text{pCO}_2$  decreased in Chenqi spring after rainfall, possibly due to more carbonate dissolution in the larger soil cover rich in limestone fragments in the spring catchment, while the pH decreased and  $\text{pCO}_2$  increased in Dengzhanhe spring after rainfall.

All the differences above show that soil cover played an important role in the karst processes. In other words, the karst hydrogeochemistry could be regulated effectively by different LULC.

#### 4.2. Variation of $\delta^{13}\text{C}_{\text{DIC}}$ values

Fig. 8 shows the variations of the carbon isotopic compositions of the dissolved inorganic carbon (DIC) in Chenqi and Dengzhanhe springs. It can be seen that both springs show similar seasonal variations in  $\delta^{13}\text{C}_{\text{DIC}}$ , i.e., in winter dry season, the DIC becomes enriched in  $^{13}\text{C}$ , while  $\delta^{13}\text{C}_{\text{DIC}}$  becomes more negative in summer rainy season. This reflected the influence of seasonal climate change on the vegetation growth and biological activity in soil, which controls the production and carbon isotope of soil  $\text{CO}_2$  (Reardon et al., 1979). However,  $\delta^{13}\text{C}$  of DIC changed from  $-11.57\text{‰}$  (ranging from  $-12.75\text{‰}$  to  $-10.21\text{‰}$ ) in rainy summer season to  $-10.59\text{‰}$  ( $-11.62\text{‰}$  to  $-9.85\text{‰}$ ) in dry winter season for Chenqi spring and it changed from  $-10.91\text{‰}$  (ranging from  $-11.56\text{‰}$  to  $-9.49\text{‰}$ ) in rainy summer season to  $-8.67\text{‰}$  (ranging from  $-9.31\text{‰}$  to  $-8.05\text{‰}$ ) in dry winter season for Dengzhanhe spring. The lower and more stable  $\delta^{13}\text{C}_{\text{DIC}}$  of Chenqi spring than Dengzhanhe spring (Fig. 8) was also possibly related to the difference in LULC between Chenqi and Dengzhanhe spring catchments

