

THE EFFECTS OF AGRICULTURAL ACTIVITIES AND ATMOSPHERIC ACID DEPOSITION ON CARBONATE WEATHERING IN A SMALL KARSTIC AGRICULTURAL CATCHMENT, SOUTHWEST CHINA

VPLIV KMETIJSKE DEJAVNOSTI IN KISLIH USEDLIN IZ ZRAKA NA PREPEREVANJE KARBONATOV NA MAJHNEM KRAŠKEM KMETIJSKEM OBMOČJU NA JUGOZAHODU KITAJSKE

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Abstract

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Yu Chen & Yongjun Jiang The effects of agricultural activities and atmospheric acid deposition on carbonate weathering in a small karstic agricultural catchment, Southwest China

In order to quantify the sources and fluxes of DIC, the effects of the use of N-fertilizers and acid deposition on carbonate weathering have been quantified by hydrochemistry and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in Qingmuguan underground river system (QRS) – a small karstic agricultural catchment of Southwest China. The results show that: (1) the significant temporal variations for major element concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in different months were observed, especially, of which the groundwater showed significant high concentrations of DIC, Ca^{2+} , Mg^{2+} , NO_3^- , SO_4^{2-} and $\delta^{13}\text{C}_{\text{DIC}}$ in rainy season and fertilizing period in the QRS; (2) the contributions of carbonate dissolution by carbonic acid to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater in different months averaged 68.5 % and 81.0 %, respectively. While the contributions of carbonate dissolution by nitric acid originated from the use of N-fertilizers and atmospheric acid deposition to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater in different months averaged 11.1 % and 6.7 %, respectively, and the contributions of carbonate dissolution by sulphuric acid originated from the atmospheric acid deposition to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater in different months averaged 20.4 % and 12.3 %, respectively; (3) the $\delta^{13}\text{C}_{\text{DIC}}$ increased obviously with $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater in the rainy season and fertilizing period indicated that the use of N-fertilizers and atmospheric acid deposition should be responsible for the elevated the $\delta^{13}\text{C}_{\text{DIC}}$ and the molar ratio of $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater in the QRS.

Key words: carbonate weathering, karst groundwater, agricultural activities, atmospheric acid deposition, Qingmuguan, Southwest China.

Izvleček

UDK 552.54:551.3.053(513)

Yu Chen & Yongjun Jiang Vpliv kmetijske dejavnosti in kislih usedlin iz zraka na preperevanje karbonatov na majhnem kraškem kmetijskem območju na jugozahodu Kitajske

Da bi določili izvor in tok DIC (raztopljen anorganski ogljik) smo vrednotili učinek uporabe dušikovih gnojil in kislih usedlin na preperevanje karbonatov. Pri tem smo se poslužili hidrokemičnih postopkov in analize $\delta^{13}\text{C}_{\text{DIC}}$ podzemne vode v kraškem zaledju reke Qingmuguan (QRS), ki je del manjšega kmetijskega območja na jugozahodu Kitajske. Rezultati so pokazali naslednje: (1) Izmerjene so bile opazne časovne spremembe v koncentraciji glavnih elementov in $\delta^{13}\text{C}_{\text{DIC}}$ v podzemni vodi v različnih mesecih; to je še posebej očitno v deževnem obdobju in času gnojenja, ko so bile zabeležene izrazito povečane koncentracije DIC, Ca^{2+} , Mg^{2+} , NO_3^- , SO_4^{2-} in $\delta^{13}\text{C}_{\text{DIC}}$; (2) Delež preperevanja karbonatov zaradi ogljikove kisline je glede na skupne koncentracije $(\text{Ca}^{2+}+\text{Mg}^{2+})$ in HCO_3^- v podzemni vodi v različnih mesecih v povprečju znašal med 68,5 % in 81,0 %. Medtem je delež preperevanja karbonatov zaradi dušikove kisline (posledica uporabe dušikovih gnojil in kislih usedlin iz zraka) glede na skupne koncentracije $(\text{Ca}^{2+}+\text{Mg}^{2+})$ in HCO_3^- v podzemni vodi v različnih mesecih v povprečju znašal med 11,1 % in 6,7 %, delež preperevanja karbonatov zaradi žveplove kisline (posledica kislih usedlin iz zraka) glede na skupne koncentracije $(\text{Ca}^{2+}+\text{Mg}^{2+})$ in HCO_3^- v podzemni vodi v različnih mesecih pa je v povprečju znašal med 20,4 % in 12,3 %; (3) Vsebnost $\delta^{13}\text{C}_{\text{DIC}}$ v podzemni vodi se v času deževne sezone občutno poveča skupaj z razmerjem $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$, obdobje gnojenja pa nakazuje, da uporaba dušikovih gnojil in usedanje kislin iz ozračja vplivajo na povišano vsebnost $\delta^{13}\text{C}_{\text{DIC}}$ in molarno razmerje $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ v podzemni vodi v rečnem sistemu QRS.

Ključne besede: preperevanje karbonatov, kraška podzemna voda, kmetijske dejavnosti, kisle usedline iz zraka, Qingmuguan, jugozahodna Kitajska.

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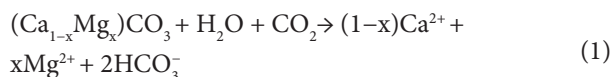
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INTRODUCTION

The geological-environmental characteristics of karst hydrological systems result in a highly vulnerable system, which is considerably sensitive to external environmental changes. While the increasing environmental pollution, both deliberate and unintentional forms as consequence of human activities, has to a great extent spoiled sensitive karst hydrological systems in Southwest China (Liu *et al.* 2006, 2008; Jiang *et al.* 2008, 2009a, 2009b; Jiang 2012; Pu *et al.* 2011). Concentrations of nitrate and sulphate of karst groundwater in southwest China increase notably as a result of large amount of chemical fertilizers used in agriculture (Liu *et al.* 2006; Jiang *et al.* 2008, 2009a, 2009b; Jiang 2012; Pu *et al.* 2011) and acid deposition (Li *et al.* 2008, 2010), which could not only influence the quality of karst groundwater, as well as the carbonate weathering process related to the global carbon cycle.

