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ORIGINAL PAPER

Stable Carbon Isotope Biogeochemistry and Anthropogenic Impacts on Karst Ground Water, Zunyi, Southwest China

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Abstract Natural and anthropogenic impacts on karst ground water, Zunyi, Southwest China, are discussed using the stable isotope composition of dissolved inorganic carbon and particulate organic carbon, together with carbon species contents and water chemistry. The waters can be mainly characterized as HCO_3–Ca type, $HCO_3 \cdot SO_4$–Ca type, or $HCO_3 \cdot SO_4$–Ca · Mg type, according to mass balance considerations. It is found that the average $\delta^{13}C_{DIC}$ values of ground waters are higher in winter (low-flow season) than in summer (high-flow season). Lower contents of dissolved inorganic carbon (DIC) and lower values of $\delta^{13}C_{DIC}$ in summer than in winter, indicate that local rain events in summer and a longer residence time of water in winter play an important role in the evolution of ground water carbon in karst flow systems; therefore, soil CO_2 makes a larger contribution to the DIC in summer than in winter. The range of $\delta^{13}C_{DIC}$ values indicate that dissolved inorganic carbon is mainly controlled by the rate of carbonate dissolution. The concentrations of dissolved organic carbon and particulate organic carbon in most ground water samples are lower than 2.0 mg C L^{-1} and 0.5 mg C L^{-1}, respectively, but some waters have slightly higher contents of organic carbon. The waters with high organic carbon contents are generally located in the urban area where lower $\delta^{13}C_{DIC}$ values suggest that urbanization has had an effect on the ground water biogeochemistry and might threaten the water quality.

Keywords Stable carbon isotope · Ground water · Carbonate weathering · Anthropogenic impacts

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1 Introduction

The carbon flux in karst areas takes place from the atmosphere or soil to ground water as HCO_3^-, and is related to the dissolution of carbonate rocks and evolution of water quality. Concentrations and isotopic compositions of carbon species in water samples are often used in studies of carbon evolution and biogeochemistry (Clark and Fritz 1997; Cane and Clark 1999; Doctor et al. 2000; Lee and Krother 2001; Li et al. 2005; Rueedi et al. 2007). The carbon system in ground water can be influenced by CO_2 dissolved in the soil, oxidation of organic matter, and dissolution of atmospheric CO_2 as well as water–rock reactions. The carbonate system evolves during subsequent organic and inorganic reactions in soils and aquifers. Microorganisms play a key role in the degradation of organic compounds and evolution of redox conditions. Under oxic conditions, aerobes use dissolved O_2 as the terminal electron acceptor in the oxidation of organic materials to produce CO_2; under anaerobic conditions, some microorganisms can utilize alternative electron acceptors (such as NO_3^-, Fe^{3+}, and SO_4^{2-}) to produce CO_2 (Clark and Fritz 1997; Fang et al. 2000). Changes in the carbon system in ground water affected by natural and anthropogenic factors could be useful to improve the best management practices for local water quality. As rainwater or surface water seeps through unsaturated soil into ground water, its chemical composition can change drastically. Isotopic composition of dissolved inorganic carbon (DIC) can be used to distinguish the main sources of DIC and is a good tracer of carbonate evolution in ground water due to the characteristic isotopic signatures of different carbon reservoirs (Clark and Fritz 1997). Stable carbon isotope values are useful in understanding the evolution of carbon biogeochemistry and controlling factors in ground water systems when combined with other ground water chemical parameters.

Ground water is the most important water resource in karst areas of Southwest China, but water quality is threatened by high population and human activities. Assessing the risk of ground water contamination by anthropogenic activity has become increasingly important. This work focuses on the evolution of carbon biogeochemistry impacted by natural and anthropogenic factors in ground waters of Zunyi, Southwest China. Here we attempt to understand carbon variations in summer (the high-flow season) and winter (the low-flow season) using the contents of carbon species and carbon isotopes, together with water chemistry.

