Influence of Anthropogenic Sulfuric Acid on Different Lithological Carbonate Weathering and the Related Carbon Sink Budget: Examples from Southwest China

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Abstract: Accurate estimate of carbonate weathering and the related carbon sink flux induced by anthropogenic H$_2$SO$_4$ is of great significance for improving understanding of the hydrogeochemical evolution and the global carbon cycle. Here, to quantitatively evaluate the influence of anthropogenic H$_2$SO$_4$ on different lithological carbonate weathering and the related carbon sink budget, karst spring water in the typical limestone and mixed limestone–dolomite catchments in Yaji and Beidiping affected by acid precipitation in southwest China were sampled monthly for the analysis of hydrochemical and $\delta^{13}$C$_{DIC}$ characteristics. Results show for the period of sampling (August 2013 to December 2014) that the average contribution rates of atmospheric inputs and carbonate weathering to total dissolved cations are 2.24% and 97.8%, and 3.09% and 96.9% in Yaji and Beidiping, respectively. The $\delta^{13}$C$_{DIC}$ values (−17.0‰ to −14.7‰) and the [Ca$^{2+}$ + Mg$^{2+}$]/[HCO$_3^-$] (0.98 to 1.25) and [Ca$^{2+}$ + Mg$^{2+}$]/[HCO$_3^-$ + SO$_4^{2-}$] (approximately 1) equivalent ratios of samples prove that H$_2$CO$_3$ and H$_2$SO$_4$ simultaneously participate in carbonate weathering. The contribution rates of H$_2$SO$_4$ to [Ca$^{2+}$ + Mg$^{2+}$] and [HCO$_3^-$] produced by carbonate weathering in Yaji and Beidiping are 0–30% and 0–18%, and 0–37% and 0–23%, with average values of 14% and 7%, and 19% and 11%, respectively, suggesting that the influence of H$_2$SO$_4$ on different lithological carbonate weathering is different. H$_2$SO$_4$ precipitation participating in carbonate weathering increases the weathering rate by 14–19%, whereas it decreases the flux of karst carbon sink by 7–11% in Southwest China. Therefore, anthropogenic acids have influenced the global carbon cycle and climate change by carbonate weathering due to the large karst areas in the world, and their influences on different lithological carbonate weathering should not be ignored in the regional and global carbon cycles in future studies.

Keywords: chemical weathering; CO$_2$ consumption; carbon cycle; sulfuric acid; hydrogeochemistry; karst

1. Introduction

Rock weathering affects the atmospheric CO$_2$ balance by consuming CO$_2$ in the atmosphere or soil and plays an important role in the global carbon cycle and climate change [1–3]. However, the carbon sink from rock weathering was considered a long-term (10$^4$–10$^6$ years) geological process in previous global carbon cycle models, and it was believed that the carbon cycle driven by lithosphere-related carbonate weathering did not actively participate in the modern carbon cycle, making no or negligible contributions to current atmospheric CO$_2$ sources and sinks [4,5]. With the deepening of research, the karst carbon sink effect has gradually been recognized. On a short time scale, due to the...
kinetics of the rapid dissolution [6,7] and high solubility [6,8,9] of carbonate, the carbon sink generated by carbonate weathering can reach up to about 0.6 Pg C/a [2,3,10,11], accounting for 18–50% of the total “residual land sink” (1.2–3.4 Pg C/a) [3,12,13]. In addition, new evidence shows that carbonate weathering based on the H2O–carbonate–CO2–aquatic phototroph interaction can form endogenous organic carbon burial through the utilization of DIC by photosynthetic organisms in the terrestrial aquatic ecosystem (biological carbon pumping), which may make the carbon sink generated by carbonate weathering important in the control of climate change at any time scale [2,3,8]. Therefore, the karst carbon sink by carbonate weathering is a key part of the global carbon budget at different time scales and thus plays an important role in climate change.

In general, soil CO2 dissolved in water can produce carbonic acid and thus dissolves carbonate rocks in the natural state following Equation (1):

$$Ca_{x}Mg_{1-x}CO_3 + H_2O + CO_2 \rightarrow xCa^{2+} + (1 - x) Mg^{2+} + 2HCO_3^- \ (0 \leq x \leq 1).$$

In this case, half of the HCO3− in water comes from carbonate rocks, and the other half is from soil CO2. This process saves soil CO2 in the form of HCO3− in water, leading to a reduction in the amount of CO2 released from the soil into the atmosphere, thereby realizing the carbon sink effect. However, in recent years, with the strengthening of human activities, in addition to carbonic acid, anthropogenic sulfuric acid has been widely involved in the geochemical cycle of carbonate rocks. The participation of sulfuric acid in carbonate weathering also increases HCO3− in water following Equation (2):

$$2Ca_{x}Mg_{1-x}CO_3 + H_2SO_4 \rightarrow 2 \times Ca^{2+} + 2(1 - x)Mg^{2+} + 2HCO_3^- + SO_4^{2-} \ (0 \leq x \leq 1).$$

But the HCO3− all comes from carbonate rocks. Considering that the residence time of SO4^{2−} (8.7 Ma) is two orders of magnitude higher than that of HCO3− (0.083 Ma) in seawater [14], sulfuric acid weathering of carbonate rocks is essentially a net release process of atmospheric CO2. Therefore, a systematic study on the role of sulfuric acid in carbonate weathering is crucial for an accurate estimate of the budgets of karst carbon sources and sinks [14].