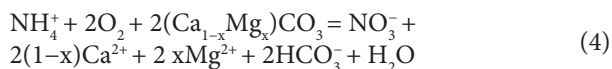
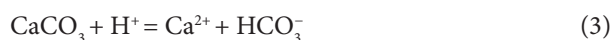
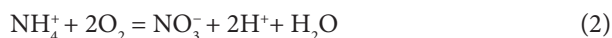
Conventionally, the DIC in karst groundwater is dominantly derived from carbonate dissolution by carbonic acid (Eq. 1), which forms from reaction of soil or atmospheric CO₂ with water.



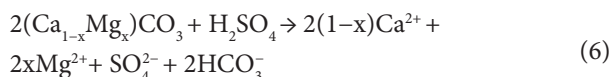
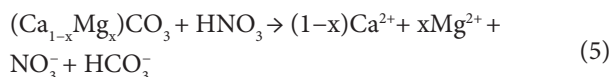
In this case, half of the DIC (generally, bicarbonate is the dominant DIC species in karst groundwater) in karst groundwater derived from soil/atmospheric CO₂ constitutes an important sink of atmospheric CO₂.

However, recently increases in the inorganic carbon flux in karst groundwater have been linked to agricultural activities and acid precipitation (Semhi *et al.* 2000; Calmels *et al.* 2007; Li *et al.* 2008, 2010; Perrin *et al.* 2008; Barnes & Raymond 2009; Ali & Atekwana 2011; Gandois *et al.* 2011; Jiang 2013; Yue *et al.* 2015).

The consequence of the use of nitrogen fertilizers (usually in the form of (CO(NH₂)₂), (NH₄)₂SO₄, NH₃ and (NH₄)₂PO₄, is the release of protons in the soil during the nitrification process. N fertiliser oxidation produces two protons for every nitrified ammonium ion and then enhances carbonate weathering. These processes can be expressed as following equations:



Acid deposition, including reactive N and sulfate, has dramatically increased worldwide in the past few decades, of which more than one third of the territory in China (Tang *et al.* 2010), especially in Southwest China, is suffering from acid deposition. Anthropogenic Nr is released to the atmosphere either as nitrogen oxides (NO_x), mainly from combustion, or as ammonia (NH₃), mainly from agriculture (Dentener *et al.* 2006; Paulot *et al.* 2013). NO_x is oxidized in the atmosphere to nitric acid (HNO₃) and ammonia can be transformed into NH₄⁺ through chemical reactions and then can be nitrified and produce proton. Sulfate is released to the atmosphere as SO_x, predominately from sulfur emissions (fossil fuel combustion) (Dentener *et al.* 2006), and SO_x can be oxidized in the atmosphere to sulfuric acid (H₂SO₄). Thus, acid deposition can impact carbonate weathering. These processes can be expressed as following equations:



In these cases, carbonate dissolution by nitric and sulphuric acids are resulting in greater DIC export, which is derived from the carbonate rather than from the CO₂ sequestration. Such enhanced carbonate weathering by anthropogenic acidity inputs could not only influence the element fluxes to riverine systems, as well as the global carbon cycle.

Thus, based on these knowledge, this paper presented the results of chemical analysis for the concentrations of major ions, DIC and δ¹³C–DIC of groundwater, and discussed: (1) to quantify the sources and fluxes of DIC in groundwater, and (2) to evaluate the effects of N–fertilizers and acid deposition on carbonate weathering in a small karstic agricultural catchment of Southwest China.

STUDY AREA

The Qingmuguan Underground River System (QRS) is located at the west of Chongqing municipality, Southwest China (Fig. 1). The underground drainage area of the system is approximately 11.4 km². The elevation of QRS is between 320~640 m above average sea level. The climate

is primarily subtropical monsoonal with a mean annual precipitation of 1100 mm and a mean air temperature of 16.5 °C. The monsoonal climate results in a rainy season from April to October and a dry season from November to March.

