Environ Earth Sci (2010) 60:893–899
DOI 10.1007/s12665-009-0226-y

ORIGINAL ARTICLE

Hydrogeochemistry and dissolved inorganic carbon isotopic composition on karst groundwater in Maolan, southwest China

Guilin Han · Yang Tang · Qixin Wu

Received: 3 January 2009 / Accepted: 23 June 2009 / Published online: 8 July 2009

Abstract The forest ecosystem in the Maolan karst forest, southwest China is the only concentrated, intact, and relatively stable karst forest ecosystem which has survived in the area at the same latitude in the world, and is a valuable karst forest plant resource as well. Groundwater samples from Maolan karst forest were collected from wells and springs during summer; and concentrations of major ions and dissolved inorganic carbon (DIC) isotopic compositions were measured. The pH values range from 7.2 to 8.3 results from the dissolution of carbonate, HCO_3^- is the dominant species of DIC in groundwater. Calcium and HCO_3^-, followed by Mg^{2+} and SO_4^{2-} dominate the chemical composition of major ions in the groundwaters. Groundwater samples have $\delta^{13}C$ values in the range from −8.1‰ to −16.6‰, which are lower than that of the other karst city groundwaters in the southwest China. Combining $\delta^{13}C_{DIC}$ ratios with measurements of HCO_3^- and pH clearly distinguishes the principal processes underlying the geochemical evolution of groundwater in Carboniferous carbonate aquifers, where processes can be both degradation of organic matters in the soil and the carbonate dissolution.

Keywords Stable carbon isotope · Dissolved inorganic carbon · Karst groundwater · Southwest China

G. Han (✉) · Y. Tang · Q. Wu
The State Laboratory of Environmental Geochemistry,
Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, China
e-mail: hanguilin@vip.skleg.cn

Y. Tang · Q. Wu
Graduate School of Chinese Academy of Sciences,
Beijing 100039, China

Introduction

Groundwater is a fundamental hydrologic component in many watersheds, feeding streams, and rivers via baseflow. The carbon flux in karst areas takes place from the atmosphere or groundwater as HCO_3^- and is related to the dissolution of carbonate rocks and evolution of water quality. Indentifying sources and sinks of dissolved inorganic carbon (DIC) species is an important step in understanding the geochemistry of groundwater systems (Chapelle and Knobel 1985; Landmeyer and Stone 1995; Li et al. 2005, 2008; Murad and Krishnamurthy 2008). This is particularly important for karst areas because bicarbonate (HCO_3^-) is frequently the major dissolved anion. The kinetics of calcite dissolution in groundwater is governed by several factors, such as pH, p_{CO_2}, surface of the solid $CaCO_3$ exposed to contact with groundwater, degree of turbulence at the contact surface, ionic strength, impurities, etc. (Plummer et al. 1978; Chou et al. 1989; Eisenlohr et al. 1999; Gonfiantini and Zuppi 2003).

In this study, the concentration of major ions and isotope composition of DIC from 31 springs and wells in Maolan National Nature Reserved Park, southwest China, are examined to determine the relative influences of calcite and soil CO_2 as C sources. This study focuses on the water chemistry and the evolution of carbon isotope impacted by natural factors in groundwaters. The aim of this study is to understand carbon variations in the typical groundwater in subtropical karst areas.

Geography, climate, and lithology of drainage catchments

Maolan in Guizhou Province, China is famous for its dense virgin evergreen forests growing on peak cluster karst. The area selected for this study is situated in the Maolan National Nature Reserved Park in the southeast of Guizhou province, southwest China, located between 25°09′20″ and 25°20′50″ of latitude north and 107°52′10″ and 108°05′40″ of longitude east (Fig. 1). This area covers approximately 200 km^2, over mountains of jagged carbonate rock with a forest-covering rate of more than 90%. A karst forest of such magnitude is rarely seen in the world. Annual rainfall at the site with virgin forest is about 1750 mm, ca 80% of which falls in monsoonal rainy season of April to September, while it is 400-mm lower in surrounding deforestation areas (Zhou 1987). The mean annual air temperature at the site is about 17°C with hot summer (June–August) and cold winter (December–February).

