Environ Geol (2007) 53:533–541
DOI 10.1007/s00254-007-0665-2

ORIGINAL ARTICLE

Major ions in typical subterranean rivers and their anthropogenic impacts in southwest karst areas, China

Fang Guo · Guanghui Jiang · Daoxian Yuan

Received: 12 June 2006 / Accepted: 29 January 2007 / Published online: 21 February 2007

Abstract Subterranean rivers contain much of the groundwater in karst and supply many local people in southwest China. The quality of groundwater in subterranean rivers is of concern because of its sensitivity to anthropogenic activity. Groundwater samples in a rural catchment were collected at the discharge point, and the concentrations of major ions including potassium, sodium, calcium, magnesium, chloride, sulfate, nitrate and bicarbonate were analyzed in this study. Rainfall and discharge were also observed at the same time. It could be concluded from the data that the concentrations of sulfate and nitrate had a peak in the rainy season when the concentrations of sodium, calcium, magnesium and bicarbonate were low. The concentrations of potassium and chloride changed randomly throughout the year. The concentration of major ions in flood process was not completely controlled by discharge. Only the concentrations of nitrate and sulfate had obviously increased during the past two decades. It was believed that dilution, eluviation, karst erosion and anthropogenic activity can explain the ion variations and hence this study helps to understand environmental problem in karst.

Keywords Karst · Subterranean river · Land use · Ions concentrations · Rainfall

F. Guo (✉) · G. Jiang · D. Yuan
Karst Dynamics Laboratory,
Institute of Karst Geology, MLR,
50 Qixing Road, Guilin 541004, China
e-mail: gfkarst@126.com

F. Guo
College of Geographical Sciences,
Southwest University, Beibei,
Chongqing 400715, China

G. Jiang
Department of earth Sciences,
Nanjing University,
22 Hankou Road, Nanjing 210093, China
e-mail: bmnxz@126.com

Introduction

Karst groundwater is becoming an increasingly important resource in many countries, including China, and currently karst aquifers contribute 25% of world-wide water supply (Kollarits et al. 2006). Karst aquifers in SW China are mainly distributed in mountainous areas including Guizhou, Guangxi, Yunnan, Hunan, Guangdong, Hubei, Sichuan Province and Chongqing. Karst covers an area of about 7.8 million km^2, with a population of 80 million. It has been found that only in Guangxi there are 3066 subterranean rivers with an annual natural water resource of about 18.08 billion m^3. There are 435 subterranean rivers and 736 karst springs with a discharge of more than 100 l/s, and the total discharge is 191 m^3/s in dry season (Yuan et al. 1991).

However in the past two decades, groundwater pollution has gradually become more of a problem, due to disposal of domestic waste from urban areas and a combination of solid, water and air pollution from industry, mining/quarrying, and over-use of pesticides and fertilizers in agricultural activities, which has endangered the safety of drinking water.

Many studies on karst water quality have been done in China. Most of them are for urban areas which suffer from industrial activities, waste water disposal, mining or quarrying. These study areas include Shuicheng basin (Yao et al. 2002), Liupanshui (Jia and Yuan 2003), Anshun city, Guizou Province and Xuzhou, Jiangshu Province. Some researchers study the variation of water quality with respect to the change of land use, showing there is some relationship between temporal or spatial variation of water quality and land-use (Jia et al.2004; Zhang and Yuan 2004; Jiang et al.2004; Gülbahar and Elhatip 2005). But little work on water pollution due to agriculture activities has so far been done in rural areas of China. In other countries, many studies indicate that the major ions or other chemical characteristics of groundwater are influenced by human activities directly or indirectly (Abu et al. 2004; Katz 2004; Frumkin 1999). In recent years, people attach more importance to the relationship between agriculture and karst, but most of them study the relation between agriculture and karst form, environment, water resources and water quality in a macroscopical view.

Groundwater quality is good as a whole in SW China, in most cases belonging to the first and second grades of national standard. But when compared with ionic concentrations of 20 years ago (background level), the concentration of major ions has demonstrably increased, showing that groundwater quality has a tendency to deteriorate (Guo et al. 2002). In order to explore the mechanisms of change of ionic concentrations, long-term monitoring (monthly or hourly) for subterranean rivers is carried out in the Guancun subterranean river. Furthermore hydrogeological surveys have been carried out from the late 1970s to the early 1980s, from which we have acquired the data of water quality in main groundwater outlets. In the current land and resources survey, the trend of variation of water quality in the past two decades can be obtained to compare with these baseline data.

Study area

Location and climate

Guancun subterranean river lies in Daliang, Rong'an County, 60 km from Liuzhou city (Fig. 1). The area of the catchment is 30.5 km^2, located between 109°19′56″ and 109°23′44″ E, and 24°51′6″ and 24°56′29″ N. The annual average temperature is 20°C, and the annual average rainfall is 1,750 mm. In the dry season (from September to February), rainfall only accounts for 11% of the annual total, and the rest occurs from March to August, with a maximum in May and June.