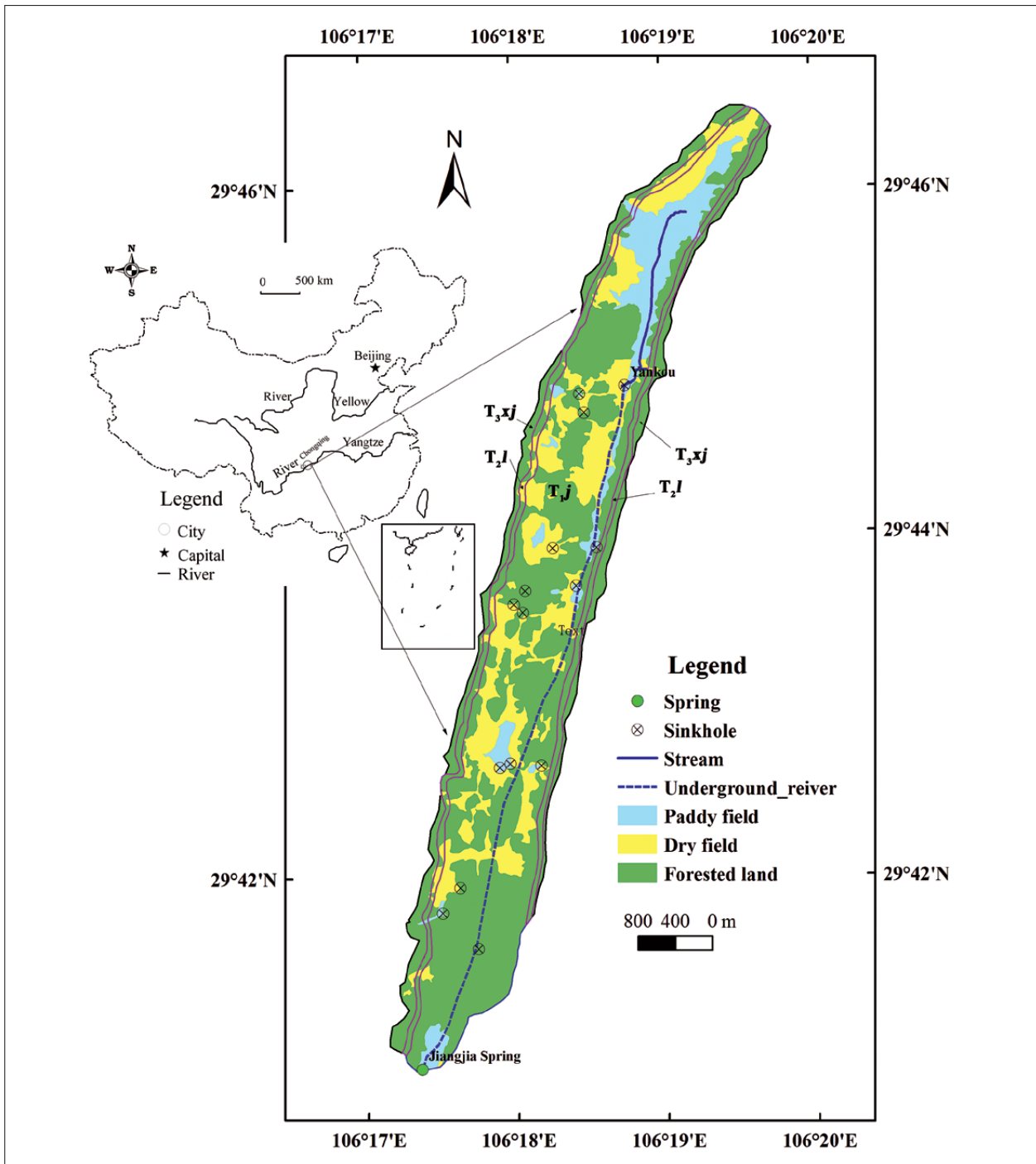


Fig. 1: Location, hydrogeological and land use map in the QRS.

GEOLOGY AND HYDROGEOLOGY

The geologic layers of the study area are shown in Fig. 1. The QURS lies in the middle part of the Wentangxia anticline, Chongqing, and the aquifers are mainly underlain by Lower and Middle Triassic strata (Fig. 1). Carbonate rocks (limestone) cover an area of 10 km² or about 88 % of the total area. The strata of the anticlinal axis are carbonate rocks of the *Lower Triassic Jialingjiang* Formation (T_{2j}), with limestone being a major lithology, whereas anticlinal wings are carbonate rocks of the Middle Triassic Leikoupo Formation (T_{2l}) and sandstones with some coal seams of the Upper Triassic Xujiahe Formation (T_{3xj}). Yellow-green calcareous clay rocks of the Lower Leikoupo (T_{2l}) overlie the *Jialingjiang* Group (T_{2j}). *No sulfate evaporates (gypsum and anhydrite) are exposed in the study area.* Due to the banded distribution of carbonate rocks and the presence of relatively impermeable sandstone at two wings combined with a vertical patulous cranny which was well developed in the anticlinal core, basic conditions exist for a formation of a karst trough valley and the development of a karst groundwater system. There are many depressions, caves, dolines and sinkholes in the catchment. In the upper stream, the surface water in Ganjiacao depression, which is the biggest depression, recharges the QURS via Yankou sinkhole. The Qingmuguan Underground River developed in the core of the karst trough valley and flowed along anticlinal axis (Lower Triassic Jialingjiang formation) in a NE–SW direction with a total length of 7.8 km. In the downstream reach of the QURS, the Jiangjia spring discharges the groundwater of the QURS. High-resolution tracer tests in the catchment indicated a single conduit

between Yankou sinkhole and Jiangjia spring (Fig. 1) (He *et al.* 2010), and the Jiangjia spring is the only outlet of the hydrological system. Flow rates of the spring have large variations around a year from 0.002 to 3.5 m³/s, with an average of 20.5 l/s. The spring water is used by individual households.

LAND USE PATTERN, VEGETATION, SOIL AND AGRICULTURAL PRACTICES

There are three land use categories (Fig. 1): forested land, paddy land and dry land. The percentages of land use were 64.9 for forested, 11.4 for paddy land and 23.7 for dry land, respectively. Paddy fields are mainly distributed in the Ganjiacao depression, and dry fields are scattered around the bottom of the valley. The crops are rice in paddy field, potato and vegetables in dry field.

Vegetation is predominantly subtropical evergreen broadleaved forests. Those plants and crops are C₃ photosynthetic type.

The dominant types of soils are mainly limestone soil and yellow soil derived from carbonate rocks and sandstones, respectively. Paddy soil are scattered in the depressions.

Farmers principally spread chemical fertilizers on soils in spring and summer seasons, mainly compound fertilizers of the N-P-K type and straight fertilizers such as urea (CO(NH₂)₂), NH₄HCO₃ and ammonium sulphate ((NH₄)₂SO₄). Typical amounts of chemical fertilizers used in the catchment are 1200 kg ha⁻¹ yr⁻¹ for rice, 600 kg ha⁻¹ yr⁻¹ for vegetables. Because soil pH and carbonate content are high, buffering with lime is not practiced.

SAMPLES AND ANALYSES

The rainfall was collected from the HOBO weather station (made by OnSET Ltd., USA) installed in the catchment, which the resolution of rainfall was 0.2 mm with a time interval of 15 min. The discharge, water temperature, pH and specific conductivity of groundwater were monitored at 15 min intervals using a Greenspan CTD 300 multi-channel data logger.

Monthly samples of groundwater were collected for analysis of major hydrochemical components and isotope in laboratory in 2013. Rainwater was collected during 3 events in the catchment from May to July, 2013.

Temperature, pH, specific conductivity (SC, at 25 °C) and dissolved oxygen (DO) of groundwater and rainwater were measured in the field using a WTW multiparameter probe (Multiline P3 PH/LF-SET) with reso-

lutions of 0.1 °C, 0.1, 1 μS cm⁻¹ and 0.1 mg L⁻¹, respectively. NH₄⁺ of groundwater and rainwater was measured in the field using a D8500 water quality multimeter (HACH, America), with resolution of 0.001mg/l. Ca²⁺ and HCO₃⁻ were determined by a test kit with a titration pipette (Aquamerck) in the field with resolutions of 2 mg/l and 0.1 mmol/l, respectively.