The tectonic of the Maolan forest is situated in the depression zone of the southwestern Jiangnan landmass of the East Yangtes craton. This zone was folded and uplifted over the sea level until the end of the Mesozoic Era. The main aquifers in the region contain homogenous carbonate. The geomorphologic types on the northwest side mainly belong to cockpit karst, which is generally 680–1010 m above sea level, with wide depressions and shallow groundwater. The geomorphologic types on the southeast side mainly belong to cone karst dolines, which are 450–770 m above sea level, with deep shapes and deep groundwater. The rock exposures in the study area are sedimentary formations of middle- and lower-Carboniferous ages in Maolan syncline. The geological map of the study area is shown in Fig. 1. The middle- and lower-Carboniferous outcrops are characterized by pure limestone rock and dolomite rock, sandstone, and clay. The karst Geomorphology, together with the forest growing on the base rock in the habitat, forms a unique natural complexity of karst forest in the subtropical region.

Sampling and analytical procedures

Thirty-one groundwater samples were collected during the period from July 23 to 28 of 2007 in summer (rainy season). The sampling locations are shown in Fig. 1. Water temperature (T), pH, and electrical conductivity (EC) were measured at the sampling sites with a portable pH and salt conductivity meter. HCO_3^- was determined using the HCl titration method within hours of sample collection. Immediately after collection some of water samples were filtered through 0.45-μm Whatman cellulose acetate membrane filters and a small portion of these samples was stored for measuring anions, while another portion was

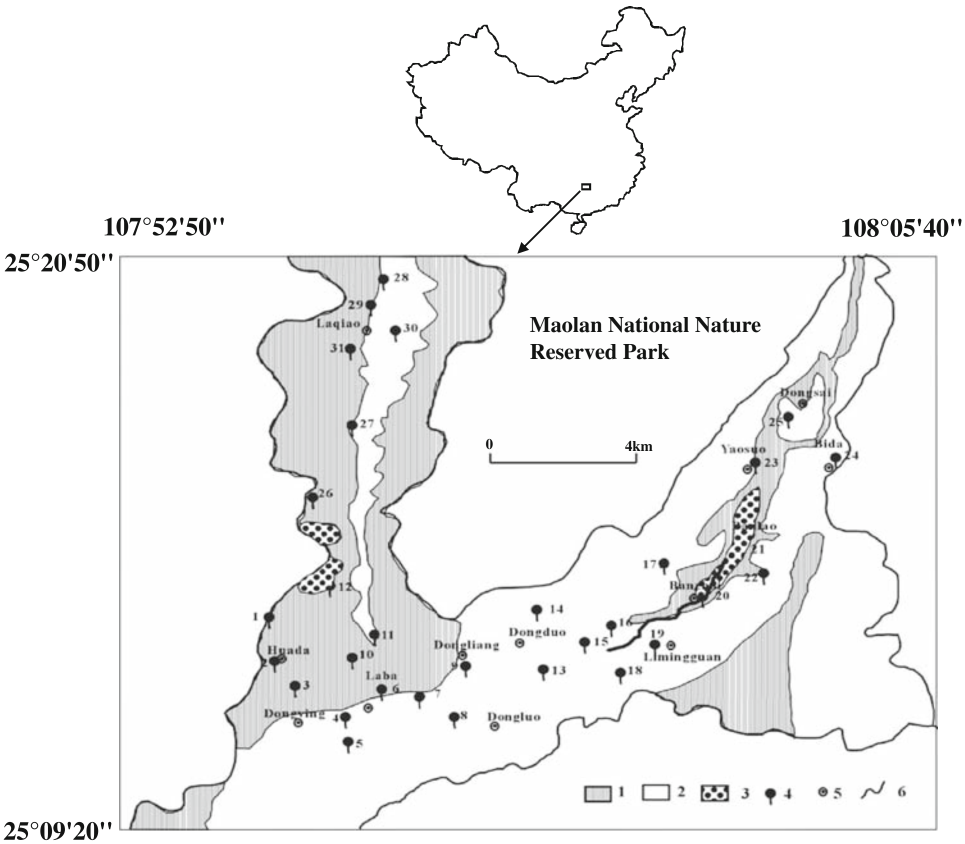

Fig. 1 Sketch map showing the lithology of Maolan National Nature Reserved Park and sampling locations and sample numbers. 1, limestone; 2, dolostone; 3, sandstone; 4, sample location; 5, village; and 6, river

acidified with ultra-purified hydrochloric acid to pH <2 after collection for measuring cations. All the samples were stored in darkness. The cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were determined by atomic absorption spectrometry (AAS), while the anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) were determined by Ion chromatography.