2 Material and Method

2.1 Site Description

The major region investigated here is located at the northeastern margin of the Yunnan-Guizhou Plateau, Southwest China (Fig. 1). The elevation of Zunyi is between 790 and 1300 m above mean sea level. The Zunyi prefecture contains diverse karstic landforms and abundant karst ground water sources. The main aquifers in the region contain homogenous carbonate rocks as well as carbonate units interbedded with clastic rocks. The strata exposed in Zunyi are mainly pre-Jurassic carbonates (limestone and dolomite), a few Jurassic clastic rocks outcrop in the center of urban area, while sulfate evaporite (gypsum) and coal seams occur locally. The carbonate rocks usually expose on the surface and soils are thin and discontinuous in the studied area. The climate is subtropical with an average temperature of 15 C and annual precipitation of about 1100 mm. The mean temperature is 24.1 C in summer and 5.5 C in winter, respectively. A monsoonal climate often results in

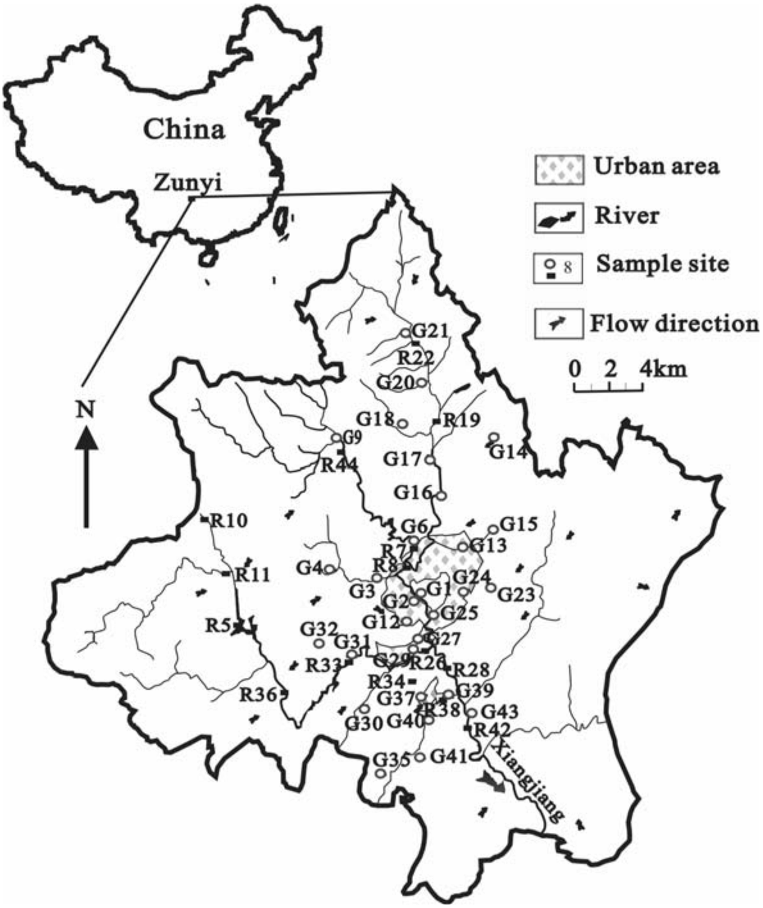


Fig. 1 Map showing the location of Zunyi and the sampling sites (G = groundwater, R = river water)

about 75% of annual precipitation during wet seasons (general from May. to Oct.) and much less during dry seasons, with about 5% of annual precipitation from Dec to Feb (Mao 1995; Han and Jin 1996).

2.2 Sampling and Analytical Methods

Water samples were collected in July and December of 2002, corresponding to the high-flow season (summer) and low-flow season (winter), respectively. The sampling sites for ground water and surface water are shown in Fig. 1. G15, G17, G39 are outlets of underground rivers. G1, G2, G13, G14 are boreholes with depth greater than 100 m. The rest of the samples are artesian wells or various types of spring. Temperature, electrical conductivity, pH values, and dissolved oxygen contents of the samples were measured on site. Alkalinity was measured by titration with HCl within 12 h. Major cations (Mg^{2+}, Ca^{2+}, K^{+}, and Na^{+}) were analyzed by atomic absorption spectrometry (AAS, PE51002, America) and the anions (SO_4^{2-}, Cl^{-}, and NO_3^{-}) by high performance liquid chromatography (HP1100, SHIMADZU, Japan).

The other water samples were filtered by pressure filtration through 0.45 μm cellulose–acetate filter paper and collected in polyethylene bottles with air-tight caps and preserved with $HgCl_2$ to prevent biological activity. The concentrations of dissolved organic carbon (DOC) were determined as CO_2 by catalytic combustion (Elementar high TOCII+N, German) after samples were acidified with HCl to remove all inorganic carbon. The typical precisions of major ions and DOC are about ±5%.