Water samples of the spring and rain were collected by injection syringes and were immediately filtered into pre-rinsed plastic containers (1 L) with 0.45 μm filter membranes for ion analyses, one of which was acidified to pH<2 with HNO₃ to preserve cation concentrations. To limit gas exchange, the plastic containers were cooled with ice. Samples for the stable carbon isotope of dissolved inorganic carbon (δ¹³C_{DIC}) analysis were filtered

into 10 mL tubes with 0.2 μm cellulose-acetate filters. Soon after collection, these samples were preserved using three drops of a saturated solution of HgCl_2 to prevent microbial alteration. All samples were kept refrigerated (below 4 $^\circ\text{C}$) until analysis.

Three representative plant samples (including the root, stem and leaf), rice, bamboo and Cyclobalanopsis, were collected in the catchment. Meanwhile, three soil CO_2 samples were collected, using a capillary tube reaching in 0.4–0.8 m depth and an evacuated glass vessel with Kontes valves, under the corresponding plants. Also, two limestone samples were collected from Lower Triassic Jialingjiang formation and Middle Triassic Leikoupo Formation, respectively.

Concentrations of major cations and anions were measured with inductively coupled plasma optical emission spectrometry (ICP-OES) with a resolution of 0.01 mg/l and ion chromatography (IC) with a resolution of 0.01 mg/l, respectively, at the Water Environmental Laboratory of Southwest University. The precision of the IC and ICP analyses was within $\pm 5\%$ for major elements.

For $\delta^{13}\text{C}_{\text{DIC}}$, using the modified method of Atkwana and Krishnamurthy (1998) for stable carbon isotope analysis of dissolved inorganic carbon, a 10 mL

water sample was injected by syringe into glass bottles that were pre-filled with 1 mL 85 % phosphoric acid and magnetic stir bars. The CO_2 was extracted and purified after cryogenic removal of H_2O using a liquid nitrogen–ethanol trap. Finally, the CO_2 was transferred cryogenically into a tube for isotope measurement.

Plant samples were ultrasonically cleaned for 15 min in deionized water, and dried in an oven at 50 $^\circ\text{C}$ for 48 h. Then, the plant samples were ground into powder with diameters less than 150 μm to ensure homogeneity, of which 1 to 2 mg was placed into stannum cups for carbon isotope analysis.

All analyses for $\delta^{13}\text{C}$ were done at the Geochemistry Laboratory of Southwest University. The carbon isotopic compositions of soil organic matter and plants were determined using an elemental analyzer coupled to an isotope-ratio mass spectrometer (EA-IRMS), and the carbon isotopic compositions of DIC, soil CO_2 and carbonate were determined using Gas Bench-linked with Delta V Plus gas stable isotope-ratio mass spectrometer (Gasbench-IRMS). The results were expressed on a conventional permil scale with respect to the Vienna Pee Dee Belemnite (V-PDB) standard. The overall experimental accuracy for $\delta^{13}\text{C}$ during this study was $\pm 0.2\%$.

RESULTS AND DISCUSSION

THE $\delta^{13}\text{C}$ OF LIMESTONE, PLANTS AND SOIL ORGANIC MATTER

Isotopic compositions ($\delta^{13}\text{C}$) of limestone, plants and soil CO_2 are shown in Tab. 1. The $\delta^{13}\text{C}$ of limestone from Jialingjiang and Leikoupo information was 0.2 ‰ and 0.3 ‰, respectively, consistent with typical values of marine limestone. The $\delta^{13}\text{C}$ of plants varied from –26.6 ‰

to –28.6 ‰ with an average value of –27.9 ‰, consistent with the major vegetation type using the C_3 carbon fixation pathway in the catchment. The $\delta^{13}\text{C}$ of soil CO_2 ranged from –22.6 ‰ to –24.3 ‰ with an average value of –23.3 ‰.

Tab. 1: Isotopic composition ($\delta^{13}\text{C}$) of limestone, plants and soil CO_2 in QURS.

Sample type		$\delta^{13}\text{C}$ (‰)
Limestone	Jialingjiang formation of Lower Triassic limestone (T ₁)	0.2
	Leikoupo Formation of Middle Triassic limestone (T ₂)	0.3
Plant	Rice	–28.6
	Bamboo	–28.4
	Cyclobalanopsis	–26.6
Soil CO_2	Soil CO_2 in a Rice field	–24.3
	Soil CO_2 in a Bamboo field	–23.1
	Soil CO_2 in a Cyclobalanopsis field	–22.6

THE $\delta^{13}\text{C}_{\text{DIC}}$ IN GROUNDWATER

From the range of pH values it can be deduced that bicarbonate (HCO_3^-) is the dominant DIC species of the groundwater in the catchment. Therefore, concentrations of total inorganic carbon are expressed as HCO_3^- in this article. As shown in Tab. 2, the $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater varied from –12.4 ‰ to –10.1 ‰ in different months, with a mean value of –11.2 ‰ in 2013 in the catchment. Also, as shown in Fig. 2, obvious positive $\delta^{13}\text{C}_{\text{DIC}}$ values of groundwater were observed in the rainy season and fertilizing period, and negative $\delta^{13}\text{C}_{\text{DIC}}$ values of groundwater were observed in the winter, suggesting the $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater was controlled by different geochemical processes in different seasons in the QURS.

Tab. 2: Major ions concentration and $\delta^{13}C_{DIC}$ of groundwater and rainwater in the QURS.