Physiographic features and hydrogeological set-up

The topography is high in the northeast and northwest with the highest of 770 m, and low in south with the lowest of 160 m. The relief is of the fengcong type (peak-cluster) with depressions represented large dolines. The underground river is developed in Rongxian Formation carbonate (D_3r, upper Devonian), which turns to surface river somewhere. Surface rivers are intermittent, only filling with water during the rainy season (Fig. 2). The depth of the water level in karst windows during the dry season ranges from 8 to 12 m, and in flood processes the water rises above the ground surface in some depressions. Rainfall is the only recharge source for groundwater in the catchment area. Seasonal fluctuation in water level corresponds to rainfall, and usually the flood decline process takes a period of about 1 week.

Land use or cover

The bottom of the depressions in the catchment are flat, productive lands. The styles of land use are paddy field, dry land, pasture and resident. The infield area is 76 ha, accounting for only 2% of the total area only. Paddy fields are 58.13 ha, accounting for 76.5% of the infield. The dry land plants are sugar cane, corn or vegetable.

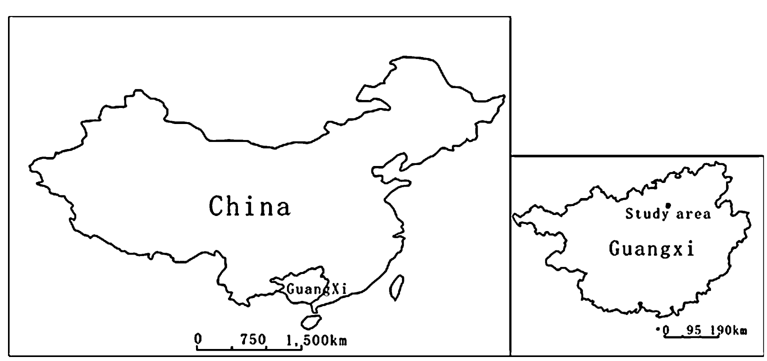

Fig. 1 Location of the study area

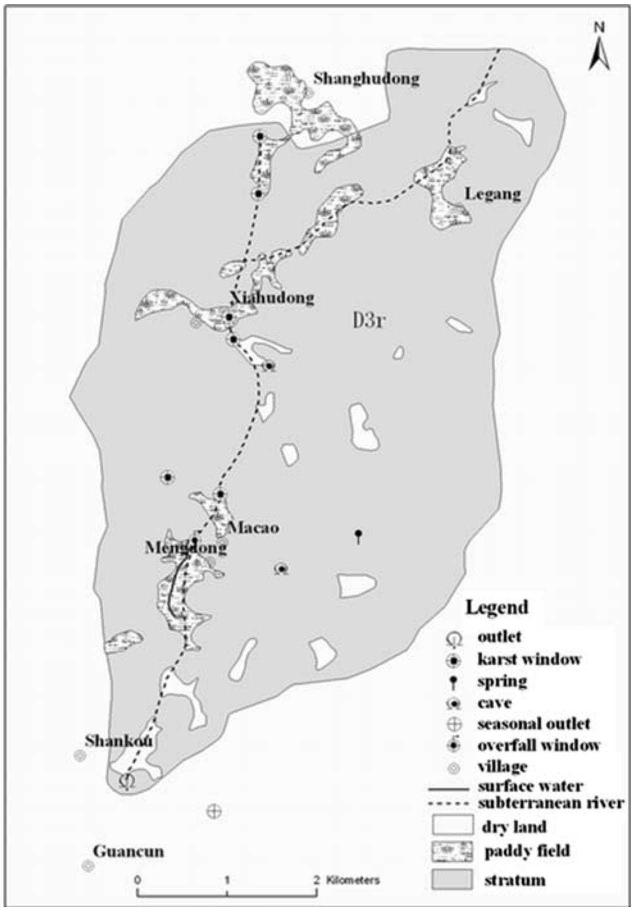

Fig. 2 Hydrogeological sketch of Guancun subterranean river catchment

Agriculture activities have a close relationship with the climate. In the catchment, farmers often fertilize dry land in February in order to plant sugar cane. The amount of compound fertilizer (K_2SO_4 included) used for the paddy field is 373–597 kg/ha before cultivating in early May. After 1 week, farmers add 5–10 kg carbamide, and after 2 weeks 5 kg more of carbamide and 7.5 kg of potassium fertilizer (KCl). Fertilizer is rarely used from then on and how much is determined by the growth of the crop. After harvest in August, most of the cropland is left undisturbed, except that some of them are planted with corn and vegetables.

There is a total population of 653 in the catchment area, but actually one-third of population is working away and they come back to their habitations only rarely. The population is less than in the 1980s.