For determination of $\delta^{13}C$ and the concentrations of dissolved inorganic carbon, CO_2 was collected in the off-line vacuum system according to the method of Atekwana and Krishnamurthy (1998). Carbon isotope ratios of the DIC were determined on a Finnigan MAT 252 mass spectrometer. A portion of this water (200–2000 ml) was filtered through a pre-combusted Whatman GF/F filter (47 mm Ø) and the volume of the water recorded. The particulate inorganic carbon on the filter was removed by adding HCl. Particulate organic carbon (POC) contents (CO_2 yield) were measured on a vacuum line manometer after combustion of the glass filters with CuO and Cu at 850 (Tao et al. 2001). The carbon isotope values are reported using the δ notation relative to PDB in permil, where

$$\delta(\text{‰}) = ((R_{\text{sample}}/R_{\text{PDB}}) - 1) \times 1000 \tag{1}$$

Routine $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ measurements have an overall precision of 0.1‰, respectively. The isotopic standards of carbonate and IAEA-C3 (cellulose) were measured as a check on reproducibility.

3 Results

3.1 Major Chemical Composition of Waters and Carbonate Weathering

The mean values of temperature of ground water are 19.9 C in summer and 15.4 C in winter, respectively. The pH values of ground water range from 6.8 to 8.4 with a median value of 7.3 lower than local river water which has a median value of 8.0. Under the pH conditions observed, bicarbonate (HCO_3^-) is the dominant DIC species. The Ca^{2+} contents in ground waters vary from 0.73 to 4.29 mmol l^{-1}, with a mean value of 2.38 mmol l^{-1} in summer and 2.49 mmol l^{-1} in winter, respectively. The SO_4^{2-} contents in ground waters range from 0.02 mmol l^{-1} to 3.24 mmol l^{-1}, with a mean value of 1.15 mmol l^{-1}. Ca^{2+} and Mg^{2+} were the dominant cations and HCO_3^- and SO_4^{2-} the dominant anions in the ground water. The waters can be mainly characterized as a HCO_3–Ca type, $HCO_3 \cdot SO_4$–Ca type, or $HCO_3 \cdot SO_4$–Ca · Mg type according to mass balance considerations (Lang 2005), indicating extensive dissolution of carbonate rocks. The outcrops in the study area are mainly carbonate rocks (limestone and dolomite) of Triassic and Permian age, with a minor amount of clastic rocks. Coal-bearing formations are also widely distributed which are enriched in sulfide minerals; oxidation of sulfide minerals such as FeS_2 will contribute sulfate to the ground water. The contributions from carbonate weathering of the study area are mainly responsible for the major chemical characteristics.

3.2 Carbon Contents and Isotopic Composition

Alkalinity was assigned as HCO_3^- due to the range of pH values. The concentrations of HCO_3^- in summer and winter are in the range of 1.63–5.96 mmol l^{-1} and 1.62–6.58 mmol l^{-1} (Table 1), averaging 4.06 and 4.22 mmol l^{-1}, respectively. The concentrations of

Table 1 The contents and isotopic compositions of carbon in Zunyi, Southwest China