Month	Rainfall mm	pH	EC $\mu S/cm$	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	HCO ₃ ⁻ mg/l	Cl ⁻ mg/l	SO ₄ ²⁻ mg/l	NO ₃ ⁻ mg/l	NH ₄ ⁺ mg/l	DO mg/l	$\delta^{13}C_{DIC}$ ‰	Contribution of carbonate dissolution by carbonic acid to total DIC in groundwater %	Contribution of carbonate dissolution by nitric acid to total DIC in groundwater %	Contribution of carbonate dissolution by sulphuric acid to total DIC in groundwater %	Theoretical $\delta^{13}C_{DIC}$ ‰
Groundwater																		
1	16.0	7.9	596	107	9.60	9.4	5.6	336.0	14.5	23.1	12.5	Nd	6.2	-12.3	88.8	3.7	7.5	-12.4
2	14.6	8.0	605	104	9.8	9.6	5.5	324.9	14.6	25.1	14.4	Nd	6.4	-12.1	87.4	4.4	8.2	-12.2
3	23.8	8.1	624	105	9.6	9.9	5.7	332.3	14.4	25.2	15.5	Nd	6.6	-12.4	89.1	4.6	6.3	-12.5
4	99.0	7.8	616	110	12.1	11.6	5.3	314.0	16.4	43.1	25.2	Nd	6.8	-10.1	73.3	7.9	18.8	-10.3
5	108.6	7.6	633	117	11.3	11.3	5.1	327.2	14.3	56.3	35.5	Nd	6.8	-10.2	73.2	10.7	16.1	-10.2
6	106.3	7.4	678	131	13.5	18.2	3.4	382.5	18.5	59.1	38.2	Nd	7.1	-10.7	77.4	9.8	12.7	-10.8
7	95.2	7.5	664	131	14.5	15.3	4.2	378.6	18.1	58.9	37.7	Nd	7.3	-10.4	75.4	9.8	14.8	-10.6
8	60.4	7.4	655	126	13.6	14.5	3.6	367.4	18.2	56.3	35.7	Nd	7.2	-10.6	76.6	9.6	13.8	-10.7
9	136.0	7.7	647	118	12.3	13.7	3.3	355.5	17.9	44.5	22.5	Nd	7.1	-11.2	81.5	6.2	12.3	-11.4
10	76.3	7.6	643	114	12.4	13.5	3.3	350.6	17.6	41.7	19.8	Nd	6.9	-11.3	83.1	5.6	11.3	-11.6
11	38.9	7.7	633	115	12.1	13.2	3.2	349.6	17.5	38.2	14.9	Nd	6.8	-11.4	82.5	4.2	13.3	-11.6
12	7.0	7.9	593	103	11.8	12.3	3.4	323.8	17.3	32.6	12.3	Nd	6.2	-11.6	84.1	3.7	12.2	-11.8
Rainwater																		
5		4.9	190	11	0.4	0.3	0.9	12.4	1.70	12.6	6.8	0.58						
6		5.1	153	12	0.3	0.2	0.7	11.5	1.80	12.4	6.6	0.54						
7		5.0	145	12	0.3	0.2	0.7	15.4	1.70	11.6	7.5	0.49						

CHEMICAL CHARACTERISTICS OF GROUNDWATER AND RAINWATER

As shown in Tab. 2, the pH values of groundwater samples in the QURS ranged from 7.4 to 8.1, averaging 7.7. The Ca²⁺ concentrations in groundwater varied from 103 mg/l to 131 mg/l, with a mean value of 115 mg/l. The Mg²⁺ concentrations varied from 9.6 mg/l to 14.5 mg/l, with a mean value of 11.9 mg/l. Ca²⁺ and Mg²⁺ dominate the cation concentrations in groundwater, accounted for 82–86 % of the total cations in groundwater. The NH₄⁺ was not detected in the groundwater samples. HCO₃⁻ was the most abundant anions, and its concentrations ranged from 314.0 mg/l to 382.5 mg/l, averaging 345.2 mg/l. The SO₄²⁻ and NO₃⁻ concentrations varied dramatically, ranging from 23.1 mg/l to 59.1 mg/l and 12.3 mg/l to 38.2 mg/l in different months, with a mean concentration of 42.0 mg/l and 23.7 mg/l, respectively. The Cl⁻ ranged from 14.3 mg/l to 18.5 mg/l, with a mean concentration of 16.6 mg/l.

Rainwater showed lower pH values, ranging from 4.9 to 5.1, typically characterized by acid rain. Concentrations of Ca²⁺, SO₄²⁻ and NO₃⁻ in rainwater ranged from 11 mg/l to 12 mg/l, 11.6 mg/l to 12.6 mg/l and 6.6 mg/l to 7.5 mg/l, respectively. And other ions concentrations were very low in rainwater.

Meanwhile, as shown in Fig. 2, pH showed lower values in rainy season and higher values in the winter, indicating pH was impacted by the dilution effect of rainwater with lower pH in the rainy season. In contrast, the concentrations of Ca²⁺, Mg²⁺, HCO₃⁻, NO₃⁻ and SO₄²⁻ in groundwater tended to be enriched in rainy season, and the dilution effect of rainfall has not been observed in these ions of groundwater, suggesting these ions were impacted by some geochemical processes which are different from other seasons.

RELATIONSHIP BETWEEN (Ca²⁺+Mg²⁺) AND HCO₃⁻ IN GROUNDWATER

As shown in Figure 3a, the molar ratio between (Ca²⁺+Mg²⁺) and HCO₃⁻ of groundwater in the QURS varied from 0.56 to 0.63 with a mean value of 0.60 in different months, which higher molar ratio between (Ca²⁺+Mg²⁺) and HCO₃⁻ of groundwater were observed in the rainy season and fertilizing period. As indicated by Equation (1), the molar ratio between (Ca²⁺+Mg²⁺) and HCO₃⁻ released into the groundwater should be 0.5, suggesting that carbonate dissolution is controlled by natural processes involving carbonic