China is one of the world’s three major acid precipitation areas after Europe and North America [15,16], and Southwest China is not only the world’s largest continuous karst area, but also one of the most important sulfuric acid precipitation areas due to the increase in energy demand, coal combustion and air pollution emissions [17,18]. In the past decade, the frequency of acid precipitation in Southern China has decreased [19], but the incidence of acid precipitation still reaches 58–66% [20,21]; thus, acid precipitation remains at a relatively severe level. In this context, Southwest China is an ideal area to study the influence of anthropogenic sulfuric acid on the weathering mechanism of carbonate rocks and the associated karst carbon sink and source effects. In recent years, more and more attention has been paid to the role of atmospheric acid precipitation (mainly sulfuric acid) in weathering of carbonate rocks. At the karst catchment scale, atmospheric acid precipitation has reduced the karst carbon sink by 4.5–19.3% [22–25], significantly changing the karst carbon cycle. Many studies contribute to clarifying the spatial distribution and importance of anthropogenic sulfuric acid in carbonate weathering. However, the decreased proportion of karst carbon sink caused by anthropogenic sulfuric acid participating in carbonate weathering still has great uncertainty, which seriously restricts the accurate assessment of the karst carbon sink effect. As we know, carbonate rocks are composed of limestone, dolomite and a series of transitional types of mixed limestone and dolomite, and the distribution of dolomite is as common as that of limestone [26,27]; thus, dolomite is an important component of carbonate rocks. Under natural conditions, the dissolution rate of dolomite is only 1/3–1/60 of that of limestone [28,29], but its solubility is usually 20–30% higher than that of limestone [6,29]. Nonetheless, the current research mainly focuses on the limestone catchment, while the related studies in other lithological carbonate catchments are relatively scarce [30]; thus, anthropogenic sulfuric acid weathering characteristics of different lithological carbonate rocks on different time scales are not yet clear. Therefore,
simply using limestone or dolomite to completely replace carbonate rocks may lead to significant uncertainty in the assessment of the influence of anthropogenic sulfuric acid on the karst carbon sink effect at regional or global scales. Therefore, it is necessary to have a more comprehensive and in-depth understanding of the impact of anthropogenic sulfuric acid on the weathering mechanisms of carbonate rocks and the associated karst carbon sink effect from the perspective of carbonate lithology so as to provide theoretical reference for the study of the global carbon cycle and climate change. In addition, the current research data on the involvement of anthropogenic sulfuric acid in carbonate weathering is mostly based on water samples collected in the rainy and/or dry seasons, with only a few studies utilizing high-frequency sampling data (e.g., monthly sampling strategy) [23,31] to study the seasonal variation pattern of the contribution of anthropogenic sulfuric acid to carbonate weathering. Such studies can reduce the uncertainty of the assessment of karst carbon sink fluxes generated by the sulfuric acid weathering of carbonate rocks and are required for a better understanding of the biogeochemistry cycle of sulfur and carbon in karst systems and its feedback to modern global climate change.

In this study, spring water samples were collected monthly for one and a half years for analyses of the hydrochemical and carbon isotopic characteristics to compare the processes of carbonate weathering by carbonic acid and sulfuric acid generated by anthropogenic activities in two small different lithological karst catchments (limestone and mixed limestone–dolomite). The main aims of the study are to (1) compare the influence on CO₂ consumption flux from carbonate weathering by anthropogenic sulfuric acid in limestone catchment with that in mixed limestone–dolomite catchment; (2) quantitatively evaluate the impact of anthropogenic sulfuric acid on carbonate weathering and the associated carbon sink budget.

2. Material and Methods

2.1. Study Area and Sampling Sites

The studied region is located in the Guilin area in northern Guangxi Province, Southwest China (Figure 1). It has a subtropical monsoon climate, with the rainy season from April to August and the dry season from September to March of the following year. The mean annual air temperature, humidity and precipitation are 19.3 °C, 78% and 1900 mm, respectively; about 70% of rainfall occurs during the rainy season [32]. The region is undergoing severe acid precipitation pollution (mainly sulfuric acid) [21,32]. There are no mining activities and no evaporite rocks in the studied area (Figure 1). The two small typical karst catchments selected (Yaji and Beidiping), approximately 20 km apart, have similar drainage areas, vegetation and degree of anthropogenic influences and the same climate but different geological settings (Figure 1).

Yaji karst spring catchment is located near Yaji Village, about 8 km southeast of Guilin City. It is a typical karst landscape, and the topography is dominated by karst peak-cluster depressions. The catchment encompasses an area of 1 km². The lithology is the Devonian Rongxian Formation (D₃r) pure limestone, which forms the karst aquifer (Figure 1a). The catchment is covered entirely by woodland and shrubland.

Beidiping karst spring catchment is located in Maocun Village, about 30 km southeast of Guilin City. The catchment is a typical karst landscape, and the topography is dominated by karst peak-cluster depressions. It covers an area of 0.8 km². The lithology is the Middle Devonian Donggangling formation (D₂d) limestone and dolomite, which forms the karst aquifer (Figure 1b). The vegetation type is woodland and shrubland, with a few scattered fruit trees in depressions.
2.2. Sampling and Analysis

The spring water in the two catchment outlets was sampled once per month from August 2013 to December 2014. The locations of the sampling springs are shown in Figure 1.

Water pH and temperature (T) were measured in situ by a hand-held multi-parameter analyzer (Multi3430, WTW, Oberbayern, Germany), with a resolution of 0.01 pH and 0.1 °C, respectively. The analyzer was calibrated for deployment using standard solutions with pH values (4, 7 and 10) before use. The concentrations of Ca$^{2+}$ and HCO$_3^-$ were measured in situ using portable testing kits (Merck Company, Darmstadt, Germany) in the field, with precisions of 1 and 6 mg/L, respectively. All samples were immediately filtered through cellulose acetate filter membranes (pore size, 0.45 µm) and kept in pre-cleaned polyethylene bottles of different sizes. One 600 mL polyethylene bottle of sample for cation analysis was acidified with ultrapurified HNO$_3$ (1:1) to pH below 2, and the other one was untreated for anion analysis. Each sample for δ$^{13}$C$_{DIC}$ was stored in 30 mL polyethylene bottle with air-tight cap, and 2–3 drops of saturated HgCl$_2$ was added to prevent microbial activity. All samples were stored in a refrigerator at 4 °C until analysis.

The concentrations of K$^+$, Na$^+$ and Mg$^{2+}$ were determined by an ICP-OES (IRIS Intrepid II XSP, Thermo Fisher Scientific, Waltham, MA, USA), and anions (Cl$^-$, SO$_4^{2-}$ and NO$_3^-$) were measured by an ion chromatograph (861 Advanced Compact IC Metrohm, Switzerland).

