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

Yu CHEN¹ & Yongjun JIANG¹,²*

Abstract
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 δ¹³C of groundwater in Qingmuguan underground river system (QURS) – a small karstic agricultural catchment of Southwest China. The results show that: (1) the significant temporal variations for major element concentrations and δ¹³C of groundwater in different months were observed, especially, of which the groundwater showed significant high concentrations of DIC, Ca²⁺, Mg²⁺, NO₃⁻, SO₄²⁻ and δ¹³C in rainy season and fertilizing period in the QURS; (2) the contributions of carbonate dissolution by carbonic acid to total concentrations of (Ca²⁺+Mg²⁺) and HCO₃⁻ 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 (Ca²⁺+Mg²⁺) and HCO₃⁻ 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 (Ca²⁺+Mg²⁺) and HCO₃⁻ of groundwater in different months averaged 20.4 % and 12.3 %, respectively; (3) the δ¹³C increased obviously with (Ca²⁺+Mg²⁺)/HCO₃⁻ 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 δ¹³C and the molar ratio of (Ca²⁺+Mg²⁺)/HCO₃⁻ of groundwater in the QURS.

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

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

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 hidrokrimičnih postopkov in analize δ¹³C. Podzemne vode v kraškem zaledju reke Quinmugan (QURS), ki je del manjšega kmetijskega območja na jugozahodu Kitajsko. Rezultati so pokazali naslednje: (1) Izmerjene so bile opazne časovne spremembe v koncentracijah glavnih elementov in δ¹³C v podzemni vodi v različnih mesecih; to je še posebej očitno v deževnem obdobju in času gnogenja, ko so bile zabeležene izrazito povečane koncentracije DIC, Ca²⁺, Mg²⁺, NO₃⁻, SO₄²⁻ in δ¹³C; (2) Delež preperevanja karbonatov zaradi oglikove kisline je glede na skupne koncentracije (Ca²⁺+Mg²⁺) in HCO₃⁻ 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 (Ca²⁺+Mg²⁺) in HCO₃⁻ 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 (Ca²⁺+Mg²⁺) in HCO₃⁻ v podzemni vodi v različnih mesecih pa je v povprečju znašal med 20,4 % in 12,3 %; (3) Vsebnost δ¹³C v podzemni vodi se v času deževne sezone občutno poveča skupaj z razmerjem (Ca²⁺+Mg²⁺)/HCO₃⁻, obdobje gnogenja pa nakazuje, da uporaba dušikovih gnojil in usage kisiln iz ozračja vplivajo na povišano vsebnost δ¹³C in molarno razmerje (Ca²⁺+Mg²⁺)/HCO₃⁻ v podzemni vodi v rečnem sistemu QURS.

Ključne besede: preperevanje karbonatov, kraška podzemna voda, kmetijske dejavnosti, kisle usedline iz zraka, Qingmuguan, jugozahodna Kitajska.
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 CO$_2$ with water.

$$\text{(Ca}_{1-x}\text{Mg}_x\text{PO}_4\text{)} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow (1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}_3^- \quad (1)$$

In this case, half of the DIC (generally, bicarbonate is the dominant DIC species in karst groundwater) in karst groundwater derived from soil/atmospheric CO$_2$ constitutes an important sink of atmospheric CO$_2$.

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(NH$_2$)$_2$), (NH$_4$)$_2$SO$_4$, NH$_3$ and (NH$_4$)$_2$PO$_4$) 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:

$$\text{NH}_4^+ + 2\text{O}_2 = \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \quad (2)$$

$$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \quad (3)$$

$$\text{NH}_4^+ + 2\text{O}_2 + 2(\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3) = \text{NO}_3^- + 2(1-x)\text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{H}_2\text{O} \quad (4)$$

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 (NOx), mainly from combustion, or as ammonia (NH$_3$), mainly from agriculture (Dentener et al. 2006; Paulot et al. 2013). NOx is oxidized in the atmosphere to nitric acid (HNO$_3$) and ammonia can be transformed into NH$_3$ through chemical reactions and then can be nitrified and produce proton. Sulfate is released to the atmosphere as SOx, predominately from sulfur emissions (fossil fuel combustion) (Dentener et al. 2006), and SOx can be oxidized in the atmosphere to sulfuric acid (H$_2$SO$_4$). Thus, acid deposition can impact carbonate weathering. These processes can be expressed as following equations:

$$(\text{Ca}_{1-x}\text{Mg}_x\text{PO}_4\text{}) + \text{HNO}_3 \rightarrow (1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + \text{NO}_3^- + \text{HCO}_3^- \quad (5)$$

$$2(\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3) + \text{H}_2\text{SO}_4 \rightarrow 2(1-x)\text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{SO}_4^{2-} + 2\text{HCO}_3^- \quad (6)$$