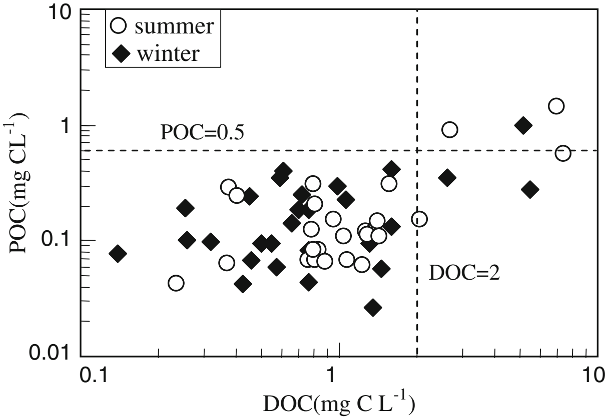
No.	pH		ALK (mmol l^{-1})		DOC (mg C l^{-1})		POC (mg C l^{-1})		δ^{13}C-DIC		δ^{13}C-POC	
	S[a]	W	S	W	S	W	S	W	S	W	S	W
G1[b]	7.5	7.1	3.11	1.62	1.10	0.77	nd	0.04	−12.9	−12.3	nd	−26.8
G2	7.1	7.0	2.34	2.54	1.07	0.57	0.07	0.06	−12.8	−10.9	−28.0	−25.3
G3	7.2	nd	4.34	3.20	1.27	0.66	0.12	0.14	−11.4	−10.8	−27.1	−19.5
G4	7.4	7.4	3.76	4.37	0.76	0.55	0.07	0.09	−10.4	−9.7	−26.2	−25.6
G6	7.5	7.3	3.19	3.92	0.96	0.77	0.15	0.19	−10.9	−11.0	−26.0	−26.3
G9	7.6	7.5	3.95	3.99	0.84	0.45	0.08	0.24	−11.0	−10.4	−28.2	−25.9
G12	7.4	7.4	1.63	2.41	0.78	0.72	0.12	0.25	−12.9	−12.4	−28.0	−20.7
G13	7.0	7.0	5.49	5.78	1.38	1.07	0.12	0.22	−10.7	−10.8	−28.7	−25.4
G14	7.1	7.1	4.45	4.58	0.82	1.60	0.07	0.13	−10.1	−10.3	−26.5	−25.7
G15	7.3	7.4	3.38	3.50	1.05	0.26	0.11	0.19	−10.7	−10.4	−26.1	−24.1
G16	7.1	7.3	3.52	4.20	0.80	0.46	0.08	0.07	−8.3	−6.3	−27.6	−25.7
G17	7.6	7.4	3.44	4.47	2.70	0.98	0.90	0.30	−10.0	−9.5	−25.0	−23.7
G18	6.8	6.9	4.48	5.70	7.42	5.50	0.56	0.28	−9.8	−7.6	−26.3	−24.1
G20	7.5	7.4	4.91	4.86	0.24	0.42	0.04	0.04	−11.2	−11.3	−27.0	−25.7
G21	7.3	7.2	5.96	5.89	0.88	0.70	0.06	0.18	−11.3	−10.8	−26.8	−25.1
G23	7.6	7.4	2.94	3.18	0.37	0.50	0.06	0.10	−10.8	−10.2	−27.3	−25.2
G24	7.5	7.2	5.73	6.58	1.24	1.30	0.06	0.09	−11.4	−12.2	−28.5	−26.0
G25	7.3	7.4	5.35	5.77	6.98	5.16	1.45	1.01	−14.4	−13.0	−25.4	−26.5
G27	7.1	7.0	5.12	4.93	1.42	0.76	0.14	0.08	−11.4	−10.8	−20.9	−27.0
G29	7.3	7.1	3.59	3.90	1.29	1.34	0.11	0.03	−11.4	−10.5	−25.4	−23.0
G30	7.3	7.3	4.62	4.53	0.38	0.59	0.29	0.35	−10.9	−10.1	−18.0	−26.1
G31	7.3	7.1	4.44	5.15	0.41	0.61	0.24	0.40	−10.6	−9.2	−19.4	−21.4
G32	7.9	7.9	3.05	1.78	0.79	0.32	0.30	0.10	−8.9	−7.2	−17.9	−21.1
G35	7.4	7.4	4.52	5.28	1.43	1.45	0.11	0.06	−11.7	−10.7	−20.2	−25.2
G37	7.4	nd	4.15	nd	2.07	nd	0.15	nd	−11.8	nd	−19.8	nd
G39	7.4	7.3	3.22	3.59	1.58	1.60	0.31	0.41	−11.9	−11.1	−26.3	−26.1
G40	8.4	7.4	3.89	2.80	3.95	2.61	nd	0.35	−10.2	−9.3	nd	−26.8
G41	7.2	7.1	5.26	5.41	0.62	0.26	nd	0.10	−11.8	−11.3	nd	−22.5
G43	7.2	7.0	3.86	4.21	0.81	0.14	0.21	0.08	−9.1	−9.2	−19.7	−22.5
S-av[c]	8.1	8.1	3.2	4.1	1.99	1.83	0.60	0.69	−9.8	−9.1	−25.6	−27.1

[a] S = summer, W = winter; [b] G = ground water; [c] S-av = average value of surface water; “nd” = not determined

HCO_3^- are generally lower in summer than in winter, reflecting the dilution effects of the rains. The contents of dissolved organic carbon and particulate organic carbon are listed in Table 1. The concentrations of DOC and POC in most ground water samples are lower than 2.0 mg C l^{-1} and 0.5 mg C l^{-1}, respectively (Fig. 2). However, some waters have high contents of organic carbon, which might suggest that natural and man-made organic compounds present a potential threat to the water quality.