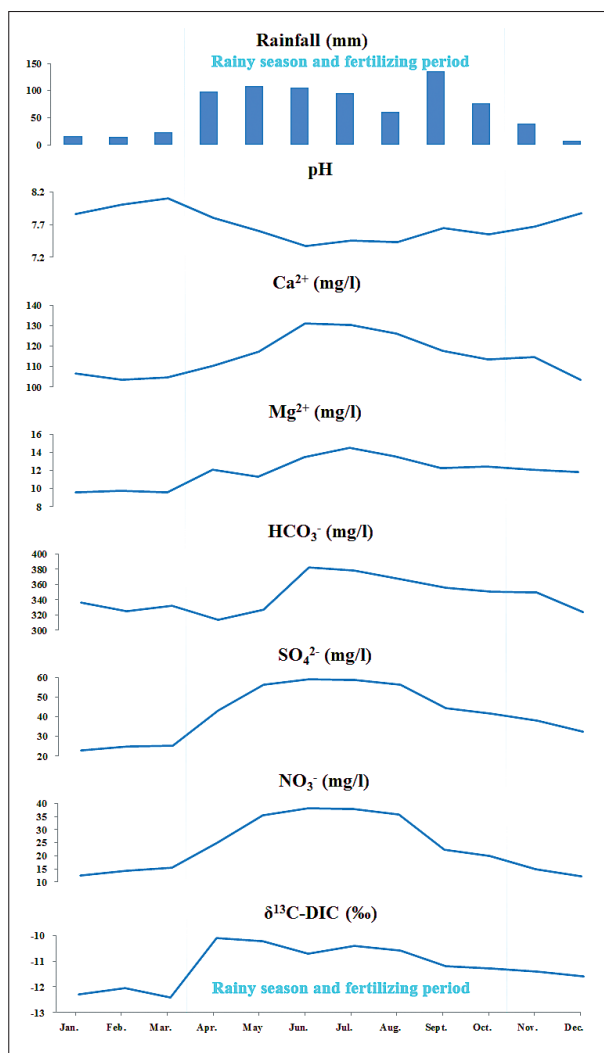


Fig. 2: Seasonal variations of rainfall and hydrogeochemistry of groundwater in 2013.

acid. However, as indicated by Equation (4), (5) and (6), the molar ratio between $(Ca^{2+}+Mg^{2+})$ and HCO_3^- released into the groundwater should be 1, suggesting that carbonate dissolution is governed by sulphuric/nitric acid. These suggested that carbonic acid could probably not be a unique weathering agent in the catchment. Mean-

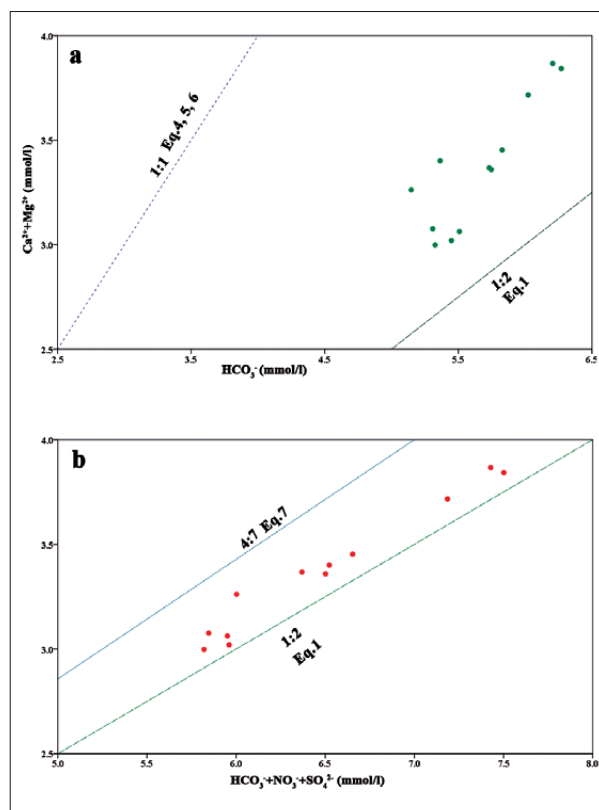


Fig. 3: Cross plot of $(Ca^{2+}+Mg^{2+})$ vs. HCO_3^- (a) and $(Ca^{2+}+Mg^{2+})$ vs. $(HCO_3^-+NO_3^-+SO_4^{2-})$ (b) in groundwater.

while, as stated in section 4.3, higher concentrations of Ca^{2+} , Mg^{2+} , HCO_3^- , NO_3^- and SO_4^{2-} of groundwater were observed the rainy season and fertilizing period, suggesting that among the different sources of protons mentioned in the introduction, fertilizers as well as atmospheric acid deposition may play an important role in the carbonate weathering in the catchment. Therefore, the questions arised whether those elements in groundwater originated from carbonate dissolution by carbonic and sulphuric/nitric acids and to which extent of carbonate dissolution were influenced by different acids in different months.

DISCUSSION

ATMOSPHERIC INPUTS

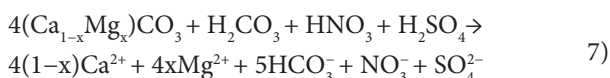
Compared to groundwater, the rainwater showed very low concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- , however, high concentrations of NO_3^- and SO_4^{2-} in the catchment. Therefore, it might be concluded that Ca^{2+} , Mg^{2+} and

HCO_3^- supplied by atmospheric inputs are low, but nitrate and sulfate inputs are significant. The highest values of nitrate and sulfate were observed during local fertilizer spreading period, suggesting that they partly originate from fertilizer inputs. Meanwhile, a significant amount

of NH_4^+ is supplied to the catchment by rainwater, but NH_4^+ was not detected in groundwater, which could be presumably nitrified in the catchment by soil bacteria and used by plants.

HYDROCHEMISTRY OF GROUNDWATER: CARBONATE DISSOLUTION BY CARBONIC ACID VERSUS SULPHURIC AND NITRIC SULPHURIC ACIDS

As atmospheric inputs of Ca^{2+} , Mg^{2+} and HCO_3^- are very low, and the silicate weathering originated from sandstone with slow dissolution can be neglected, the concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- were mainly originated from carbonate dissolution in the catchment. If the contributions of carbonic, sulphuric and nitric acids in equimolar amounts to the carbonate dissolution were considered, carbonate dissolution becomes (Eq. 7):



In this case, the molar ratio between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- , and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{HCO}_3^- + \text{NO}_3^- + \text{SO}_4^{2-})$ in groundwater should be 4/5 (0.8) and 4/7 (0.571). However, the molar ratio between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- , $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{HCO}_3^- + \text{NO}_3^- + \text{SO}_4^{2-})$ of groundwater in different varied from 0.56 to 0.63 with a mean value of 0.60, and from 0.51 to 0.54 with a mean value of 0.52 (Figs. 3a and 3b), which deviate from the expected the molar ratio of 0.8 and 0.57, respectively, indicating carbonate dissolution in those groundwaters controlled by carbonic, sulphuric and nitric acids in different ratios. Meanwhile, it could be assumed that all NO_3^- in groundwater could be derived from the nitrification of fertilizer and atmospheric NH_4^+ , and oxidation of atmospheric NO_x , due to other NO_3^- sources in the catchment.