For determination of $\delta^{13}C_{DIC}$, groundwater was filtered by pressure filtration through 0.45-μm cellulose acetate filter membrane to avoid the potential influence of carbonate mineral particles. Samples were then collected in polyethylene bottles with airtight caps and preserved with $HgCl_2$ to prevent biological activity. Using a modification of the method of Atekwana and Krishnamurthy (1998), a 10-ml water sample was injected by syringe into glass bottles that were prefilled with 1-ml 85% phosphoric acid and that had magnetic stir bars. No detectable gases were produced by unwanted reaction between glass and acid, when the glass bottles with 1-ml 85% phosphoric acid were allowed to stand for several hours. The acid-water reaction begins immediately upon injection. CO_2 was extracted into a vacuum line in the laboratory at 50°C, while stirring for 10 min. It was then cryogenically separated from H_2O by being passed sequentially through an N_2-cooled ethanol trap and then frozen into a manometer cold finger by a liquid N_2 trap. Finally, the CO_2 was transferred cryogenically into a tube for isotope measurement. Carbon isotope ratios of the DIC were determined on a Finnigan MAT 252 mass spectrometer (Li et al. 2005). The carbon isotope values are reported using the δ notation relative to PDB in per mil, where

$$\delta^{13}C(‰) = \left[\left(R_{\mathrm{sample}} - R_{\mathrm{PDB}}\right)/R_{\mathrm{PDB}}\right] \times 1000$$

Routine $\delta^{13}C_{DIC}$ measurements have an overall precision of 0.1%. The isotopic standards of carbonate and IAEA-C3 (cellulose) were measured as a check on reproducibility. A number of duplicate samples were measured and the results show that the differences were less than the range of measurement accuracy.

Results and discussion

Major elements hydrogeochemistry

The chemical compositions and C isotopic ratios of groundwater samples collected from Maolan karst area are reported in Table 1. The pH values of water samples in the study area ranges from 7.2 to 8.3, averaging 7.7. The pH values reflect the influence of the soil water that incorporates a large amount of CO_2 and of the dissolution of carbonate bedrock.

The Ca^{2+} concentrations in groundwaters vary from 1163 to 2538 μmol/l, with a mean value of 1552 μmol/l. The Mg^{2+} concentrations vary from 53 to 1353 μmol/l, with a mean value of 431 μmol/l. In general, Ca^{2+} and Mg^{2+} dominate the cation concentrations of these waters, accounts for 95–99% of the total cations in the groundwater samples. HCO_3^- was the most abundant anions, and its concentrations vary from 2.1 to 4.9 mmol/l, averaging 3.4 mmol/l. The second abundant anion is SO_4^{2-}, with variation range from 112 to 1104 μmol/l, and a mean concentration of 258 μmol/l. The chemistry of the majority of the groundwater is characterized by a calcium–magnesium and bicarbonate type, with the following ionic sequences: $HCO_3^- > SO_4^{2-} > Cl^-$. The concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- in groundwater are generally higher than those in the surface water (Han and Liu 2004) indicating extensive dissolution of carbonate rocks and greater solubility of the dissolved solutes probably because of lower pH of groundwater. The aquifers are Carboniferous limestone and dolomite, indicating the important contributions of carbonate weathering.