The partial pressure of carbon dioxide (pCO$_2$) in ground waters is a function of soil respiration, which increases pCO$_2$ and dissolution of carbonate. pCO$_2$ and calcite saturation ratio are calculated according to chemical equilibrium equations (Clark and Fritz

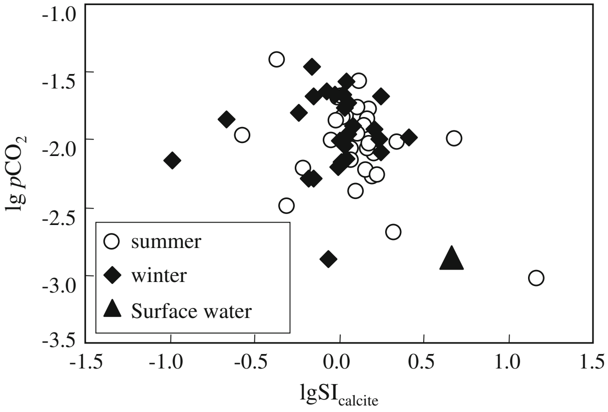
Fig. 2 Plots showing the relationship between DOC and POC in Zunyi ground water



1997). The $p\mathrm{CO}_2$ in ground water ranges from $10^{-3.02}$ to $10^{-1.42}$ (atm) in summer and from $10^{-2.88}$ to $10^{-1.46}$ (atm) in winter, with mean values of $10^{-2.04}$ (atm) and $10^{-1.95}$ (atm), respectively, which are higher than that of the atmosphere. The mean value of $p\mathrm{CO}_2$ in surface water was $10^{-2.85}$ (atm) which was lower than that in most of the ground water. The $\mathrm{lgSI}_{\mathrm{calcite}}$ value in most of the waters was a little higher than 0 (Fig. 3), which shows a little saturation in waters.

The δ^{13}C values of the DIC in ground waters range from −14.4‰ to −8.3‰ with a mean value of −11.1‰ in summer and from −13.0‰ to −6.3‰ with a mean value of −10.3‰ in winter. In general, ground waters have lower δ^{13}C values in summer than in winter (Fig. 4), which suggests that the soil CO_2 (mainly biogenic, hence enriched in ^{12}C) makes a larger contribution to the DIC of ground water in summer than in winter. The values are generally lower than that measured in Guiyang (Li et al. 2005) and in karst aquifers of northern Cyrenaica, Libya (Gonfiantini and Zuppi 2003), but are higher than that in ground water of the Raisin River watershed (Cane and Clark 1999), ground water in northeastern Lower Michigan contaminated by fuel hydrocarbons (Fang et al. 2000), and urban ground water in the British Midlands (Rueedi et al. 2007). The δ^{13}C values have no clear correlation with DIC concentrations (not shown), which has also been reported by Cane and Clark (1999) and Li et al. (2005). The δ^{13}C values of the POC in ground waters range from −28.7‰ to −17.9‰ in summer and from −27.0‰ to −19.5‰ in winter.

Fig. 3 Relationship between $\mathrm{lgSI}_{\mathrm{calcite}}$ and $\mathrm{lg}p\mathrm{CO}_2$ in Zunyi ground water



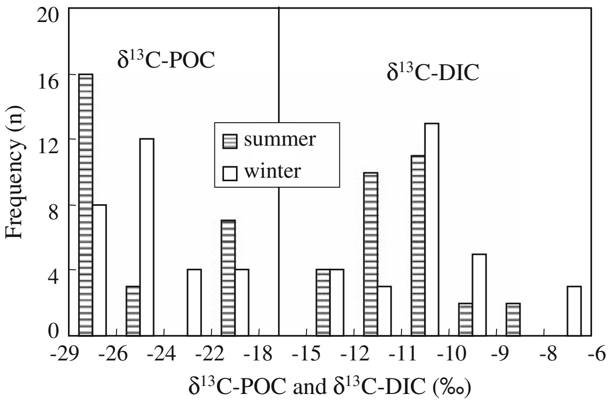


Fig. 4 Histogram of the $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ in Zunyi ground water