Materials and methods

Guancun subterranean river was selected for the study. An automated instrument (CDTP300) produced by Greenspan Co. Australia was used to auto-monitor water level, water temperature, pH, electrical conductivity and precipitation at the outlet of the subterranean river (once per 15 min) during the sample collection period. From Jun 2004, measurements of pH, EC, water temperature were made in the field using a pH/Cond 340i WTW Meter; Ca^{2+} and HCO_3^- were measured using portable testing box in situ monthly. The discharge was measured at a gauging station using a rectangle weir about 100 m away from the outlet. Water samples were collected monthly from June 2004 to October 2006 for determining the concentration of K, Na, Ca, Mg, Cl, SO_4, NO_3, NO_2 and NH_4 in the laboratory of Institute of Karst Geology, China. The two floods in May and June-July 2005 were sampled between one and four times per day. In the first flood ten samples were obtained within 4 days, and 31 samples within 17 days in the second flood. One to three groundwater samples were collected per day for determining nitrate from April to October 2006. Water chemistry data of 1978 and 1980 was collected from the Liuzhou Hydrogeology Team. Land use and human activity in the catchment area were surveyed seasonally.

Results

The component of groundwater

The groundwater in the study area was of Ca-HCO_3 type. Among the major ions, Ca and HCO_3 were the dominant component, and Mg, Na, K, Cl, SO_4 and NO_3 were of secondary abundance, other components being present at much lower concentration. Ca, HCO_3 and Mg were mostly derived from rock weathering, so all factors that affect karst erosion would have an impact on the concentration of these ions. The concentrations of K, Na, Cl, SO_4 and NO_3 in the rock were less than those in water and soil, while they were equal in soil and groundwater, showing that they mostly came from soil.

Change of ionic concentration in flood process

The analysis below is based on Figs. 3, 4, 7, and 8. The first observed flood occurred just after a period of fertilizer application in paddy fields. Even though it rained frequently and water level fluctuated considerably, K concentrations did not have a continuous decrease, but sometimes ascended. The high water level did not correspond with low concentrations of K. Following the decline of water level in June, K concentration decreased. The lowest concentration of K

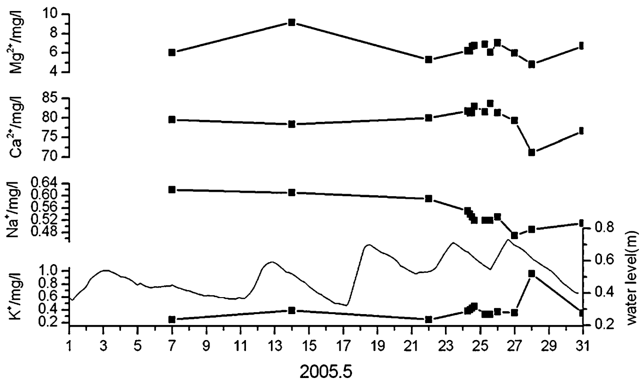

Fig. 3 Variation of cation concentrations in flood process, May 2005

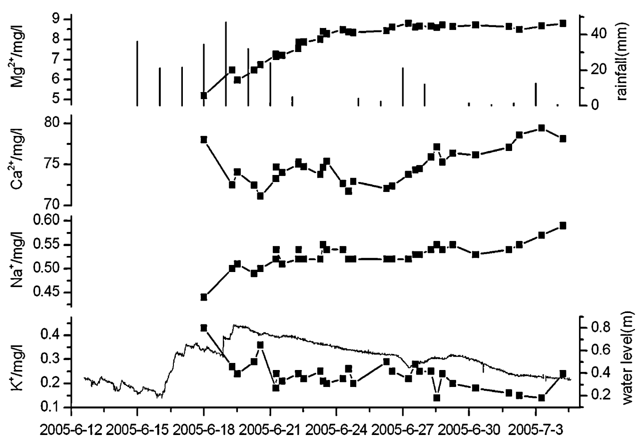

Fig. 4 Variation of cation concentrations during floods, June-July 2005

was 0.14 mg/l, while K concentration of rainwater in June was 0.19 mg/l, indicating that K had been diluted completely. It also indicated that K was an active cation and would not reside in soil for a long time.

Na was also sensitive to rain. Rainfall in May did not result in a change of Na concentration at the beginning, but rainfall from late May to June led to rapid decreases in Na concentration. Na concentration increased at the end of the monitoring, a pattern that is more like rock-derived ions. This may be explained by that fissure water with higher Na concentration discharging after conduit water, so Na concentration increased as conduit water ended and fissure water entered the river. The variation of K and Na in the May flood could not be explained by dilution or karst erosion and so is likely to relate to application of fertilizers in April.

The concentration of calcium declined after a slight rise in the first observed flood, but then it ascended. In the second rainstorm the concentration of calcium first decreased and then increased at the end. This was attributed to dilution and $CaCO_3$ dissolution (karst erosion). The variation of Mg concentration was similar to Ca because both of them were derived from karst erosion. However, the concentration of Mg was lower than that of Ca, as a result Mg derived from soil was also important to the variation of its concentration. Mg concentration increased gradually in June, while Ca concentration decreased briefly during the increase.