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 CO$_2$ 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 $\delta^{13}$C–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.
The Qingmuguan Underground River System (QURS) 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 QURS 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 QURS.
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.j), with limestone being a major lithology, whereas anticlinal wings are carbonate rocks of the Middle Triassic Leikoupo Formation (T.l) and sandstones with some coal seams of the Upper Triassic Xujiahe Formation (T.xf). Yellow-green calcareous clay rocks of the Lower Leikoupo (T.l) overlie the Jialingjiang Group (T.j). 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 Ganjiaocao 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 internal of 15 min. The discharge, water temperature, pH and specific conductivity of groundwater were monitored at 15 min intervals using a Greenspan CTDP 300 multi-channel data logger.

Monthly samples of groundwater were collected for analysis of major hydrochemical components and isotopes 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 resolutions 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 (δ¹³CDOC) 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 HgCl₂ to prevent microbial alteration. All samples were kept refrigerated (below 4 °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 CO₂ 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 ±5 % for major elements.

For δ¹³C, using the modified method of Atekwnana 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 CO₂ was extracted and purified after cryogenic removal of H₂O using a liquid nitrogen–ethanol trap. Finally, the CO₂ 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 °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 δ¹³C 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 CO₂ 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 δ¹³C during this study was ±0.2 ‰.

RESULTS AND DISCUSSION

THE δ¹³C OF LIMESTONE, PLANTS AND SOIL

ORGANIC MATTER

Isotopic compositions (δ¹³C) of limestone, plants and soil CO₂ are shown in Tab. 1. The δ¹³C of limestone from Jininglingjiang and Leikoupo information was 0.2 ‰ and 0.3 ‰, respectively, consistent with typical values of marine limestone. The δ¹³C of plants varied from −26.6 ‰ to −28.6 ‰ with an average value of −27.9 ‰, consistent with the major vegetation type using the C₄ carbon fixation pathway in the catchment. The δ¹³C of soil CO₂ ranged from −22.6 ‰ to −24.3 ‰ with an average value of −23.3 ‰.

THE δ¹³C DIC IN GROUNDWATER

From the range of pH values it can be deduced that bicarbonate (HCO₃⁻) is the dominant DIC species of the groundwater in the catchment. Therefore, concentrations of total inorganic carbon are expressed as HCO₃⁻ in this article. As shown in Tab. 2, the δ¹³C 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 δ¹³C DIC values of groundwater were observed in the rainy season and fertilizing period, and negative δ¹³C DIC values of groundwater were observed in the winter, suggesting the δ¹³C DIC of groundwater was controlled by different geochemical processes in different seasons in the QURS.

Tab. 1: Isotopic composition (δ¹³C) of limestone, plants and soil CO₂ in QURS.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>δ¹³C‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td></td>
</tr>
<tr>
<td>Jilingjiang formation of Lower Triassic limestone (T₁jl)</td>
<td>0.2</td>
</tr>
<tr>
<td>Leikoupo Formation of Middle Triassic Limestone (T₁jl)</td>
<td>0.3</td>
</tr>
<tr>
<td>Plant</td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>−28.6</td>
</tr>
<tr>
<td>Bamboo</td>
<td>−28.4</td>
</tr>
<tr>
<td>Cyclobalanopsis</td>
<td>−26.6</td>
</tr>
<tr>
<td>Soil CO₂</td>
<td></td>
</tr>
<tr>
<td>Soil CO₂ in a Rice field</td>
<td>−24.3</td>
</tr>
<tr>
<td>Soil CO₂ in a Bamboo field</td>
<td>−23.1</td>
</tr>
<tr>
<td>Soil CO₂ in a Cyclobalanopsis field</td>
<td>−22.6</td>
</tr>
</tbody>
</table>
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 Ca\(^{2+}\) concentrations in groundwater varied from 103 mg/l to 131 mg/l, with a mean value of 115 mg/l. The Mg\(^{2+}\) concentrations varied from 9.6 mg/l to 14.5 mg/l, with a mean value of 11.9 mg/l. Ca\(^{2+}\) and Mg\(^{2+}\) dominate the cation concentrations in groundwater, accounted for 82–86 % of the total cations in groundwater. The NH\(_4\)\(^+\) was not detected in the groundwater samples. HCO\(_3\)\(^-\) 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 SO\(_4\)\(^{2-}\) and NO\(_3\)\(^-\) 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 Ca\(^{2+}\), SO\(_4\)\(^{2-}\) and NO\(_3\)\(^-\) 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 Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\)\(^-\), NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) 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.