Figure 1. Hydrogeological diagram of the Yaji (a) and Beidiping (b) karst catchments.
Switzerland). The uncertainties of all analyses were within ±5%. The carbon isotopic composition of DIC ($\delta^{13}$C$_{\text{DIC}}$) was analyzed using a GasBench II interfaced with a Finnigan MAT-253 mass spectrometer (Thermo Fisher Scientific, USA) with a precision better than ±0.1‰, based on replicate measurements of an internal laboratory standard. Results are reported by the delta (δ) notation relative to the international Vienna Peedee Belemnite (VPDB) using per mil (‰), where

$$\delta^{13}\text{C} (\%o) = (R_{\text{sample}}/R_{\text{PDB}} - 1) \times 1000 \quad (3)$$

The normalized inorganic charge balance (NICB) value of samples was calculated using the following formula:

$$\text{NICB} = \left(\frac{TZ^+ - TZ^-}{TZ^+ + TZ^-}\right) \times 100\% \quad (4)$$

where $TZ^+ = \text{Na}^+ + \text{K}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+}$ and $TZ^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{HNO}_3^- + \text{NO}_3^-$ in meq/L.

Evapotranspiration factor ($Ef$) was calculated using the following formula:

$$Ef = \frac{P}{(P - E)} \quad (5)$$

where $P$ represents precipitation (mm) and $E$ represents evaporation (mm).

2.3. pCO$_2$ and Calcite and Dolomite Saturation Indexes

The water temperature, pH and concentrations of Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, Cl$^-$, HCO$_3^-$ and SO$_4^{2-}$ were processed with the program WATSPEC [33] to calculate the partial pressure value of CO$_2$ (pCO$_2$) and the saturation indexes of calcite (SIC) and dolomite (SID) in spring water. pCO$_2$ is assumed to be in equilibrium with the sampled spring waters and was calculated using the following equation:

$$p\text{CO}_2 = ([\text{HCO}_3^-][\text{H}^+)/(/K_1K_h) \quad (6)$$

where $K_1$ and $K_h$ are the temperature-dependent dissociation constants between DIC species.

SIC and SID were calculated using the following equations:

$$\text{SIC} = \log \left(\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_c}\right) \quad (7)$$

$$\text{SID} = \log \left(\frac{([\text{Ca}^2+][\text{Mg}^{2+}][\text{CO}_3^{2-}])}{K_d}\right) \quad (8)$$

where $K_c$ and $K_d$ are the equilibrium constants of calcite dissolution and dolomite dissolution, respectively.

2.4. Calculation of the Effect of Anthropogenic H$_2$SO$_4$ on Carbonate Weathering and Carbon Sink

According to Equations (1) and (2), $d_1$ (mmol/L) carbonic acid and $d_2$ (mmol/L) sulfuric acid together participate in carbonate weathering and thus can be written as:

$$(d_1 + 2d_2)\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3 + d_1\text{H}_2\text{SO}_4 + d_1\text{H}_2\text{CO}_3 \rightarrow (d_1 + 2d_2)\times \text{Ca}^{2+} + (d_1 + 2d_2)(1 - x)\text{Mg}^{2+} + 2d_1\text{HCO}_3^- + d_2\text{SO}_4^- \quad (0 \leq x \leq 1) \quad (9)$$

Therefore, the concentrations of Ca$^{2+}$, Mg$^{2+}$ and HCO$_3^-$ (in mmol/L) produced by carbonate weathering can be expressed as:

$$a(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{carbonate weathering}} = d_1 + 2d_2 \quad (10)$$

$$a(\text{HCO}_3^-)_{\text{carbonate weathering}} = 2d_1 + 2d_2 \quad (11)$$

The value of $d_1$ can be calculated by the following formula:

$$d_1 = \text{Equation (11)} - \text{Equation (10)} = a(\text{HCO}_3^-)_{\text{carbonate weathering}} - a(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{carbonate weathering}} \quad (12)$$
The contribution rate of carbonate weathering by $\text{H}_2\text{CO}_3$ to $[\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate weathering}}$ ($k_1$) and $[\text{HCO}_3^-]_{\text{carbonate weathering}}$ ($k_2$) in spring water can thus be quantified by the following formulas:

$$k_1 = \frac{d_1}{a(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{carbonate weathering}}}$$  
$$k_2 = 2\frac{d_1}{a(\text{HCO}_3^-)_{\text{carbonate weathering}}}$$

The contribution rate of $\text{H}_2\text{SO}_4$ weathering of carbonate rocks to $a(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{carbonate weathering}}$ ($S_1$) and $a(\text{HCO}_3^-)_{\text{carbonate weathering}}$ ($S_2$) in spring water can thus be quantified by the following formulas:

$$S_1 = 1 - \frac{d_1}{a(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{carbonate weathering}}}$$  
$$S_2 = 1 - 2\frac{d_1}{a(\text{HCO}_3^-)_{\text{carbonate weathering}}}$$

3. Results

The monthly major ion ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{Na}^+$, $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$) concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ of samples in Yaji and Beidiping are shown in Table 1. The pH values of spring water in Yaji and Beidiping ranged from 6.88 to 7.22 and from 6.93 to 7.26, with average values of 7.03 and 7.07, respectively. Thus, the pH values of the two catchments are similar and all close to or higher than 7, showing the importance of carbonate weathering. The temperatures of karst spring water in Yaji and Beidiping were 19.4–22.9 °C and 19.0–19.8 °C, respectively. Thus, the seasonal dynamic variations of water temperatures in the two catchments were both small, which were similar to the annual average air temperature of 19.6–20.4 °C in the Guilin area [34], reflecting that the temperature of karst spring water was mainly controlled by the local mean temperature. The normalized inorganic charge balance (NICB) values of all samples were within 10%, indicating that the contribution of organic ligands to the charge balance can be negligible, and the measured results were reliable [1,25]. The total cationic charges ($TZ^+$) of samples in Yaji and Beidiping varied from 5.04 to 6.59 meq/L and from 4.68 to 7.86 meq/L, with average values of 5.79 and 6.40 meq/L, respectively, which were 4.6 times and 5.1 times higher than the average $TZ^+$ value of the rivers in the world (1.25 meq/L) [35], respectively, reflecting strong chemical weathering. It is worth noting that the average $TZ^+$ values of Yaji and Beidiping karst water were both significantly higher than that of the Banzhai karst underground river in Guizhou ($TZ^+ = 5.13$ meq/L) [36] and that of the main underground rivers in Guangxi ($TZ^+ = 4.05$ meq/L) [37] without sulfuric acid participating in carbonate weathering, while similar to that of karst water in the Pingguo area, Guangxi, where sulfuric acid was involved in carbonate weathering ($TZ^+ = 6.01$ meq/L) [25]. This suggests that sulfuric acid may be involved in the weathering processes of carbonate rocks in Yaji and Beidiping.