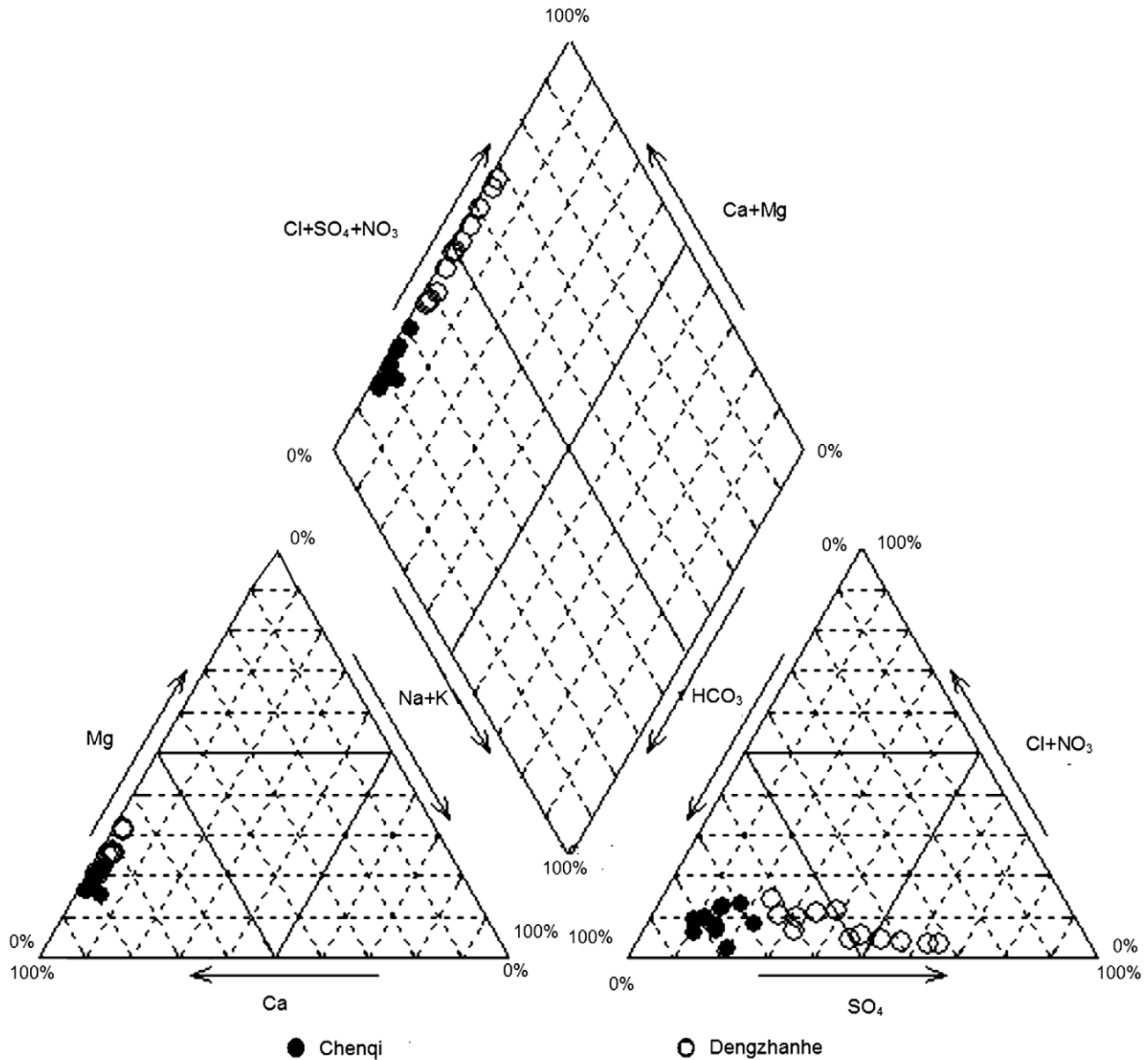


Fig. 6. Piper diagram showing the chemical compositions and types of water for Chenqi and Dengzhanhe springs.

as stated before, i.e., the larger soil cover and distribution of the paddy land in the discharge area in the Chenqi spring catchment produced and kept more  $\text{CO}_2$  and lower  $\delta^{13}\text{C}$  values in the soil-aquifer system, while in the Dengzhanhe spring catchment area, there was less soil cover and the paddy land was located mainly in the recharge area, both of which contributed to the release of  $\text{CO}_2$  with lighter carbon from water.

Because  $\delta^{13}\text{C}$  values are quite different in various carbon pools, it is very useful to trace the source and evolution of carbon in groundwater by carbon isotope (Friz et al., 1989). The sources of groundwater DIC include atmosphere  $\text{CO}_2$ , soil  $\text{CO}_2$  derived from soil respiration and decay of organic carbon, and the dissolution of carbonate rocks. The atmosphere  $\text{CO}_2$  is absorbed by rain and then infiltrated to the groundwater. A great quantity of  $\text{CO}_2$  generated by the decay of organic carbon and plant root respiration enters into groundwater system and reacts with water to form carbonic acid. The carbonic acid will interact with carbonate min-

eral and further form bicarbonate. Therefore, there might be a kind of relationship between  $\delta^{13}\text{C}_{\text{DIC}}$  and DIC (Rightmire and Hanshaw, 1973). This has been shown in Fig. 9. What is more interesting is the difference in the sign of relation coefficients between the two springs: the relationship between the  $\delta^{13}\text{C}_{\text{DIC}}$  and DIC for Chenqi spring was negative though the coefficient was only 0.2, while it was positive for Dengzhanhe spring. The reason for this difference might be explained by the difference in soil  $\text{CO}_2$  and dilution effects (Liu et al., 2007) between the paired catchments. Due to the difference in soil cover and land use pattern as stated before, soil  $\text{CO}_2$  effect dominated dilution effect in Chenqi catchment, while dilution effect dominated soil  $\text{CO}_2$  effect in Dengzhanhe catchment, which resulted in the higher DIC concentration in Chenqi catchment and lower DIC concentration in Dengzhanhe catchment in summer rainy season. However, on the other hand, the  $\delta^{13}\text{C}_{\text{DIC}}$  value depended on only soil  $\text{CO}_2$  effect in the open system of karst according to Deines et al. (1974). Therefore, the sign of relation