The analysis below is based on Figs. 5, 6, 7 and 8. The concentration of Cl was unstable in May, but it became constant during rainstorms in June. The change from unsteadiness to steady indicated that Cl may be affected by fertilization. Fertilizer transferred to the subterranean river when it rained, making for fluctuations in Cl concentration. The Cl concentration in soil approached the normal level in June, so the concentration did not continue to fluctuate. The concentration of SO_4 increased after fertilization, showing that fertilizer may also have a great impact on it. When it rained in June, rapid recharge induced a SO_4 decrease; however SO_4 concentration reached a high level again soon. The variation of HCO_3 concentration was similar to Ca. Because HCO_3 and Ca were both derived from carbonate rock, they had a close relationship with karst erosion. The concentration of NO_3 had a tendency to fall from May to June because of dilution by several big rainfalls. Nitrate fluctuated during the flood process in late May, however it kept steady in late June. This was very similar to Cl and may be explained by both of them being greatly affected by fertilizer input.

The main facts controlling variation of concentration were rainfall and human activity. Of course, apart from fertilizers, soil erosion also could lead to concentration increases, which is related to the intensity of rainfall and vegetation. Sloping fields in the catchment area gave priority to forest cover in the 1970s. From the 1980s people cut firewood for charcoal gradually for business resulting in reduction of forest. From the 1990s a large scale of grazing and calcite mining intensified the degradation of vegetation.

Fertilizer was poured into the catchment area from February to May, which included N (in the form of NO_3 due to nitrification process), P (PO_4), K, Cl and S (SO_4). These contaminations entered the subterranean river along with rainwater. After moving through conduits they were discharged by the outlet. The concentration of major ions had their own patterns of variation. Observation in the two flood events showed that (1) K and Cl increased in May, while they continuously declined in June; (2) SO_4 did not decrease in the flood of May and still kept a high concentration in the flood of June; (3) NO_3 did not decrease greatly

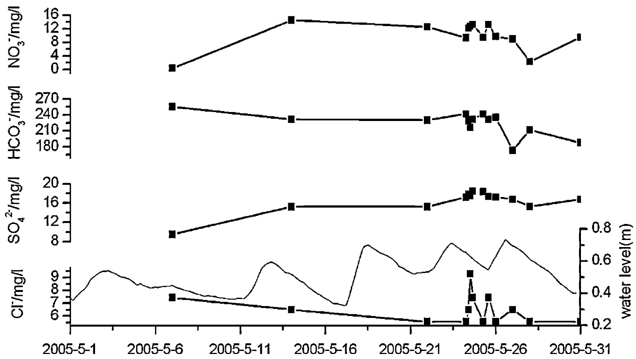

Fig. 5 Anion concentrations variation and water level in May, 2005

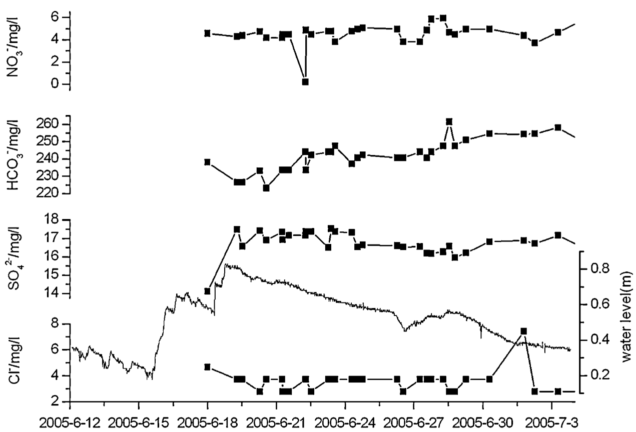

Fig. 6 Anion concentrations variations and water level in June-July, 2005

in the May flood. These phenomena could be explained by application of fertilizers in April. Correlation coefficient calculations for the eight ions showed that the highest relative degree was Mg–HCO_3 ($R^2 = 0.5214$), second was K–SO_4 ($R^2 = 0.2654$), and K–Cl ($R^2 = 0.1358$) was also higher compared with the rest ions. All of these facts indicated that K, NO_3, SO_4 and Cl in the subterranean river were likely derived from fertilizer.

The change of ion concentrations monthly and during the past two decades

The two former samples were collected in April 14, 1978 and May 28, 1980. The current data was compared with the previous data, indicating some of the ions had increased, whilst some had no change. The lowest concentration of K was 0.14 mg/l appearing during a flood process in July, and the highest was 1.2 mg/l, with the average of 0.36 mg/l. The concentration of potassium was close to the average in most of the period, except several very high points appearing in Nov 2004, May and Oct 2005, and Jan and Feb 2006. The data in 1978 and 1980 were within the range of variation (Fig. 9).

Sodium varied in the range of 0.36–1.52 mg/l, with an average of 0.64 mg/l. The concentration of sodium was low in rainy season and high in dry season. The value in 1978 and 1980 were in the current range (Fig. 10).

The range of calcium and bicarbonate were 71.1–90.0 mg/l, 173.9–289.0 mg/l respectively, with the average of 77.7 mg/l and 243.0 mg/l. The patterns of seasonal change about these ions were similar to sodium (Figs. 11, 16). High concentration of Mg occurred in the dry season and low concentrations in the rainy season, with the range and average of 4.81–14.4 mg/l and 8.23 mg/l, respectively. The baseline data were within the range of variation values (Fig. 12).