The cationic composition of spring water was mainly $\text{Ca}^{2+}$, accounting for 91.2–99.3% (mean: 98.2%) and 77.3–87.6% (mean: 82.6%) of the total cationic equivalent concentration in Yaji and Beidiping, respectively (Figure 2). $\text{Mg}^{2+}$ was the second most abundant cation in spring water, accounting for 4.24–6.15% (mean: 5.24%) and 6.75–17.7% (mean: 13.1%) of the total cationic equivalent concentration in Yaji and Beidiping, respectively (Figure 2). $\text{HCO}_3^-$ was the main anion in spring water, accounting for 92.4–95.1% (mean: 93.7%) and 94.9–97.2% (mean: 96.4%) of the total anionic equivalent concentration in Yaji and Beidiping, respectively (Figure 2). The contents of other anions and cations were all very low (Figure 2). The hydrochemical composition in Yaji and Beidiping reflected that the typical hydrochemical characteristics were controlled by carbonate weathering [38].

The $\delta^{13}\text{C}_{\text{DIC}}$ values of samples in Yaji and Beidiping varied from −17.0 to −14.7‰ and from −16.1 to −15.3‰, with average values of −16.2‰ and −15.8‰, respectively.
Table 1. Major ion chemical concentrations and $\delta^{13}_{\text{DIC}}$ of spring water in Yaji and Beidiping karst catchments.

<table>
<thead>
<tr>
<th>Location on the Map</th>
<th>Date</th>
<th>T (°C)</th>
<th>pH</th>
<th>K$^+$</th>
<th>Na$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>HCO$_3^-$</th>
<th>NO$_3^-$</th>
<th>SIC</th>
<th>SID</th>
<th>TZ$^+$</th>
<th>TZ$^-$</th>
<th>$\delta^{13}_{\text{DIC}}$</th>
<th>pCO$_2$</th>
<th>NICB</th>
<th>S$_1$</th>
<th>S$_2$</th>
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<td>0.31</td>
<td>0.24</td>
<td>0.24</td>
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<td>0.89</td>
<td>14.3</td>
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Notes: (1) NICB = (TZ⁺ - TZ⁻) / (TZ⁺ + TZ⁻) × 100%, where TZ⁺ = Na⁺ + K⁺ + 2Mg²⁺ + 2Ca²⁺ and TZ⁻ = Cl⁻ + 2SO₄²⁻ + HNO₃⁻ + NO₃⁻ in meq/L, respectively. (2) S¹: Contribution ratio of carbonate weathering by H₂SO₄ to [Ca²⁺ + Mg²⁺] carbonate weathering in spring water. (3) S²: Contribution ratio of carbonate weathering by H₂SO₄ to [HCO₃⁻] carbonate weathering in spring water. (4) SIC: Saturation index of calcite. (5) SID: Saturation index of dolomite. (6) pCO₂: The partial pressure of CO₂. (7) u.d. means under detection limit.
4. Discussion

4.1. Sources of Dissolved Load

In general, dissolved loads in water systems mainly come from the weathering of minerals, atmospheric deposition and anthropogenic inputs [1,25,35,39]. All samples in Yaji and Beidiping plotted in the range of rock weathering (Figure 3), indicating that the hydrochemical composition of spring water was mainly controlled by rock weathering. The aquifers in the Yaji and Beidiping catchments are all composed of carbonate rocks; thus, carbonate weathering controlled the hydrochemical composition of spring water. Generally, the input pathways of human activities to river solutes mainly include atmospheric acid deposition, domestic sewage and waste discharge from agricultural and industrial activities [1,40,41]. However, there are no industrial activities in the Yaji and Beidiping catchments; thus, industrial waste discharge can be ruled out. In addition, on the one hand, there are no human habitation and farmland distributions in the Yaji catchment, which excludes the inputs of agricultural activities and domestic sewage. There is only a small amount of farmland and human habitation in the Beidiping catchment; thus, the impacts of agricultural activities and the inputs of domestic sewage on the spring water chemistry were relatively very small and thus can be ignored, and on the other hand, the studied area is located in the area with severe acid rain pollution [21,32,42]. Therefore, human activities mainly affect the dissolved loads in the spring water through atmospheric acid deposition [15,25]. Thus, the dissolved ions in spring water in Yaji and Beidiping mainly come from atmospheric inputs and carbonate weathering.

The straightforward method [43] was employed to calculate the contributions of carbonate weathering and atmospheric inputs to the chemical composition of the spring water. For any element X, the following mass budget equation in spring water can be assumed as:

$$[X]_{\text{spring}} = [X]_{\text{atm}} + [X]_{\text{carb}}$$  \hspace{1cm} (17)

where [X] stands for concentration of ions in mmol/L, atm refers to atmospheric inputs, carb refers to carbonate weathering.

Figure 2. Piper diagram showing the relative proportions of major ions in the Yaji and Beidiping karst catchments.
The figure is adapted from [44]. Total dissolved solid (TDS) was calculated using equation: 
\[ \text{TDS} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^- \] (mg/L).

Chloride is the most commonly used reference element to calculate the atmospheric inputs to the hydrogeochemical composition [1]. The annual average precipitation (P) and evaporation (E) of the studied area are 1900 mm [21] and 1255 mm [45], respectively, according to Equation (5), the evapotranspiration factor (Ef) is 2.9. Yu [42] and Zhu [21] reported that the Cl\(^-\) concentration of rainwater in the studied area ranged from 2.34 to 224 \(\mu\)mol/L. According to the formula:

\[ [X]_{\text{atm}} = (Ef) \times [X]_{\text{rain}} = 2.9 \times [X]_{\text{rain}} \] (18)

where \([X]_{\text{rain}}\) stands for the concentration of element X in rainwater.