Most of the waters had low NO_3^- and Cl^- concentrations, which were considered as indicators of human activities (urban and agricultural settlements), except for samples 22 and 23 (Table 1). Chloride content in the groundwater ranges from 0.12 to 67.9 μmol/l. When compare to surface water (Han and Liu 2004), the Cl^- concentrations in groundwater are clearly poorer in all the samples, likely reflecting no anthropogenic inputs. Cl^- ions in groundwater probably reflect atmospheric inputs because Cl^- ions do not have any significant lithological origin. The concentrations of NO_3^- of a total of 31 groundwater samples range from 0.03 to 2.41 mg/l, which are lower than accepted drinking water limit of 45 mg/l NO_3^-. There are good correlation between NO_3^- and Cl^- ($R = 0.99$), suggesting that they have same origin.

Saturation index and C isotope

From the range of pH values it can be deduced that bicarbonate (HCO_3^-) is the dominant DIC species. Therefore, concentrations of total inorganic carbon are expressed as HCO_3^- in this article. The partial pressure of carbon dioxide (p_{CO_2}) in groundwaters is a function of soil respiration, which increases p_{CO_2} and dissolution of carbonate. p_{CO_2}, saturation indexes of calcite (SIC), and saturation indexes of dolomite (SID) ratio are calculated according to chemical equilibrium equations (Clark and Fritz 1997; Liu et al. 2007).

$$p_{CO_2} = \frac{(HCO_3^-)(H^+)}{K_H K_1}$$

Table 1 Major ions concentration and $\delta^{13}C$ values of the DIC in ground water of Maolan, City