4 Discussion

4.1 Seasonal Variation of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$

As indicated by Fig. 4, the $\delta^{13}C_{DIC}$ ranges from −14.4‰ to −6.3‰. About 48% of ground water samples had $\delta^{13}C_{DIC}$ lower than −12‰ and 38% between −12‰ and −11‰ in summer. Meanwhile, about 25% of samples had $\delta^{13}C_{DIC}$ lower than −12‰ and 46% between −12‰ and −11‰ in winter. The difference observed suggested that there is considerable variation in $\delta^{13}C_{DIC}$ during the hydrological year, which is in line with other results (Cane and Clark 1999; Doctor et al. 2000). Cane and Clark (1999) considered that lower $\delta^{13}C_{DIC}$ during periods of high water table reflected local recharge by direct infiltration though the fields. Dilution effects are common due to high precipitation during the summer in the karst areas of Southwest China (Liu and Yuan 2000). Aquilina et al. (2006) have outlined a major role for the epikarst reservoir during karst recharge. Epikarst aquifer has an important influence on ground water carbon in highly karstified carbonate areas due to the connection between the rain and deep flow (Lee and Krother 2001). Lee and Krother (2001) have reported that $\delta^{13}C_{DIC}$ values were lower in epikarst waters than in base flow. The subsurface flow may be affected by differential mixing between "old" water stored in matrix porosity and epikarst waters as well as soil waters. Within the karst flow systems of Southwest China, transport of rain, surface and ground water progresses quickly making the residence time of groundwater relatively short in summer (Han and Jin 1996). The residence time of ground water in winter is longer than in summer because of less rain in winter, Southwest China, which might yield more positive $\delta^{13}C_{DIC}$ values in winter due to prolonged isotopic exchange between water and carbonate. The lower contents of DIC and lower values of $\delta^{13}C_{DIC}$ in summer than in winter confirm that local rain events in summer and a longer residence of water in winter affect the evolution of ground water carbon in karst systems of Southwest China. Therefore, there might be more soil CO_2 recharge to Zunyi ground water due to frequent rain events during the wet season, which suggested that ground water has more chance to gain soil CO_2 in summer.

Most C_3 plants have $\delta^{13}C$ values that range from −24 to −30‰ with an average value of about −27‰ and C_4 plants have $\delta^{13}C$ values that range from −10 to −16‰ with an average value of about −12.5‰ (Vogel 1993). As indicated by Fig. 4, the range of $\delta^{13}C_{POC}$ from −28.7‰ to −17.9‰ suggest that POC was mainly derived from C_3 plants with only a minor proportion of POC derived from C_4 plants. There is some difference between $\delta^{13}C_{POC}$ in winter relative to summer, which might suggest either that there is some new organic carbon derived from C_3 plants or that there has been input of household waste into the ground water system following summer rains, although there is little variation of POC contents between the two seasons. The seasonal variation of $\delta^{13}C$–POC suggests that the degradation of organic carbon in ground waters or saturated zone might play an important role on carbon evolution in the groundwater system.

4.2 Carbon Evolution and Controlling Factors

Carbon interactions in karst ground water begin with carbonate dissolution mainly driven by soil CO_2 and continue with subsequent organic and inorganic reactions in soils and aquifers (Clark and Fritz 1997). Carbonate dissolution is the main process affecting carbon system evolution due to the high ratio of dissolved inorganic carbon versus organic carbon in ground water. So ground water chemistry is mainly controlled by water/rock reactions, and ground water DIC sources can be easily attributed to one of several sources: (1) soil CO_2 derived from the decay of terrestrial vegetation and respiration of plant roots, which is dissolved in surface and rain water and then infiltrates the subsurface water system; (2) carbonate bedrock (limestone and dolomite) weathering by carbonic acid and sulfuric acid as well as organic acids derived from the root zone (Yoshimura et al. 2001; Han and Liu 2004). Acid rain emerged as an important environmental problem in the southwestern China and rain water there shows high contents of SO_4^{2-} and lower pH (Larssen et al. 2006). Han and Liu (2006) have reported that the sulfate concentrations range from 30 to 300 μmol l^{-1} with a median value of 80 μmol l^{-1} in rain of Guiyang; (3) Dissolution of atmospheric CO_2. 4) Oxidation of organic matter in ground water. The various sources of DIC and their evolution are described in the following equations:

1. Dissolution of CO_2 (including soil CO_2 and atmospheric CO_2) and oxidation of organic matter.

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{2}$$

$$CH_2O + O_2 \rightarrow H_2CO_3 \tag{3}$$

2. Weathering of carbonate bedrock by acids (e.g., carbonic, sulfuric, or organic acids).

a. $$(Ca_{1-x}Mg_x)CO_3 + H_2CO_3 \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \tag{4}$$

b. $$2(Ca_{1-x}Mg_x)CO_3 + H_2SO_4 \rightarrow 2(1-x)Ca^{2+} + 2xMg^{2+} + 2HCO_3^- + SO_4^{2-} \tag{5}$$

Each of these sources has a distinctive stable carbon isotopic composition: (1) $\delta^{13}C$ of CO_2 derived from oxidation of organic matter is similar to that of organic matter in the soil. C_3 plants make up most of the vegetation in the studied area and might be the key factor in controlling the $\delta^{13}C$ value of CO_2 according to the measured range of $\delta^{13}C_{POC}$ in ground water. $\delta^{13}C$ of soil CO_2 can be assumed to be −23‰ by reference to other studies (Cerling et al. 1991; Clark and Fritz 1997); (2) the average $\delta^{13}C$ values of the carbonate rocks were reported to be near +1.8‰ in Guizhou (Li et al. 2002). The isotope composition of HCO_3^- by dissolution of the carbonate rock from sulfuric acid is similar to that of the rock; (3) atmospheric CO_2 normally has an isotopic composition of $\delta^{13}C = -8‰$, but has little influence on the carbon isotopic composition of ground water because of the high pCO_2 in ground water relative to that in the atmosphere and the lower pH values of rain in Southwest China (Larssen et al. 2006). Precipitation of calcite would impact the inorganic dissolved carbon in waters (Szramek and Walter 2004). The $lgSI_{calcite}$ value in most waters was a little higher than 0 showing that calcite precipitation was not a major process. Precipitation could cause $\delta^{13}C_{DIC}$ to shift by less than 0.5‰ in the HCO_3^- reservoir once isotopic fractionation and the contribution of HCO_3^- for DIC are considered (Zhang et al. 1995), and so can be ignored. The ratios of Ca versus Mg were generally higher than 1 and the median value was about 4, suggesting that incongruent dissolution of dolomite was not notable. The mean $\delta^{13}C$ values of DIC in the ground waters are −11.1‰ in summer and −10.3‰ in winter, which is near the combined average $\delta^{13}C$ values of the soil CO_2 and the carbonate. Therefore, it is considered that $\delta^{13}C_{DIC}$ is mainly controlled by two primary sources: soil CO_2 and the dissolution of carbonate minerals.

Whether groundwater behaves as an open or closed system has an important role in shifting $\delta^{13}C_{DIC}$ values and these conditions can be distinguished using DIC concentrations, pCO_2, as well as $\delta^{13}C_{DIC.}$ The dissolved inorganic carbon was calculated following equations and constants of chemical equilibrium using water chemistry, showing that HCO_3^- generally contributes more than 90% of DIC. Under closed system conditions, the value of $\delta^{13}C_{DIC}$ would be close to −11‰ (average of the soil CO_2 and the carbonate) due to the fact that there is no continual CO_2 infiltration from the soil. The value of $\delta^{13}C_{DIC}$ will be close to or lower than −14‰ under open system conditions according to the fractionation between DIC (HCO_3^- + H_2CO_3) and soil CO_2 (Zhang et al. 1995). Clark and Fritz (1997) thought that closed system conditions are typical of recharge areas where infiltration to the water table is fast (e.g. karst), so the fast reaction of carbonate dissolution mainly affect the shift of $\delta^{13}C_{DIC}$ in Zunyi ground waters due to the range of $\delta^{13}C_{DIC}$ values.

4.3 Anthropogenic Impacts on Carbon Evolution

Batiot et al. (2003) have shown that the contents of total organic carbon are generally lower than 3 mg/l in most of the waters in the Vaucluse karst system. In this study, the concentrations of DOC and POC in most ground water samples are lower than 2.0 mg C l^{-1} and 0.5 mg C l^{-1}, respectively. The recommended maximum level of total organic carbon in potable water of Finland is 2 mg l^{-1} (Ministry of Social Affairs and Health 1994). The ground waters with high contents of organic carbon above 2 mg C l^{-1} were all located at the center of Zunyi or near petrol station, such as G25, G40, and G18, implying that point-source pollution was the key problem. So the higher organic carbon contents in some ground waters might suggest water quality being degraded.