Thus, the Cl\(^-\) concentration from atmospheric inputs in spring water was calculated to be 6.79–650 \(\mu\)mol/L. In the studied catchments, the Cl\(^-\) concentrations of spring water ranged from 12.6 to 43.4 \(\mu\)mol/L; the values were all within the range of that from atmospheric inputs. Additionally, in the two catchments, there are no evaporite rocks, and the foregoing discussion shows that human activities mainly affect the dissolved loads in the spring water through atmospheric acid deposition. Thus, the Cl\(^-\) in the spring water was only derived from atmospheric inputs [46,47]. Similar to Cl\(^-\), the K\(^+\) (1.11–18.1 \(\mu\)mol/L) and Na\(^+\) (8.1–26.5 \(\mu\)mol/L) contents in the spring water were within the ranges of K\(^+\) (3.42–99.6 \(\mu\)mol/L) and Na\(^+\) (1.89–329 \(\mu\)mol/L) contents from atmospheric inputs [21,42], respectively. Therefore, all K\(^+\) and Na\(^+\) in the spring water came from atmospheric inputs. Thus, Equation (17) can be simplified as follows:

\[ [\text{Cl}^-]_{\text{spring}} = [\text{Cl}^-]_{\text{atm}} \] (19)
\[ [\text{Na}^+]_{\text{spring}} = [\text{Na}^+]_{\text{atm}} \] (20)
\[ [\text{K}^+]_{\text{spring}} = [\text{K}^+]_{\text{atm}} \] (21)
\[ [\text{Ca}^{2+}]_{\text{spring}} = [\text{Ca}^{2+}]_{\text{atm}} + [\text{Ca}^{2+}]_{\text{carb}} \] (22)
\[ [\text{Mg}^{2+}]_{\text{spring}} = [\text{Mg}^{2+}]_{\text{atm}} + [\text{Mg}^{2+}]_{\text{carb}} \] (23)

The Ca\(^{2+}\) and Mg\(^{2+}\) from atmospheric inputs in spring water were calculated by using the average molar ratios of precipitation in the Guilin area (Ca\(^{2+}\)/Cl\(^-\) = 2.21, Mg\(^{2+}\)/Cl\(^-\) = 0.34) [21]. Thus, \([\text{Ca}^{2+}]_{\text{atm}}\) and \([\text{Mg}^{2+}]_{\text{atm}}\) can be calculated as follows:

\[ [\text{Ca}^{2+}]_{\text{atm}} = (\text{Ca}^{2+}/\text{Cl}^-) \times [\text{Cl}^-]_{\text{atm}} = 2.21 \times [\text{Cl}^-]_{\text{atm}} \] (24)
\[ [\text{Mg}^{2+}]_{\text{atm}} = (\text{Mg}^{2+}/\text{Cl}^-) \times [\text{Cl}^-]_{\text{atm}} = 0.34 \times [\text{Cl}^-]_{\text{atm}} \] (25)
After the atmospheric input correction, the rest of the Ca$^{2+}$ and Mg$^{2+}$ came from carbonate weathering. Thus, [Ca$^{2+}$]$_{\text{carb}}$ and [Mg$^{2+}$]$_{\text{carb}}$ can be simplified as follows:

$$[\text{Ca}^{2+}]_{\text{carb}} = [\text{Ca}^{2+}]_{\text{spring}} - [\text{Ca}^{2+}]_{\text{atm}} = [\text{Ca}^{2+}]_{\text{spring}} - 2.21 \times [\text{Cl}^{-}]_{\text{atm}} \quad (26)$$

$$[\text{Mg}^{2+}]_{\text{carb}} = [\text{Mg}^{2+}]_{\text{spring}} - [\text{Mg}^{2+}]_{\text{atm}} = [\text{Mg}^{2+}]_{\text{spring}} - 0.34 \times [\text{Cl}^{-}]_{\text{atm}} \quad (27)$$

Therefore, the contributions of atmospheric inputs and carbonate weathering to the dissolved cationic TDS (mg/L) in spring water can be calculated (Figure 4). The contributions of cations from atmospheric inputs and carbonate weathering in Yaji and Beidiping varied from 0.26 to 3.05% (mean: 2.24%) and from 97.0 to 99.7% (mean: 97.8%) and from 2.12 to 4.45% (mean: 3.09%) and from 94.5 to 97.9% (mean: 96.9%), respectively. The results fully proved that the dissolved loads of the karst spring water were controlled by carbonate weathering, which is consistent with the results of the Gibbs diagram (Figure 3) and the fact that aquifer lithology is composed of carbonate rocks in the two catchments.

![Figure 4](https://keelingcurve.ucsd.edu/)

**Figure 4.** The contributions of different sources (atmosphere, carbonate) to the total dissolved cations of the samples in the Yaji (a) and Beidiping (b) karst catchments.

### 4.2. Anthropogenic Source of H$_2$SO$_4$

Generally, SO$_4^{2-}$ in karst water is derived from atmospheric deposition, anthropogenic inputs, sulfide oxidation and dissolution of evaporites [22,25,31,41]. However, sulfate and sulfide minerals were not found in our study catchment, which is consistent with the reports of previous research in the study area [32,48]. The influences of sulfide oxidation and dissolution of evaporites on the chemical composition of spring water, thus, can be ruled out. According to the discussion above, the impacts of anthropogenic inputs, such as waste discharge from agricultural and industrial activities and domestic sewage inputs to the spring water, can be neglected. According to a previous study [14], sulfuric acid in precipitation mainly comes from the reaction between free radicals (OH, H$_2$O$_2$) and SO$_2$ from automobile exhaust and coal combustion in the atmosphere. In the studied area, the SO$_4^{2-}$ of precipitation was identified as the most important acidogenic anion and varied from 1.64 to 90.0 mg/L [21,42]. The SO$_4^{2-}$ in spring water in the studied catchments varied from 4.88 to 17.7 mg/L (Table 1), which were all within that range. Therefore, H$_2$SO$_4$ in spring water mainly comes from atmospheric acid precipitation. This is consistent with the fact that the study area was significantly affected by sulforic acid precipitation [21,32,42]. Still, $\delta^{34}$SO$_4$ and $\delta^{18}$OSO$_4$ will help to improve interpretations about the sources of SO$_4^{2-}$, and it will be useful to study additional isotopic tracers ($\delta^{34}$SO$_4$ and $\delta^{18}$OSO$_4$) in the future.