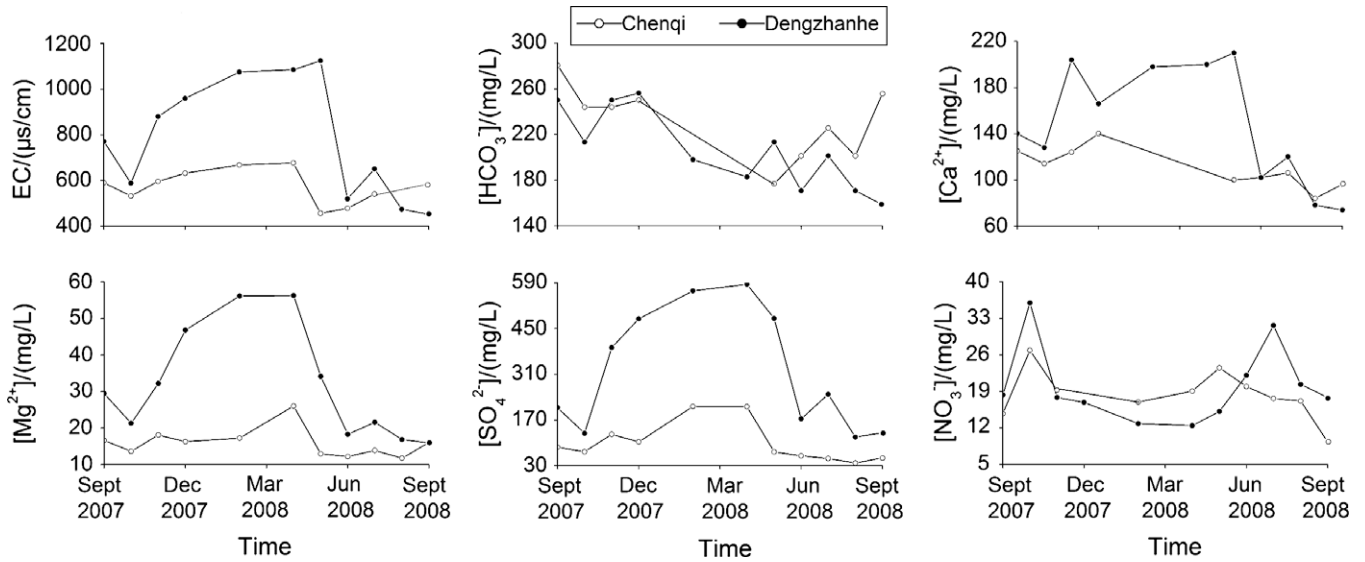


Fig. 7. Comparison of major ions variations between Chenqi and Dengzhanhe springs during the hydrological year period of 2007–2008.

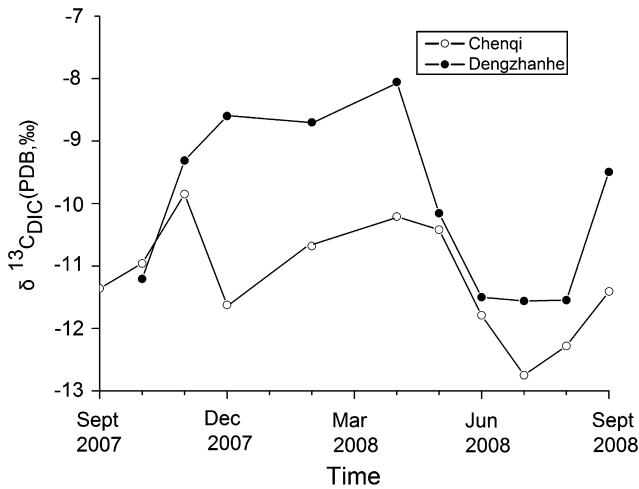


Fig. 8. Comparison of seasonal variations of  $\delta^{13}\text{C}_{\text{DIC}}$  between Chenqi and Dengzhanhe springs during the hydrological year period of 2007–2008.