Thus, based on the (1), (5) and (6), the concentrations of $[\text{Ca}^{2+} + \text{Mg}^{2+}]$ and HCO_3^- in groundwater resulted from the carbonate dissolution by carbonic, nitric and sulphuric acids can be calculated by following equations:

$$\begin{aligned} [\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate dissolution by carbonic acid}} &= \\ 1/2[\text{HCO}_3^-]_{\text{carbonate dissolution by carbonic acid}} &= \\ [(\text{HCO}_3^-)_{\text{groundwater}} - (\text{Ca}^{2+} + \text{Mg}^{2+})]_{\text{groundwater}} & \end{aligned} \quad (8)$$

$$\begin{aligned} [\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate dissolution by nitric acid}} &= \\ [\text{HCO}_3^-]_{\text{carbonate dissolution by nitric acid}} = [\text{NO}_3^-]_{\text{groundwater}} & \end{aligned} \quad (9)$$

$$\begin{aligned} [\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate dissolution by sulphuric acid}} &= \\ [\text{HCO}_3^-]_{\text{carbonate dissolution by sulphuric acid}} &= \\ 2(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{groundwater}} - (\text{HCO}_3^-)_{\text{groundwater}} - & \\ (\text{NO}_3^-)_{\text{groundwater}} & \end{aligned} \quad (10)$$

The calculated results are presented in Tab. 2. The contributions of carbonate dissolution by carbonic acid to total concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- of groundwater in different months varied from 57.7 % to 80.4 % with mean percentage of 68.5 %, and from 73.2 % to 89.1 % with a mean percentage of 81 %, respectively. While the contributions of carbonate dissolution by nitric and sulphuric acids to total concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- of groundwater in different months varied from 6.4 % to 16.8 % with a mean percentage of 11.1 %, and 3.7 % to 10.7 % with a mean percentage of 6.7 %, and from 11.3 % to 29.7 % with a mean percentage of 20.4 % and 6.3 % to 18.8 % with a mean percentage of 12.3 %, respectively. Especially, the contributions of carbonate dissolution by carbonic acid to total concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- of groundwater averaged only 63 % and 77 %, while the contributions of carbonate dissolution by nitric and sulphuric acids to total concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- of groundwater averaged 37 % and 23 % in rainy season and fertilizing period (from Apr. to Oct.). Therefore, based on the hydrochemical data, it can be concluded that carbonate dissolution was not only controlled by carbonic acid, but also by sulphuric and nitric acids introduced by the use of N-fertilizers and atmospheric acid deposition in the catchment.

THE $\delta^{13}\text{C}_{\text{DIC}}$ IN GROUNDWATER: CARBONATE DISSOLUTION BY CARBONIC ACID VERSUS NITRIC AND SULPHURIC ACIDS

Because the contribution of atmospheric CO_2 to the DIC of groundwater was minor due to the high partial pressure of CO_2 in groundwater, the DIC of groundwater in the catchment had two primary sources, soil CO_2 and carbonate bedrock. The $\delta^{13}\text{C}$ of soil CO_2 and limestone averaged -23.3 ‰ and 0.25 ‰, respectively. Meanwhile, groundwater showed higher DO (Dissolved oxygen) concentrations in different months, indicating it is an open karst system. In general, the fractionation of the carbon isotope composition was around $+9$ ‰ between soil gas CO_2 and HCO_3^- (Deines 2004; Zhang *et al.* 1995). Therefore, DIC in groundwater originated from carbonate dissolving by CO_2 in the catchment was expected to have $\delta^{13}\text{C}_{\text{DIC}}$ value of around -14 ‰. While the $\delta^{13}\text{C}_{\text{DIC}}$ had identical values to the $\delta^{13}\text{C}$ of carbonate (0.25 ‰) which DIC was derived from carbonate dissolving by sulfur acid or nitric acid. Thus, the $\delta^{13}\text{C}_{\text{DIC}}$ in ground-

water approaching a value of -14‰ indicated the DIC resulted from carbonate dissolving by soil CO_2 , while the $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater varying from 0‰ to -14‰ suggested the DIC resulted from carbonate dissolving by soil CO_2 , HNO_3 and H_2SO_4 in the catchment. As shown in Tab. 2, the $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater varied from -12.4‰ to -10.1‰ in different months, which deviate from the expected the $\delta^{13}\text{C}_{\text{DIC}}$ (-14‰) of groundwater which DIC is derived from carbonate dissolving by natural soil CO_2 , suggesting that the DIC of groundwater not only resulted from carbonate dissolving by natural soil CO_2 , but also from carbonate dissolving by sulfur and nitric acids in the catchment in the QURS.

Thus, given the $\delta^{13}\text{C}_{\text{soil CO}_2}$ (-23.3‰), $\delta^{13}\text{C}_{\text{carbonate}}$ (0.25‰) and fractionation of isotopic compositions ($+9\text{‰}$) in groundwater system, the theoretical $\delta^{13}\text{C}_{\text{DIC}}$ value of groundwater that DIC was derived from different sources (carbonate dissolution and soil CO_2) can be calculated by the following equation:

$$\delta^{13}\text{C}_{\text{DIC}} = \left[\frac{\sum_0^i (mC_i)(\delta^{13}\text{C}_i)}{\sum_0^i (mC_i)} \right] \quad (11)$$

where $\delta^{13}\text{C}_{\text{DIC}}$ is the theoretical $\delta^{13}\text{C}_{\text{DIC}}$ value of groundwater, mC_i is the molality of added DIC from the i th source (carbonate dissolution by carbonic acid and sulphuric/nitric acids, respectively), and the $\delta^{13}\text{C}_i$ is $\delta^{13}\text{C}$ composition of added DIC from the i th source (soil CO_2 and carbonate).