The low value of Cl appeared after rainfall in Jul 2005 and in Jan 2006, while the high value was in March and May 2005 with the range of 2.34–9.29 mg/l and average of 4.60 mg/l. Although the concentration in 1978 was within the current range, its concentration of 1980 was much lower than the current lowest value (Fig. 13).

The concentration of sulfate in the rainy season was higher than that in the dry season, with the range of 3.90–20.5 mg/l and the average 14.5 mg/l. The concentration in 1980 was below the current range. Its concentration in 1978 was lower than that in Apr 2005 and 2006, though it was within the current range. So the concentration of sulfate has increased (Fig. 14).

Several points had much lower concentration of nitrate than their neighbors, while the shortest sampling interval between them was only half an hour. Ignoring these outliers, nitrate concentration ranged from 2.56 to 15.4 mg/l with an average of 6.60 mg/l. The values in 1978 and 1980 were much lower than the current value, especially than the concentration in the rainy season, showing that NO_3 increased (Fig. 15).

In summary, it could be concluded that the concentrations of nitrate and sulfate had obviously increased, and the rest six ions had no evident increase. Three facts were considered to be responsible for the change: (1) The change in fertilizer. In the former period only organic manure made of excrement was used in the fields, and now the fertilizer was popular; (2) Increase in the amount of livestock. The number of goats in the catchment had reached 3000, with a result of great manure spreading in pasture; (3) Reduction in vegetation and soil erosion. The vegetation was the only source of energy before use of firedamp. Soil erosion accelerated on the slopes without the protection of vegetation.

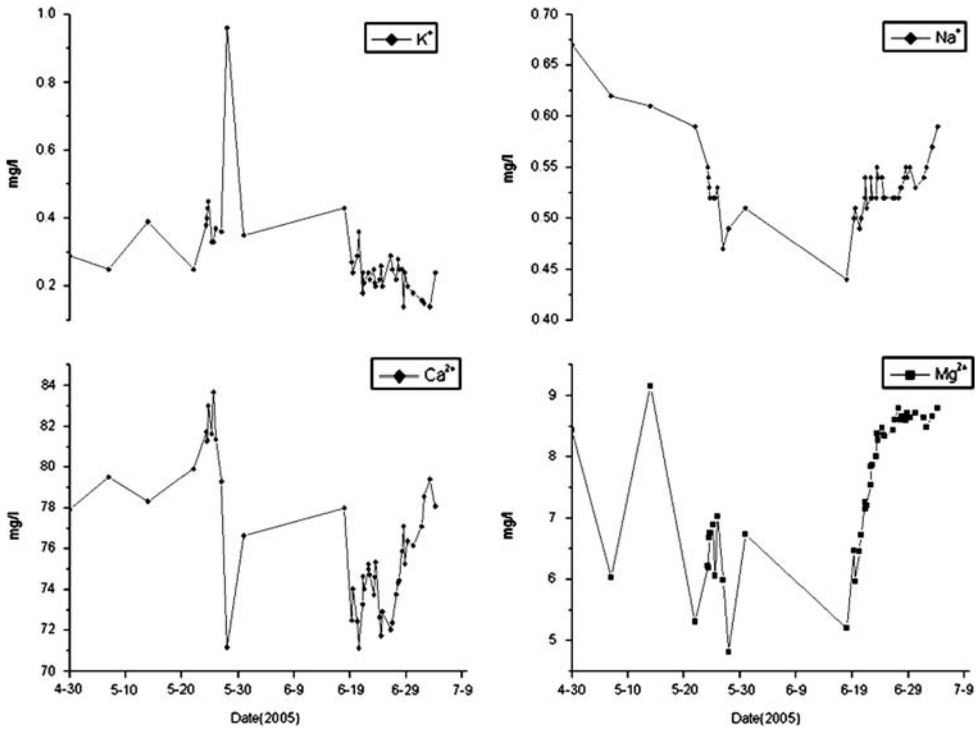

Fig. 7 Variations in cation concentration affected by recharge of rainfall after fertilization