Sample number	Date (year-month-date)	Longitude	Latitude	EC (μS/cm)	pH	T (°C)	HCO_3 (mmol/l)	K^+ (μmol/l)	Na^+ (μmol/l)	Ca^{2+} (μmol/l)	Mg^{2+} (μmol/l)	Cl^- (μmol/l)	NO_3^- (μmol/l)	SO_4^{2-} (μmol/l)	$\delta^{13}C$
1	2007-7-23	107°6.581′	25°13.042′	383	7.85	21.1	3.32	3.28	11.62	1283.96	542.88	6.45	3.69	174.47	−14.57
2	2007-7-23	107°57.403′	25°13.037′	347	8.34	21.2	3.33	8.01	14.32	1163.12	648.39	12.05	6.89	150.54	−13.55
3	2007-7-23	107°56.140′	25°12.432′	379	7.15	21.2	3.35	3.05	11.05	1308.55	501.06	4.43	2.53	133.44	−16.63
4	2007-7-23	107°56.449′	25°12.274′	345	7.69	24.7	3.32	3.68	12.37	1588.07	220.28	2.37	1.36	135.65	−14.01
5	2007-7-23	107°56.301′	25°12.290′	308	7.81	20.7	3.05	3.02	9.11	1328.64	325.76	6.24	3.57	137.72	−14.04
6	2007-7-23	107°56.260′	25°12.111′	311	8.05	19.1	3.23	3.01	10.06	1212.50	555.95	9.02	5.16	153.76	−13.19
7	2007-7-23	107°56.146′	25°12.135′	339	7.8	21.7	3.02	5.31	10.13	1311.50	372.84	17.54	10.03	147.87	−14.8
8	2007-7-23	107°55.370′	25°12.437′	393	7.44	20.6	3.42	4.69	13.08	1724.00	298.77	16.20	9.26	288.74	−14.86
9	2007-7-23	107°55.025′	25°12.379′	376	7.48	20.4	3.41	8.46	13.47	1580.25	319.86	9.86	5.64	217.11	−15.72
10	2007-7-23	107°54.435′	25°12.587′	405	7.42	21.4	3.42	65.26	75.06	1878.75	155.56	47.04	26.89	337.28	−11.49
11	2007-7-23	107°54.226′	25°13.264′	305	7.98	22.4	2.13	12.48	40.21	1451.50	114.40	16.98	9.71	490.78	−9.23
12	2007-7-23	107°54.453′	25°13.279′	280	7.8	25.8	2.32	14.75	34.74	1320.10	91.18	12.14	6.94	239.95	−9.26
13	2007-7-23	107°54.009′	25°14.370′	345	7.98	24.7	3.43	6.12	14.55	1728.42	289.24	10.47	5.98	295.95	−8.11
14	2007-7-23	107°54.145′	25°16.102′	396	7.56	20.6	3.85	15.10	24.80	1468.50	687.65	14.78	8.45	185.10	−13.96
15	2007-7-24	108°00.555′	25°15.014′	408	7.41	22.3	4.15	2.48	9.54	1192.00	1021.40	0.12	0.61	114.68	−12.84
16	2007-7-24	108°00.238′	25°14.206′	359	7.67	21.1	3.02	9.43	23.37	1759.03	126.10	15.50	8.86	364.03	−11.6
17	2007-7-24	108°01.207′	25°13.063′	365	7.78	20.2	3.72	7.32	13.12	1354.50	692.18	21.12	12.07	168.83	−12.09
18	2007-7-24	108°01.011′	25°13.511′	402	8.05	22.1	4.13	36.33	27.46	1919.11	306.84	11.53	6.59	192.13	−15.34
19	2007-7-24	108°01.231′	25°13.273′	372	7.47	19	3.35	8.73	16.51	1670.50	220.58	11.09	6.34	199.22	−15.67
20	2007-7-24	108°01.505′	25°14.051′	572	7.53	20.5	3.75	118.46	165.35	2538.00	394.08	45.37	25.94	1104.20	−13.34
21	2007-7-24	108°01.414′	25°14.065′	504	7.32	20.9	3.15	7.09	44.37	2002.73	176.89	16.96	9.70	585.97	−13.86
22	2007-7-24	108°02.830′	25°15.002′	387	7.56	20.4	3.82	49.72	76.04	2207.75	191.36	54.87	31.37	455.72	−12.97
23	2007-7-24	108°03.121′	25°16.245′	412	7.47	20.8	3.85	3.64	15.56	1455.02	656.41	67.91	38.83	175.68	−14.84
24	2007-7-24	108°03.562′	25°07.146′	522	7.72	22.6	4.92	3.06	14.15	1334.38	1352.77	11.70	6.69	221.94	−9.97
25	2007-7-24	108°01.527′	25°16.396′	399	7.3	20.2	3.32	2.64	15.97	1928.90	52.61	8.42	4.82	271.67	−16.28
26	2007-7-27	107°58.330′	25°18.063′	313	7.57	18.3	3.05	2.53	9.54	1499.54	151.07	0.77	0.44	111.59	−11.1
27	2007-7-27	107°57.341′	25°18.112′	364	7.53	18.2	3.55	4.02	13.06	1394.47	608.50	22.80	13.04	233.21	−15.48
28	2007-7-27	107°56.197′	25°19.110′	353	8.15	21	3.65	27.81	27.90	1457.20	564.98	22.01	12.58	178.79	−13.47
29	2007-7-27	107°56.324′	25°18.329′	388	7.54	18.4	3.22	2.84	9.33	1205.59	572.95	3.94	2.25	166.48	−15.77
30	2007-7-27	107°56.457′	25°18.370′	413	7.76	19.1	3.93	3.00	12.22	1274.50	932.51	11.35	6.49	194.09	−14.25
31	2007-7-28	108°03.414′	25°17.196′	316	7.84	19.2	3.23	7.94	13.21	1557.10	213.42	17.95	10.26	158.02	−14.05

$$\mathrm{SIC} = \log\left(\frac{(\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-})}{K_{\mathrm{calcite}}}\right)$$

$$\mathrm{SID} = \log\left(\frac{(\mathrm{Ca}^{2+})(\mathrm{Mg}^{2+})(\mathrm{CO}_3^{2-})^2}{K_{\mathrm{dolomite}}}\right)$$

where parenthesis denotes species activity in mol/l and K_{H} and K_1 are the temperature-dependent Henry's Law and first dissociation constants for CO_2 gas in water, respectively. K_{calcite} and K_{dolomite} are the temperature-dependent equilibrium constant for calcite and dolomite, respectively (Stumm and Morgan 1981; Liu et al., 2007). If $\mathrm{SI} > 0$, water is supersaturated with respect to the mineral; if $\mathrm{SI} < 0$, water is aggressive to the mineral; and if $\mathrm{SI} = 0$, the equilibrium reaches.