### CHEMICAL CHARACTERISTICS OF GROUNDWATER AND RAINWATER

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#### RELATIONSHIP BETWEEN (Ca\(^{2+}\)+Mg\(^{2+}\)) AND HCO\(_3\)\(^-\) IN GROUNDWATER

As shown in Figure 3a, the molar ratio between (Ca\(^{2+}\)+Mg\(^{2+}\)) and HCO\(_3\)\(^-\) 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 (Ca\(^{2+}\)+Mg\(^{2+}\)) and HCO\(_3\)\(^-\) of groundwater were observed in the rainy season and fertilizing period. As indicated by Equation (1), the molar ratio between (Ca\(^{2+}\)+Mg\(^{2+}\)) and HCO\(_3\)\(^-\) released into the groundwater should be 0.5, suggesting that carbonate dissolution is controlled by natural processes involving carbonic
However, as indicated by Equation (4), (5) and (6), the molar ratio between \((\text{Ca}^{2+} + \text{Mg}^{2+})\) and \(\text{HCO}_3^-\) 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-

while, as stated in section 4.3, higher concentrations of \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{HCO}_3^-\), \(\text{NO}_3^-\) and \(\text{SO}_4^{2-}\) 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 \(\text{Ca}^{2+}, \text{Mg}^{2+}\) and \(\text{HCO}_3^-\), however, high concentrations of \(\text{NO}_3^-\) and \(\text{SO}_4^{2-}\) in the catchment. Therefore, it might be concluded that \(\text{Ca}^{2+}, \text{Mg}^{2+}\) and \(\text{HCO}_3^-\) 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\textsubscript{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 ACIDS**

As atmospheric inputs of Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and HCO\textsubscript{3} are very low, and the silicate weathering originated from sandstone with slow dissolution can be neglected, the concentrations of Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and HCO\textsubscript{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):

$$4(Ca_{1-x}Mg_x)CO_3 + H_2CO_3 + HNO_3 + H_2SO_4 \rightarrow 4(1-x)Ca^{2+} + 4xMg^{2+} + 5HCO_3^- + NO_3^- + SO_4^{2-}$$ (7)

In this case, the molar ratio between (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{3} and (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and (HCO\textsubscript{3}+NO\textsubscript{3}+SO\textsubscript{4}\textsuperscript{2-}) in groundwater should be 4/5 (0.8) and 4/7 (0.571). However, the molar ratio between (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{3}, (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and (HCO\textsubscript{3}+NO\textsubscript{3}+SO\textsubscript{4}\textsuperscript{2-}) of groundwater in different months 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\textsubscript{3} in groundwater could be derived from the nitrification of fertilizer and atmospheric NH\textsubscript{3}, and oxidation of atmospheric NO\textsubscript{x}, due to other NO\textsubscript{3} sources in the catchment.

Thus, based on the (1), (5) and (6), the concentrations of [Ca\textsuperscript{2+}+Mg\textsuperscript{2+}] and HCO\textsubscript{3} in groundwater resulted from the carbonate dissolution by carbonic, nitric and sulphuric acids can be calculated by following equations:

$$[Ca^{2+}+Mg^{2+}]_{groundwater} \times \delta^{13}C_{DIC}$$

$$\delta^{13}C_{DIC} = \delta^{13}C_{DIC}^{soil}$$

$$\delta^{13}C_{DIC}^{soil} = \delta^{13}C_{DIC}^{watershed}$$

$$\delta^{13}C_{DIC}^{watershed} = \delta^{13}C_{DIC}^{catchment}$$

$$\delta^{13}C_{DIC}^{catchment} = \delta^{13}C_{DIC}^{soil}$$

The calculated results are presented in Tab. 2. The contributions of carbonate dissolution by carbonic acid to total concentrations of (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{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 acid to total concentrations of (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{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 (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{3} of groundwater averaged only 63 % and 77 %, while the contributions of carbonate dissolution by nitric and sulphuric acids to total concentrations of (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) and HCO\textsubscript{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 δ\textsuperscript{13}C\textsubscript{DIC} IN GROUNDWATER: CARBONATE DISSOLUTION BY CARBONIC ACID VERSUS NITRIC AND SULPHURIC ACIDS**