### 4.3. Hydrochemical Evidence of Sulfuric Acid Participation in Carbonate Weathering

The partial pressure of CO$_2$ (pCO$_2$) values in spring water ranged from 16,558 to 38,194 ppmv, which were 39.4–90.9 times higher than that in atmosphere (about 420 ppmv, [https://keelingcurve.ucsd.edu/](https://keelingcurve.ucsd.edu/), accessed on 6 June 2023), and the pCO$_2$ values in spring...
water were within the range of that in soil in karst area (1057–80,000 ppmv) [34,49,50], showing that the spring water equilibrated with pCO$_2$ in soil rather than atmosphere. Therefore, karst spring water HCO$_3^−$ was likely to come from the soil CO$_2$ and carbonate rocks. The pCO$_2$ in the karst dynamic system not only controls the pH but also drives the karstification process [10,51]. Generally, when CO$_2$ enters a karst dynamic system, the increased pCO$_2$ promotes carbonate weathering, resulting in a decrease in pH value and an increase in Ca$^{2+}$ and HCO$_3^−$ concentrations in karst water, otherwise carbonate minerals will deposit, resulting in an increase in pH and a decrease in Ca$^{2+}$ and HCO$_3^−$ concentrations in karst water [2]. In the studied karst catchments, the pH values of spring water had a negative correlation with pCO$_2$ values (Figure 5), indicating the control of CO$_2$ concentration on the pCO$_2$ and pH values of karst spring water [2]. As shown in Figure 6, the pCO$_2$ had a negative correlation with SIC and SID, respectively, suggesting the control of pCO$_2$ on calcite and dolomite dissolution in spring water. Meanwhile, the SIC had a significant positive correlation with SID in the spring water (Figure 7), showing that calcite and dolomite dissolution may be synchronous in the catchments. All of the SIC values of samples were around 0 (Table 1), reflecting that the calcite dissolution in spring water was sufficient and reached the saturation state, which means that the “transport-limited” regime dominated the hydrochemical evolution in the catchments [52]. Therefore, runoff was a restrictive factor for calcite dissolution in the studied catchments due to the subtropical monsoon climate. The calcite dissolution products are easily transported to the karst water system in the monsoon season when rainfall is relatively heavy. Unlike the SIC, the SID values of karst spring water in Yaji and Beidiping were all less than 0 (Figure 7), indicating that the dolomite dissolution was insufficient and in an undersaturated state, which means that the “kinetic-limited” regime dominated the dolomite dissolution in the spring water [52]. This is consistent with the fact that the dissolution rate of dolomite is much lower than that of calcite [28]. It is worth noting that the pCO$_2$ of karst spring water had no correlation with Ca$^{2+}$ and HCO$_3^−$, respectively (Figure 8), which was different from the obvious positive correlation between Ca$^{2+}$ and HCO$_3^−$ from carbonate weathering by carbonic acid and pCO$_2$ of karst water, respectively [36,53,54], showing that the Ca$^{2+}$ and HCO$_3^−$ in karst spring water were not only from carbonate weathering by carbonic acid but also come from gypsum mineral weathering and/or carbonate weathering by anthropogenic acids [25,31]. Considering that there is no gypsum mineral in the stratum of the study area [32,48], anthropogenic acids may participate in carbonate weathering. Anthropogenic acids that dissolve carbonate rocks include sulfuric acid and nitric acid [25,41]. As the NO$_3^−$ only accounted for 0.33–1.64% of the total anionic equivalent concentration and the corresponding concentrations were very low (≤6.65 mg/L) in the studied karst spring water, the contribution of nitric acid to carbonate weathering in spring water is negligible; thus, sulfuric acid may participate in carbonate weathering.

![Figure 5. The relationship between pH and pCO$_2$ of karst spring in the Yaji and Beidiping karst catchments.](image-url)
Figure 5. The relationship between pH and $pCO_2$ of karst spring in the Yaji and Beidiping karst catchments.

Figure 6. Relationships of SIC vs. $pCO_2$ (a) and SID vs. $pCO_2$ (b) in the Yaji and Beidiping karst catchments.

Figure 7. Relationships of SIC and SID in the Yaji and Beidiping karst catchments.

Figure 8. Relationships of $Ca^{2+}$ vs. $pCO_2$ (a) and $HCO_3^-$ vs. $pCO_2$ (b) in the Yaji and Beidiping karst catchments.

The foregoing discussion shows that carbonate weathering controls the chemical composition of the spring water. According to Equation (1), when carbonate rocks are only weathered by carbonic acid, the equivalent ratio of $[Ca^{2+} + Mg^{2+}]/[HCO_3^-]$ in water should be equal to 1. However, the ratios of spring water samples, except for two values (0.98 and 0.99), varied from 1.01 to 1.25 (Figure 9a), showing that the carbonate rocks were not weathered by carbonic acid only. Other acids, thus, should be involved in carbonate weathering. Generally, except carbonic acid, nitric acid and sulfuric acid play an important role in carbonate weathering in karst areas [25,31,41,55,56]. However, as mentioned above, the contribution of nitric acid to carbonate weathering in spring water can be negligible; thus, sulfuric acid may be involved in carbonate weathering. According to Equations (1) and (2), if carbonate weathering is controlled by both carbonic acid and...
sulfuric acid, the [Ca$^{2+}$ + Mg$^{2+}$]/[HCO$_3^-$ + SO$_4^{2-}$] equivalent ratio should be equal to 1. Figure 9b shows the [Ca$^{2+}$ + Mg$^{2+}$]/[HCO$_3^-$ + SO$_4^{2-}$] equivalent ratios of samples were all close to 1, thereby implying that sulfuric acid was also involved in the carbonate weathering. As depicted in Figure 10, the data distribution was mainly controlled by the two end-members of carbonate weathering by sulfuric acid and carbonic acid, proving that the influence of carbonate weathering by sulfuric acid on the chemical composition of spring water was considerable. Therefore, sulfuric acid participated in carbonate weathering in the Yaji and Beidiping catchments. In addition, the data distributions of the samples were all far away from the gypsum dissolution line (Figure 10), which coincides with the fact that no evaporite minerals such as gypsum exist in the studied catchments.