The p_{CO_2} in groundwater ranges from $10^{-3.9}$ to $10^{-1.87}$ (atm), with mean values of $10^{-2.40}$ (atm), which are higher than that of the atmosphere. The SIC values in most of the water samples were higher than 0 (Fig. 2), except sample 3. But the SID values in most of the water samples were lower than 0 (Fig. 2). It shows that most of springs are saturated in calcite and some of springs are undersaturated in dolomite. The fact that the waters are undersaturated in dolomite indicates that dolomite can dissolve in this system. Dolomite dissolution is likely to add Ca^{2+}, Mg^{2+}, and HCO_3^- to the solution, while calcite precipitation is necessary to keep the observed calcite saturation.

The $\delta^{13}C$ values of the DIC in groundwaters range from −16.6‰ to −8.1‰ with a mean value of −13.4‰, which suggests that biogenic CO_2 makes a larger contribution to the DIC. The $\delta^{13}C$ values of groundwater samples are generally lower than that measured in Guiyang city (Li et al. 2005), Zunyi city (Li et al. 2008) and in karst aquifers of northern Cyrenaica, Libya (Gonfiantini and Zuppi 2003), but are higher than that in groundwater of the Raisin River watershed (Cane and Clark 1999), groundwater in northeastern Lower Michigan contaminated by fuel hydrocarbons (Fang et al. 2000) and urban groundwater in the British Midlands (Rueedi et al. 2007). The $\delta^{13}C$ values have clear correlation with concentrations of HCO_3^- (Fig. 3), which is different from the results reported by Cane and Clark (1999) and Li et al. (2005, 2008).

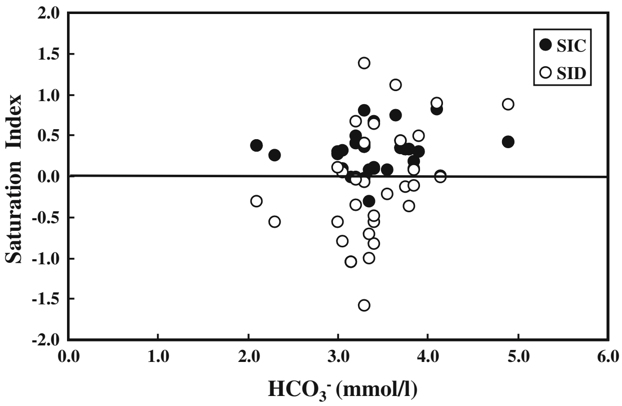

Fig. 2 Saturation index (SI) of calcite and of dolomite versus HCO_3^- of all the collected samples

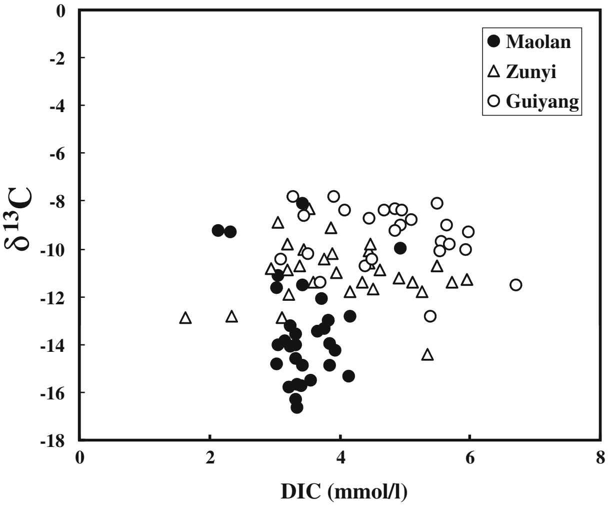

Fig. 3 varation in concentration with isotopic composition of DIC in Maolan ground water. Data sources are Li et al. (2005) for Guiyang and Li et al. (2008) for Zunyi

Carbon evolution and controlling factors

The carbon isotopic composition of the aqueous carbon is a direct reflection of the geochemical history of a groundwater. This evolution begins in the recharge environment and continues in the subsurface where mineral water interaction will dominate. Bacterial processes can further modify the isotopic composition of the aqueous carbon (Fritz et al. 1989). Carbon interactions in karst groundwater 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; Li et al. 2008). The isotopic constraints of DIC in groundwater depend on several major processes: (1) oxidation of organic matter, (2) dissolution of carbonate minerals in soils, (3) exchanges with atmospheric carbon dioxide and kinetic effects at water/atmosphere interface, and (4) photosynthetic activity. Because different source of DIC and geological materials have different isotopic compositions, stable carbon isotopes on DIC are useful as tracers of DIC sources and evolution in groundwater (Chapelle and Knobel 1985; Clark and Fritz 1997; Cane and Clark 1999).