Because the contribution of atmospheric CO\textsubscript{2} to the DIC of groundwater was minor due to the high partial pressure of CO\textsubscript{2} in groundwater, the DIC of groundwater in the catchment had two primary sources, soil CO\textsubscript{2} and carbonate bedrock. The δ\textsuperscript{13}C of soil CO\textsubscript{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\textsubscript{2} and HCO\textsubscript{3}. Therefore, DIC in groundwater originated from carbonate dissolving by CO\textsubscript{2} in the catchment was expected to have δ\textsuperscript{13}C\textsubscript{DIC} value of around –14 ‰. While the δ\textsuperscript{13}C\textsubscript{DIC} had identical values to the δ\textsuperscript{13}C of carbonate (0.25 ‰), which DIC was derived from carbonate dissolving by sulfur acid or nitric acid. Thus, the δ\textsuperscript{13}C\textsubscript{DIC} in ground-
THE EFFECTS OF AGRICULTURAL ACTIVITIES AND ATMOSPHERIC ACID DEPOSITION ON CARBONATE...

The significant temporal variations for major element concentrations and $\delta^{13}C_{DIC}$ 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$^{2+}$, and atmospheric acid deposition could be responsible for the elevated DIC concentrations and $\delta^{13}C_{DIC}$ of groundwater in the catchment. Meanwhile, an intense positive relationship between the $\delta^{13}C_{DIC}$ and (Ca$^{2+}$+Mg$^{2+}$)/HCO$_3^-$ was observed (Fig. 4). The $\delta^{13}C_{DIC}$ increased obviously with (Ca$^{2+}$+Mg$^{2+}$)/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 $\delta^{13}C_{DIC}$ and the molar ratio of (Ca$^{2+}$+Mg$^{2+}$)/HCO$_3^-$ of groundwater. Also, as indicated by Fig. 4, the $\delta^{13}C_{DIC}$ varying from −10‰ to −12.5‰, with a variational molar ratio between (Ca$^{2+}$+Mg$^{2+}$) and HCO$_3^-$ of 0.53 to 0.63 of groundwater in different months, indicated the carbonate was dissolved by soil CO$_2$ (from C$_3$ vegetation), HNO$_3$ and H$_2$SO$_4$ in the catchment. Thus, the evidences from both of the chemical data and $\delta^{13}C_{DIC}$ 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.
Mg²⁺, NO₃⁻, SO₄²⁻ and δ¹³C(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 (Ca²⁺+Mg²⁺) and HCO₃⁻ 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 (Ca²⁺+Mg²⁺) and HCO₃⁻ 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 (Ca²⁺+Mg²⁺) and HCO₃⁻ of groundwater averaged only 63 % and 77 %, while the contributions of carbonate dissolution by nitric and sulphuric acids to total concentrations of (Ca²⁺+Mg²⁺) and HCO₃⁻ of groundwater averaged 37 % and 23 % in rainy season and fertilizing period (from Apr. to Oct.).

The temporal variations of δ¹³C(DIC) in groundwater (varying from −12.4 ‰ to −10.1 ‰) in different months deviated from the expected the δ¹³C(DIC) (−14 ‰) of groundwater which DIC is derived from carbonate dissolving by natural soil CO₂, suggesting that the DIC of groundwater not only resulted from carbonate dissolving by natural soil CO₂, but also from carbonate dissolving by sulfur and nitric acids in the QURS. Meanwhile, the δ¹³C(DIC) increased obviously with (Ca²⁺+Mg²⁺)/HCO₃⁻ 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 δ¹³C(DIC) and the molar ratio of (Ca²⁺+Mg²⁺)/HCO₃⁻ of groundwater in the QURS.

Thus, the evidences from both of the hydrochemical data and δ¹³C(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 (Ca²⁺+Mg²⁺) 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.

ACKNOWLEDGMENTS

This work is financially supported by National Natural Science Foundation of China (Grant Nos. 41472321 and 41172331), and IGCP598.

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