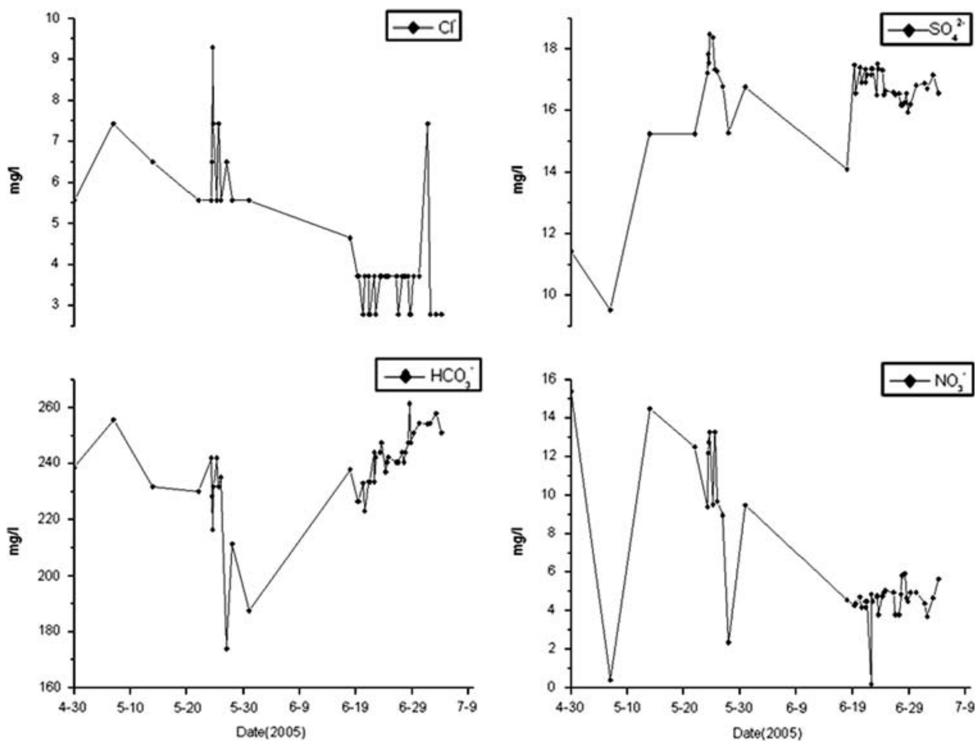

Fig. 8 Variation in anion concentration affected by recharge of rainfall after fertilization

Discussion

Concentrations of major ions in the subterranean river were affected both by the seasonal climatic cycle and by human activity; rainfall was the most important factor. Precipitation recharge led to changes of ionic concentration; the type of variation that occurred was determined by the processes of dilution, karst erosion and eluviation. Dilution reduced concentrations, whilst karst erosion caused increases for calcium, magnesium