Atmospheric CO_2 normally has an isotopic composition of $\delta^{13}C = -7‰$ but has little influence on $\delta^{13}C$ of groundwater because of its low partial pressure in the subsurface (Grossman 1997). Carbon isotopes in marine limestone and dolostones have been extensively reported in the literature and show typical marine values close to 0% since the end of the Proterozoic (Telmer and Veizer 1999). In general, the δ^{13}C of CO_2 derived from the respiration of the plant roots is similar to that of CO_2 from degradation of organic matter in the soil, the C isotopic composition of soil CO_2 reported by previous studies are close to $-24 \pm 2‰$ (Cerling et al. 1991; Aucour et al. 1999).

Thus, the δ^{13}C value of groundwater that inorganic carbon derives from different sources (carbonate dissolution and degradation of organic matters) can be calculated from a simple isotope balance equation (Chapelle and Knobel 1985):

$$\delta^{13}\mathrm{C}_{\mathrm{final}} = \frac{\sum_{0}^{i}(\mathrm{mC}_i)(\delta^{13}\mathrm{C}_i)}{\sum_{0}^{i}(\mathrm{mC}_i)}$$

where mC_i is the molality of added DIC from the *i*th source and $\delta^{13}\mathrm{C}_i$ is δ^{13}C composition of added DIC from the *i*th source.

According to above equation, the calculated results show that 34–68% (mean value is 56 ± 9%) of the DIC in the groundwater is from degradation of organic matters in the soil. This is consistent with the fact that dense virgin evergreen distribute in Maolan.

Conclusions

The use of chemical composition and C isotopic techniques in the investigation of major karst springs in Maolan carbonate aquifer systems has provided useful information about the characteristics of groundwater in these areas. The groundwater chemistry in the Maolan aquifer systems was mainly controlled by carbonate dissolution. The water can be mainly characterized as HCO_3–Ca type according to mass balance considerations. HCO_3^- is the main species of DIC in groundwater. HCO_3^- in the groundwater comes from dissolution of carbonate ($\delta^{13}C = 0‰$) and dissolution of soil gas CO_2 ($\delta^{13}C = -24‰$). Mass balance and isotope balance calculations show that most about 56 ± 9% of the DIC in the groundwater is from degradation of organic matters in the soil. The values of $\delta^{13}C_{DIC}$ observed in groundwater imply that human activities have no effect on the carbon evolution. Hence, the compositions of carbon isotope in Maolan groundwater represent the composition of the typical groundwaters in subtropical karst areas.

Acknowledgments This study was supported jointly by the Innovation Program of Chinese Academy of Sciences (No. KZCX-YW-306) and Ministry of Science and Technology of China (Grant No. 2006CB403206) as well as the Chinese National Natural Science Foundation (Nos. 40673010, 40721002).

References

Atekwana EA, Krishnamurthy RV (1998) Seasonal variations of dissolved inorganic carbon and δ^{13}C of surface waters: application of a modified gas evolution technique. J Hydrol 205:265–278. doi:10.1016/S0022-1694(98)00080-8

Aucour AM, Sheppard SMF, Guyomar O, Wattelet J (1999) Use of δ^{13}C to trace origin and cycling of inorganic carbon in the Rhône river system. Chem Geol 159:87–105. doi:10.1016/S0009-2541(99)00035-2

Cane G, Clark ID (1999) Tracing ground water recharge in an agricultural watershed with isotopes. Ground Water 37:133–139. doi:10.1111/j.1745-6584.1999.tb00966.x

Cerling TE, Solomon DK, Quade J (1991) On the isotopic composition of carbon in soil carbon dioxide. Geochim Cosmochim Acta 55:3403–3405. doi:10.1016/0016-7037(91)90498-T