Li et al (2005) found that $\delta^{13}C_{DIC}$ shifted with higher anthropogenic component in Guiyang. Fang et al. (2000) have shown there were lower values of $\delta^{13}C_{DIC}$ in ground water contaminated by fuel hydrocarbons relative to other ground waters. The lower values of $\delta^{13}C_{DIC}$ were observed in urban areas indicated by Fig. 5, with a similar distribution in winter (not shown), which means that urban anthropogenic inputs have an effect on carbon in ground water and so threaten water quality. Frequent pumping and the degradation of organics from domestic origin increases the CO_2 content of the vadose or infiltration zone flowing into urban ground water because of the high use rate of the waters for drinking or industry, and might lead to a slightly more negative value of $\delta^{13}C_{DIC}$ in urban ground waters.

5 Summary

The carbonate system evolves with weathering reactions driven by CO_2 dissolved from the soil and subsequent organic/inorganic reactions in soils and aquifers. The studied area is mainly characterized by karst landforms in Southwest China. The results have shown that

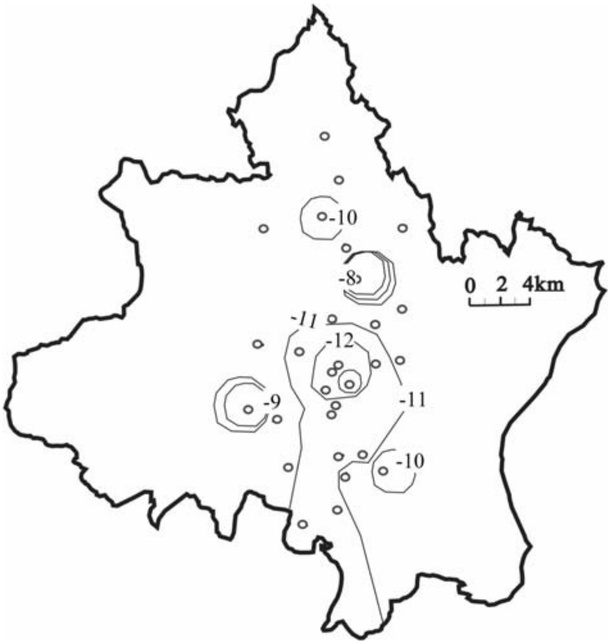


Fig. 5 Contours of $\delta^{13}C_{DIC}$ (‰) of Zunyi ground water in summer. Contour interval is 1‰ of $\delta^{13}C_{DIC}$ value

water chemistry was mainly controlled by carbonate dissolution. The mean values of HCO_3^- in winter (low-flow season) and summer (high-flow season) are 4.22 and 4.06 mmol l^{-1}, respectively, reflecting the dilution effects of the heavy monsoon rains. The average $\delta^{13}C_{DIC}$ values of ground water are −10.3‰ in winter and −11.1‰ in summer. There are lower contents of DIC and lower values of $\delta^{13}C_{DIC}$ in summer than in winter, indicating that local rain events in summer and a longer water residence time in winter play an important role in ground water carbon evolution in karst flow systems of Southwest China. Therefore, soil CO_2 makes a larger contribution to the DIC in summer than in winter due to more rain. The concentration of DOC and POC in most ground water samples is lower than 2.0 mg C l^{-1} and 0.5 mg C l^{-1}, respectively, but some waters have high contents of organic carbon. The degradation of organic carbon might affect the carbon evolution according to variations in the $\delta^{13}C_{POC}$ between the two seasons, but more work is needed to confirm this. The waters with high contents of organic carbon are generally located in the urban area, indicating that dealing with point sources of pollution will be the first challenge in controlling pollution in Zunyi ground water. The lower values of $\delta^{13}C_{DIC}$ observed in the urban area imply that urban anthropogenic activities have an effect on the carbon evolution of ground water and might threaten water quality. Hence, carbon isotope studies together with analyses of water chemistry are useful to gain a better understanding of natural and anthropogenic influences on water quality.

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