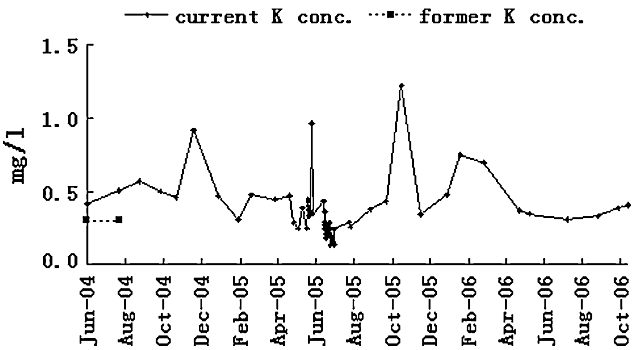

Fig. 9 Variation of K concentration compared with the former data

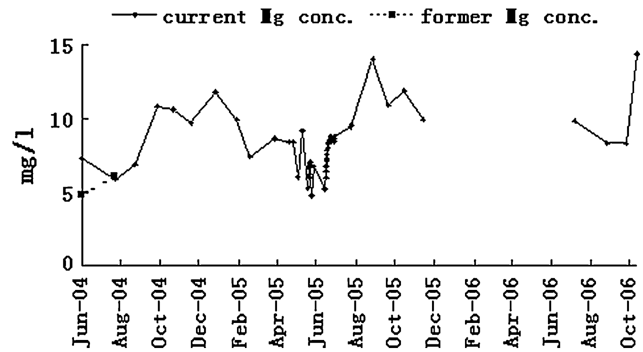

Fig. 12 Variation of Mg concentration compared with the former data

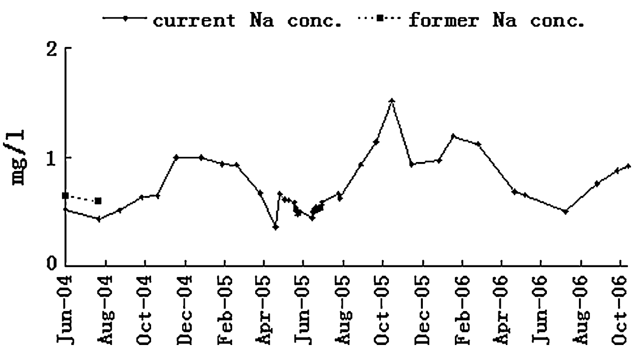

Fig. 10 Variation of Na concentration compared with the former data

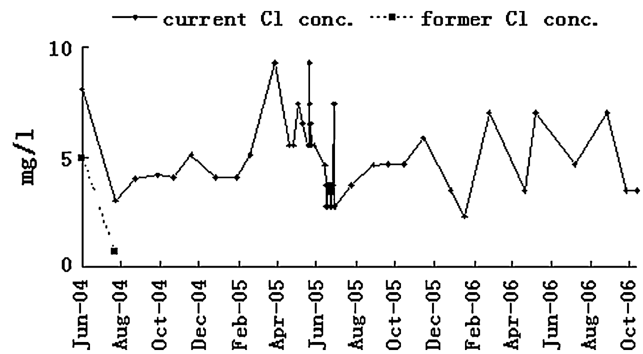

Fig. 13 Variation of Cl concentration compared with the former data

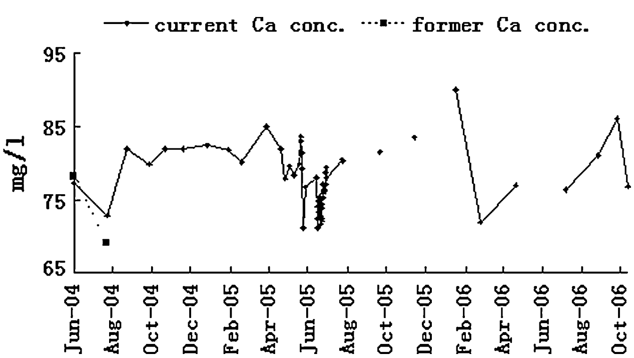

Fig. 11 Variation of Ca concentration compared with the former data

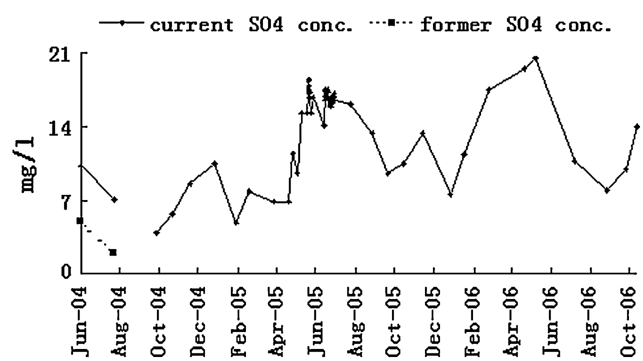

Fig. 14 Variation of SO_4 concentration compared with the former data

and bicarbonate, and the eluviation from soil led to increases in many ions including calcium, magnesium, sodium and potassium.

The ions accumulated in soil during the dry season. Fertilizer was used mostly in April and May, which led to sharp increases in soil ion concentrations. Ions in soil moved into the aquifer with rainwater when it rained. As a result, the concentrations of nitrate and sulfate increased correspondingly (Figs. 14, 17). So fertilization was attributed to the peaks of their concentrations. The concentrations attained their former values after repeated washing by rainfall.

The saturation index of calcite in the dry season was higher than that in the rainy season, for the concentrations of HCO_3, Mg and Ca were high and low correspondingly (Fig. 18). The proportions of the total of Na^+ and K^+ in cations were high in the dry season and low in the rainy season since they were strongly leached by rainfall, and the anthropogenic influence was too limited to find. Their variations only reflected the

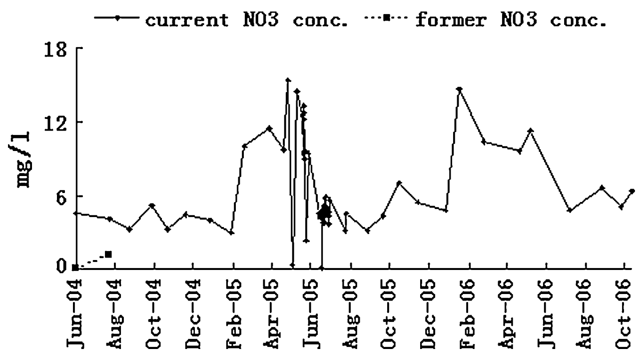

Fig. 15 Variation of NO_3 concentration compared with the former data

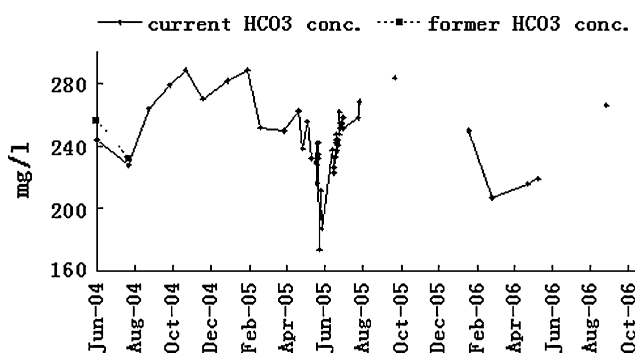

Fig. 16 Variation of HCO_3 concentration compared with the former data

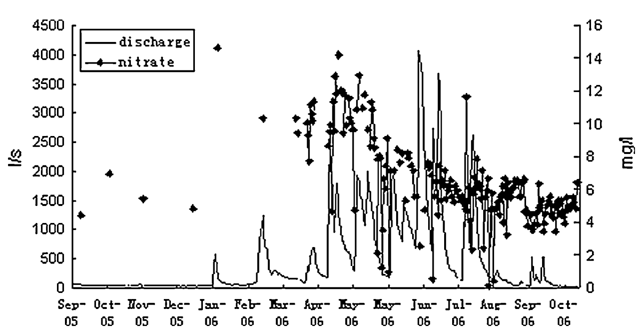

Fig. 17 The relation between discharge and variation of NO_3 concentration

mechanism of dilution. The variation of total proportion of Cl, SO_4 and NO_3 in anions closely corresponded with human activity (Figs. 19, 20).

The concentration of ions was a basic parameter for water quality. However it was difficult to compare current concentrations with the baseline values of 1978–1980 because the concentration of ions were variable through 1 year in karst aquifer and improved methods of comparison would be useful. The data presented in this paper should provide a useful point of comparison for study of new sites of discharge of karst conduit water.