Chapelle FH, Knobel LL (1985) Stable carbon isotopes of HCO_3^- in the aquia aquifer, Maryland: evidence for an isotopically heavy source of CO_2. Ground Water 23:592–599. doi:10.1111/j.1745-6584.1985.tb01507.x

Chou L, Garrels RM, Wollast R (1989) Comparative study of the kinetics an mechanisms of dissolution of carbonate minerals. Chem Geol 78:269–282. doi:10.1016/0009-2541(89)90063-6

Clark ID, Fritz P (1997) Environmental isotopes in hydrogeology. LEWIS Publishers, New York 328

Eisenlohr L, Meteva K, Gabrovsek F, Dreybrodt W (1999) The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H_2O–CO_2 solutions. Geochim Cosmochem Acta 63:989–1002. doi:10.1016/S0016-7037(98)00301-9

Fang JS, Barcelona MJ, Krishnamurthy RV, Atekwana EA (2000) Stable carbon isotope biogeochemistry of shallow sand aquifer contaminated with fuel hydrocarbons. Appl Geochem 15:157–169. doi:10.1016/S0883-2927(99)00037-2

Fritz P, Fontes JC, Frape SK, Louvat D, Michelot JM, Balderer W (1989) The isotope geochemistry of carbon in groundwater at Stripa. Geochim Cosmochem Acta 53:1765–1775. doi:10.1016/0016-7037(89)90297-4

Gonfiantini R, Zuppi GM (2003) Carbon isotope exchange rate of DIC in karst groundwater. Chem Geol 197:319–336. doi:10.1016/S0009-2541(02)00402-3

Grossman EI (1997) Stable carbon isotopes as indicators of microbial activity in aquifers. In: Hurst CJ, Knudson GR, McInerney MJ, Stetzenbach LD (eds) Manual of environmental microbiology. American Society for Microbiology, Washington, DC, pp 565–567

Han G, Liu C-Q (2004) Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. Chem Geol 204:1–21. doi:10.1016/j.chemgeo.2003.09.009

Landmeyer JE, Stone PA (1995) Radiocarbon and δ^{13}C values related to ground-water recharge and mixing. Ground Water 33:227–234. doi:10.1111/j.1745-6584.1995.tb00277.x

Li S-L, Liu C-Q, Tao F-X, Lang Y-C, Han G (2005) Carbon biogeochemistry of ground water, Guiyang, southwest China. Ground Water 43:494–499

Li S-L, Liu C-Q, Lang Y-C, Tao F, Zhao Z, Zhou Z (2008) Stable carbon isotope biogeochemistry and anthropogenic impacts on karst ground water, Zunyi, southwest China. Aquat Geochem 14:211–221. doi:10.1007/s10498-008-9033-4

Liu Z, Li Q, Sun H, Wang J (2007) Seasonal, diurnal and storm-scale hydrochemical variations of typical epikarst spring in subtropical karst areas of SW China: soil CO_2 and dilution effects. J Hydrol 337:207–223. doi:10.1016/j.jhydrol.2007.01.034

Murad AA, Krishnamurthy RV (2008) Factors controlling stable oxygen, hydrogen and carbon isotope ratios in regional groundwater of eastern United Arab Emirates (UAE). Hydrol Process 22:1922–1931. doi:10.1002/hyp.6776

Plummer LN, Wigley TML, Parkhurst DL (1978) The kinetics of calcite dissolution in CO_2-water systems at 5 to 60°C and 0.0 to 1 atm CO_2. Am J Sci 278:179–216

Rueedi J, Cronin AA, Taylor RG, Morris BL (2007) Tracing sources of carbon in urban groundwater using $\delta^{13}C_{TDIC}$ ratios. Environ Geol 52:541–557. doi:10.1007/s00254-006-0486-8

Stumm W, Morgan JJ (1981) Aquatic chemistry, 2nd edn. Wiley, New York

Telmer K, Veizer J (1999) Carbon fluxes, p_{CO_2} and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives. Chem Geol 159:61–86. doi:10.1016/S0009-2541(99)00034-0

Zhou Z (1987) Scientific survey of the Maolan karst forest. Guihzou People's Publishing House, Guiyang