![Figure 9. Relationships of HCO$_3^-$ vs. Ca$^{2+}$ + Mg$^{2+}$ (a) and HCO$_3^-$ + SO$_4^{2-}$ vs. Ca$^{2+}$ + Mg$^{2+}$ (b) in the Yaji and Beidiping karst catchments.](image)

![Figure 10. Equivalent ratios of [Ca$^{2+}$ + Mg$^{2+}$]/[HCO$_3^-$] vs. [SO$_4^{2-}$]/[HCO$_3^-$] in springs draining the Yaji and Beidiping karst catchments.](image)

4.4. Carbon Isotopic (13C$_{DIC}$) Evidence of Sulfuric Acid Weathering of Carbonate Rocks

As discussed above, the spring water HCO$_3^-$ in the studied catchments originated from the soil CO$_2$ and carbonate weathering. The $\delta^{13}$C value of soil CO$_2$ in karst areas ranged from $-18.3$ to $-36\%$ [34,57–59] with a median value of $-27.2\%$ (Figure 11). On the other hand, the $\delta^{13}$C value of marine carbonate rocks is about $0\%$ [56,59,60]. Due to the low solubility of CO$_2$ in pure water [61], the theoretical HCO$_3^-$ concentration in pure water at normal temperature and pressure is about 0.6 mg/L [61]; thus, its contribution to spring water HCO$_3^-$ can be ignored because the HCO$_3^-$ concentrations in spring water were three–four orders of magnitude higher than 0.6 mg/L. In a closed system, according to Equation (1), the theoretical $\delta^{13}$C value of HCO$_3^-$ formed by carbonate weathering by carbonic acid only is $-13.6\%$ ($-27.2\%/2$) (Figure 11). While in an open system,
the fractionation of $\delta^{13}\text{C}$ is about +9‰ between soil CO$_2$ and HCO$_3^-$ [62,63]; thus, the theoretical $\delta^{13}\text{DIC}$ value is $-18.2\%$ (−27.2‰ + 9‰) (Figure 11). According to Equation (2), the theoretical end-member value of carbonate weathering by sulfuric acid is $\delta^{13}\text{DIC} = 0\%$. In the studied catchments, the HCO$_3^-$ concentrations of the spring water were plotted in Figure 11; the characteristics of all samples are high HCO$_3^-$ concentrations, and the carbonate weathering will not produce the observed high concentrations of HCO$_3^-$ in a closed system [64]. Moreover, the $\rho$CO$_2$ in spring water in Yaji and Beidiping is much higher than that in the atmosphere, indicating adequate CO$_2$ [65,66]. These results suggest that carbonated weathering is probably completed in an open system [64]. This is why all $\delta^{13}\text{DIC}$ values in spring water are significantly lower than $-13.6\%$ (Figure 11). As shown in Figure 11, the sampling points were all located between the two end-members of sulfuric acid and carbonic acid weathering of carbonate rocks in an open system, fully proving that sulfuric acid participated in carbonate weathering.

Figure 11. Variation of $\delta^{13}\text{DIC}$ vs. HCO$_3^-$ shows the response of $\delta^{13}\text{DIC}$ to HCO$_3^-$ evolution in springs draining the Yaji and Beidiping karst catchments. These include: (1) soil CO$_2$ originating from degradation of organic matter with $\delta^{13}\text{CO}_2 = -27.2\%$ [34,57–59]; (2) open system equilibration of HCO$_3^-$ with soil CO$_2$ originating from degradation of organic matter; (3) carbonate weathering by H$_2$CO$_3$ produced from soil zone CO$_2$ in closed system; and (4) carbonate weathering by H$_2$SO$_4$ according to the $\delta^{13}\text{C}$ value of marine carbonate rock (0‰) [56,59,60].

In order to quantify the contributions of soil CO$_2$ and carbonate rocks to the HCO$_3^-$ in the spring water, using the isotope mass-balance bimodal mixing model, we assumed that the isotopic composition ratios of soil CO$_2$ and carbonate rocks were $x$ and $1 - x$, respectively. Therefore, the $\delta^{13}\text{DIC}$ value of spring water can be expressed as:

$$\delta^{13}\text{DIC}_{\text{spring water}} = x \times \delta^{13}\text{C}_{\text{soil CO}_2} + (1 - x) \times \delta^{13}\text{C}_{\text{carbonate rocks}}$$ (28)

In the studied catchments and other karst areas of Guangxi and Southwest China, the mean $\delta^{13}\text{C}$ value of karst soil CO$_2$ is about $-23\%$ [56,67], while the $\delta^{13}\text{C}$ value of marine carbonate rocks is around $0\%$ [56,60]. Based on the two end-members of $\delta^{13}\text{C}$ values, the calculated results show (Figure 12) that carbon from carbonate rocks in Yaji and Beidiping accounted for 26–36% and 30–33% of the HCO$_3^-$ in spring water, with average values of 29% and 31%, respectively. Many studies have shown that more soil CO$_2$ converted into carbonic acid participates in carbonate weathering in the rainy season than that in the dry season due to enhanced root respiration and microbial activities in the warm and wet summer season [36,68,69], resulting in a relatively lower proportion of carbonate rocks than that of soil CO$_2$ participating in carbonate weathering. However, the average proportions of carbon from carbonate rocks in the rainy season accounted for 30% and 32% of the spring water HCO$_3^-$, and the proportions in the dry season were 29% and 31% in Yaji and Beidiping, respectively, reflecting the contribution of carbonate rocks to
the spring water $\text{HCO}_3^-$ in the rainy season almost coincided with that in the dry season. The seasonal variation characteristics are probably linked to the sulfuric acid involved in carbonate weathering. As discussed above, sulfuric acid in the studied catchments mainly came from acid precipitation. Moreover, about 70% of rainfall occurs during the rainy season [32]. Therefore, more sulfuric acid participates in the weathering process of carbonate rocks in the rainy season than that in the dry season, finally resulting in nearly identical contributions of carbonate rocks to the spring water $\text{HCO}_3^-$ in both rainy and dry seasons. Yet, it is worth noting that about 70% of rainfall occurs during the rainy season, and the mean frequency of acid precipitation is up to 66.3% [21], meaning that monsoon acidic rainfall can significantly enhance the weathering of carbonate rocks.