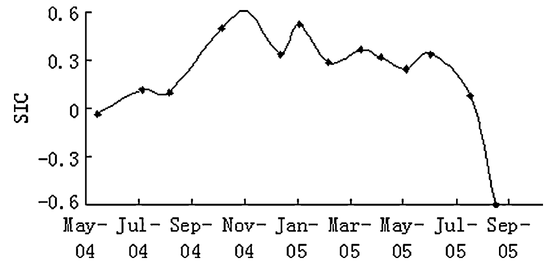

Fig. 18 Variation of calcite saturation index in 2004–2005

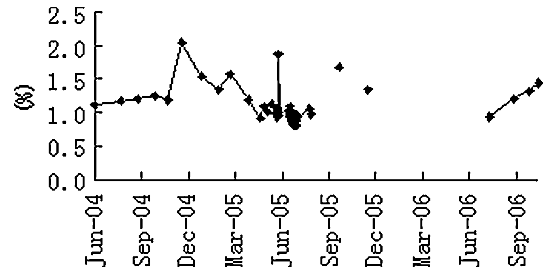

Fig. 19 Variation of (K + Na) proportion (%) in cations monthly

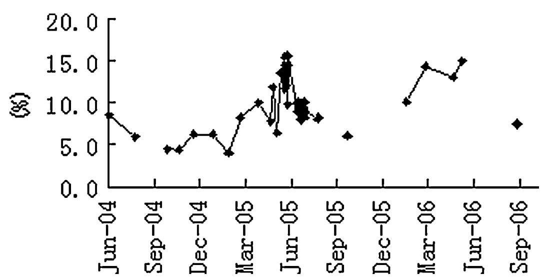

Fig. 20 Variation of (SO_4 + Cl + NO_3) proportion (%) in anions monthly

Conclusion

The variations of concentration on three kinds of time scale were discussed. (1) The variation of concentration was not completely controlled by the discharge in a flood. (2) The concentration variations of sodium, calcium, magnesium, sulfate, nitrate and bicarbonate corresponded to rainy and dry seasons, but the concentration variations of potassium and chloride did not. (3) Only the concentrations of sulfate and nitrate had increased obviously during the past two decades, and the concentrations of the rest six ions could not be judged.

Acknowledgments Financial support was provided by China Geological Survey: Groundwater and Environmental Geology Survey in Southwest Karst Areas (1212010340104) and Monitoring and Environmental Sensitivity Evaluation for Karst Groundwater (1212010634805). We would like to thank the reviewers who read the first draft of this paper for their constructive comments to further improve the manuscript. Thanks are also due to Professor Chris Groves, Ian J. Fairchild, Beth Medley and Jichun Wu for their help to polish the language of the paper and Prof. Yushi Lin, Mr. Jinliang Wang, Ms. Li Shu and Mr. Ke Li for their field assistance.

References

Abu Maila Y, EI-Nahal I, Al-Agha MR (2004) Seasonal variations and mechanisms of groundwater nitrate pollution in the Gaza Strip. Environ Geol 47(1):84–90

Frumkin A (1999) Interaction between karst, water and agriculture over the climatic gradient of Israel. Int J Speleol 28(1/4):99–100

Guo F, Jiang G, Pei J et al (2002) Assessment on the water qualities of major subterranean rivers in Guangxi and their changing trend (in Chinese). Carsologica Sinica 21(3):195–201

Gülbahar N, Elhatip H (2005) Estimation of environmental impacts on the water quality of the Tahtalidam watershed in Izmir, Turkey. Environ Geol 47(5):725–728

Jia Y, Yuan D (2003) The impact of landuse change on karst water in Shuicheng basin of Guizhou Province (in Chinese). ACTA Geographica Sinica 58(6):831–838

Jia Y, Diao Ch, Yuan D (2004) The influence of land use on karst water quality of buried karst region-A case of Conglin karst ridge-trough at Fuling Town (in Chinese). J Nat Res 19(4):455–461

Jiang Y, Yuan D, Zhang Gi et al (2004) Effects of landuse change on groundwater quality in karst watershed-A case study in Xiaojiang watershed in Yunnan Province (in Chinese). J Nat Res 19(6):707–715

Katz BG (2004) Sources of nitrate contamination and age of water in large karstic springs of Florida. Environ Geol 46(6–7):689–706

Kollarits S, Kusching G, Veselic M (2006) Decision support systems for groundwater protection: innovative tools for resource management. Environ Geol 49(6):840–848

Yao Ch, Yang G, Jiang Zh, Yuan D (2002) Human activities and their effects on geological environment in shuicheng basin, guizhou province (in Chinese). Urban Environ Urban Ecol 15(5):1–3

Yuan D, Zhu D, Weng J et al (1991) Karst of China. Geological Publishing House, Beijing pp 171

Zhang Ch, Yuan D (2004) Hydrochemical variation of typical karst subterranean stream basin and its relationship with landuse change-a case study of subterranean stream basin, puding county, guizhou province (in Chinese). J Soil Water Conserv 18(5):134–137