The calculated results of the theoretical $\delta^{13}\text{C}_{\text{DIC}}$ values of groundwater are shown in Tab. 2. The measured $\delta^{13}\text{C}_{\text{DIC}}$ value of monthly groundwater sample is much closed to its corresponding calculated $\delta^{13}\text{C}_{\text{DIC}}$ value. Thus, the elevated $\delta^{13}\text{C}_{\text{DIC}}$ (varying from -11.1‰ to -10.3‰ with an average of -10.6‰) of groundwater in the rainy season and fertilizing period suggested that carbonate dissolving was significantly influenced by nitric and sulphuric acids originated from the use of N-fertilizers and atmospheric acid deposition in the catchment.

As indicated in Fig. 2, the $\delta^{13}\text{C}_{\text{DIC}}$ increased with DIC in groundwater collected from the rainy season and fertilizing period, indicating that the use of N-fertilizers

and atmospheric acid deposition could be responsible for the elevated DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in the catchment. Meanwhile, an intense positive relationship between the $\delta^{13}\text{C}_{\text{DIC}}$ and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ was observed (Fig. 4). The $\delta^{13}\text{C}_{\text{DIC}}$ increased obviously with $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ in groundwater collected from the rainy season and fertilizing period, indicating that the use of N-fertilizers and atmospheric acid deposition could be responsible for the elevated the $\delta^{13}\text{C}_{\text{DIC}}$ and the molar ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater. Also, as indicated by Fig. 4, the $\delta^{13}\text{C}_{\text{DIC}}$ varying from -10‰ to -12.5‰ , with a variational molar ratio between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- of 0.53 to 0.63 of groundwater in different months, indicated the carbonate was

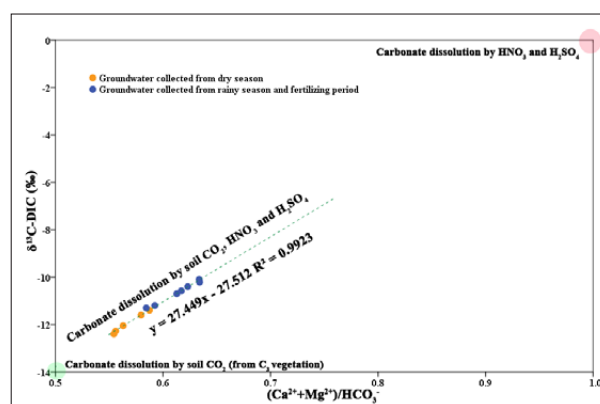


Fig. 4: Cross plot of (a) $\delta^{13}\text{C}_{\text{DIC}}$ vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater in different seasons.

dissolved by soil CO_2 (from C_3 vegetation), HNO_3 and H_2SO_4 in the catchment. Thus, the evidences from both of the chemical data and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in different months indicated that carbonate dissolution was controlled by natural carbonic acid, and nitric and sulphuric acids originated from the use of N-fertilizers and atmospheric acid deposition in the QURS.

CONCLUSIONS

Although the results of this study are preliminary and the effects of the use of N-fertilizers and acid deposition on carbonate weathering have been quantified in a small karstic agricultural catchment of Southwest China.

The significant temporal variations for major element concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in different months were observed in the QURS. The groundwater collected in rainy season and fertilizing period showed significant high concentrations of DIC, Ca^{2+} ,

Mg^{2+} , NO_3^- , SO_4^{2-} and $\delta^{13}\text{C}_{\text{DIC}}$. These temporal variations could be attributed to carbonate dissolution by natural carbonic acid, and nitric and sulphuric acids introduced by the use of N-fertilizers and atmospheric acid deposition in the QURS.

The contributions of carbonate dissolution by carbonic acid to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater in different months averaged 68.5 % and 81 %, respectively. While the contributions of carbonate dissolution by nitric and sulphuric acids originated from the use of N-fertilizers and atmospheric acid deposition to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater in different months averaged 11.1 % and 6.7 %, and 20.4 % and 12.3 %, respectively. Especially, the contributions of carbonate dissolution by carbonic acid to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater averaged only 63 % and 77 %, while the contributions of carbonate dissolution by nitric and sulphuric acids to total concentrations of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- of groundwater averaged 37 % and 23 % in rainy season and fertilizing period (from Apr. to Oct.).

The temporal variations of $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater (varying from -12.4 ‰ to -10.1 ‰) in different months

deviated from the expected the $\delta^{13}\text{C}_{\text{DIC}}$ (-14 ‰) of groundwater which DIC is derived from carbonate dissolving by natural soil CO_2 , suggesting that the DIC of groundwater not only resulted from carbonate dissolving by natural soil CO_2 , but also from carbonate dissolving by sulfur and nitric acids in the QURS. Meanwhile, the $\delta^{13}\text{C}_{\text{DIC}}$ increased obviously with $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater in the rainy season and fertilizing period, indicating that the use of N-fertilizers and atmospheric acid deposition should be responsible for the elevated the $\delta^{13}\text{C}_{\text{DIC}}$ and the molar ratio of $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ of groundwater in the QURS.

Thus, the evidences from both of the hydrochemical data and $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater in different months indicated that carbonate dissolution was not only controlled by natural carbonic acid, but also by sulphuric and nitric acids introduced by the use of N-fertilizers and atmospheric acid deposition in the QURS. More important is that not only the concentrations of nitrate and sulphate in karst groundwater have been elevated, but also the exports of inorganic carbon and $(\text{Ca}^{2+}+\text{Mg}^{2+})$ have been enhanced due to carbonate weathering by nitric and sulphuric acids originated from the use of N-fertilizers and atmospheric acid deposition in the catchment.

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