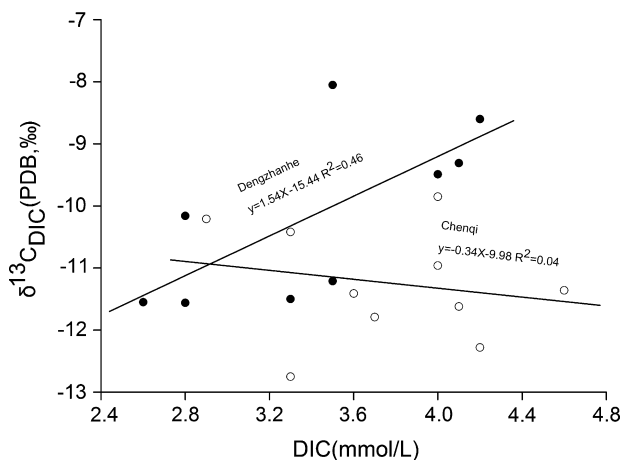


Fig. 9. Comparison of relationship between  $\delta^{13}\text{C}_{\text{DIC}}$  and DIC between Chenqi and Dengzhanhe springs.

coefficient between the  $\delta^{13}\text{C}_{\text{DIC}}$  and DIC for the two springs was just opposite. However, for further explanation more data are needed for future work.

### 5. Conclusions

The present study provides important information on the collection of continuous karst hydrochemical data and the hydrogeochemical response to different land use and land cover changes in the paired karst spring catchments of Chenqi and Dengzhanhe at Puding, Guizhou Province, SW China during the hydrological year of September 2007–September 2008. Marked seasonal and storm-scale variations are observed for pH, conductivity,  $\text{CO}_2$  partial pressures and calcite saturation indexes of the two springs. These findings indicated that both the two springs are dynamic and variable systems.

However, there were differences in the magnitude and direction of the variations of these features between the two springs.

The higher  $\text{pCO}_2$  and  $\text{HCO}_3^-$  concentration and lower pH,  $\text{SI}_c$  and  $\delta^{13}\text{C}$  in Chenqi spring than those in Dengzhanhe spring tend to be related to the difference in LULC between Chenqi and Dengzhanhe spring catchments: in the Chenqi spring catchment, there was larger (>10%) soil cover and the paddy land was located in the discharge area, both of which produced and kept more  $\text{CO}_2$  (a major driving agent for the karst processes) and lower  $\delta^{13}\text{C}$  in the soil-aquifer system, while in the Dengzhanhe spring catchment area, there was larger bare carbonate rock occurrence and the paddy land was located mainly in the recharge area.

Moreover, the pH increased and  $\text{pCO}_2$  decreased generally in Chenqi spring after rainfall, possibly due to more carbonate dissolution in the larger soil cover rich in limestone fragments in the spring catchment, while the pH decreased and  $\text{pCO}_2$  increased generally in Dengzhanhe spring after rainfall.

All these differences show that soil cover and land use pattern play important roles in the karst processes. In other words, the karst hydrogeochemistry and the karst-related carbon cycle could be regulated effectively by different LULC.

In addition, the higher concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and conductivity of Dengzhanhe spring were due to the dissolution of more gypsum and dolomite minerals in the strata of Dengzhanhe spring catchment. Therefore, the karst hydrogeochemical parameters, including pH, conductivity,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{pCO}_2$ ,  $\text{SI}_c$ ,

and  $\delta^{13}\text{C}_{\text{DIC}}$ , could serve as good indicators of different LULC and the other environmental changes.

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