![Figure 12. Carbonate contribution ratio versus date in the Yaji and Beidiping karst catchments.](image)

4.5. Effect of Anthropogenic $\text{H}_2\text{SO}_4$ on Carbonate Weathering and Carbon Sink

Since the study area is severely affected by acid precipitation and the $\text{HCO}_3^-$ concentrations in precipitation are almost non-existent [21,32,42], precipitation contributes little to the spring water $\text{HCO}_3^-$. Therefore, the $\text{HCO}_3^-$ in spring water was mainly controlled by carbonate weathering.

According to Equations (12)–(16), the quantified results are shown in Table 1 (see $S_1$ and $S_2$ parameters). The contribution rate of $\text{H}_2\text{CO}_3$ weathering of carbonate rocks to the spring water $[\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate weathering}}$ and $[\text{HCO}_3^-]_{\text{carbonate weathering}}$ in Yaji and Beidiping ranged from 70 to 100% and from 82 to 100%, and from 63 to 100% and from 77 to 100%, with average values of 87% and 93%, and 81% and 89%, respectively. The contribution rate of $\text{H}_2\text{SO}_4$ weathering of carbonate rocks to the spring water $[\text{Ca}^{2+} + \text{Mg}^{2+}]_{\text{carbonate weathering}}$ and $[\text{HCO}_3^-]_{\text{carbonate weathering}}$ in Yaji and Beidiping ranged from 0 to 30% and from 0 to 18%, and from 0 to 37% and from 0 to 23%, with average values of 14% and 7%, and 19% and 11%, respectively. Therefore, the participation of sulfuric acid in carbonate weathering increased the weathering rate by 14% and 19% while decreasing the karst carbon sink by 7% and 11% in Yaji and Beidiping, respectively. These different effects of anthropogenic $\text{H}_2\text{SO}_4$ on carbonate weathering and karst carbon sink are probably linked to the different lithological carbonate weathering in the Yaji and Beidiping karst catchments (Figure 1). Many studies have shown that the carbonate weathering within karst aquifers and karst catchments is remarkably influenced by different carbonate minerals; that is, under normal pressure and temperature, the solubility of dolomite is usually 20–30% higher than that of limestone [6,28], but the dissolution rate of dolomite is only $1/3$–$1/60$ of that of limestone [28], resulting in varying degrees of water–rock interactions. The aquifer lithology in the Yaji karst catchment is only composed of the D3r pure limestone (Figure 1), and the SIC values of the spring water ranged from −0.11 to 0.24 with an average value of 0.05, indicating that the $\text{CaCO}_3\cdot\text{CO}_2\cdot\text{H}_2\text{O}$ system within the karst aquifer had reached equilibrium and the water–rock interaction was sufficient. In contrast, the aquifer lithology in the Beidiping karst catchment is composed of the D2d limestone and dolomite, and the dolomite is an important part of the karst aquifer. However, the SIC values of
the spring water in Beidiping were all less than 0, with SIC values around 0 (Figure 7), suggesting that the CaMg(CO$_3$)$_2$-CO$_2$-H$_2$O system within the karst aquifer had not reached equilibrium and the water–rock interaction was insufficient. As a result, the weathering intensity of carbonate rocks in Beidiping was less than that in Yaji. Therefore, in the Yaji and Beidiping karst catchments with similar climate, hydrology, vegetation coverage, acid rain pollution and drainage area, with the participation of anthropogenic sulfuric acid from acid precipitation, the increased proportion of carbonate weathering rate and the reduced proportion of karst carbon sink flux in Yaji were both lower than those in Beidiping. Theoretically, if the CaMg(CO$_3$)$_2$-CO$_2$-H$_2$O system within the karst aquifer reaches equilibrium, the karst carbon sink effect produced by weathering of dolomite with higher solubility is stronger than that of limestone [68,70,71]. Then, under similar conditions, when the same amount of anthropogenic sulfuric acid participates in carbonate weathering, the reduced proportion of the karst carbon sink effect in the limestone catchment should be higher than that in the dolomite catchment. Considering that carbonate rocks are composed of limestone, dolomite and a series of transitional types of mixed limestone and dolomite, and the distribution of dolomite is as common as that of limestone [26,27], simply replacing carbonate rocks with a type of carbonate rock, thus, can lead to increased uncertainty in the assessment of the chemical weathering flux induced by anthropogenic sulfuric acid. Therefore, it is imperative to understand more comprehensively the impact process and mechanism of anthropogenic acids on karst carbon sinks from the perspective of carbonate lithology, further improving the accuracy of the assessment of karst carbon sink flux in karst catchments in future studies.

The Yaji and Beidiping karst catchments are fairly typical in the karst region of Southwest China, and anthropogenic sulfuric acid from acid precipitation participating in carbonate weathering is extensively reported in many other karst systems in the world [15,72,73]; thus, the results of this research are probably applied to most karst systems. If the Yaji and Beidiping karst catchments are taken as end-members of the typical limestone catchment and the mixed limestone and dolomite catchment, respectively, the sulfuric acid from acid precipitation can decrease the karst carbon sink flux by 7–11% by carbonate weathering, which is consistent with the previous findings of about 4.5–19.3% reduction in the karst carbon sink caused by sulfuric acid precipitation in Southwest China [22–25], showing that anthropogenic sulfuric acid plays an important role in the weathering processes of carbonate rocks. At present, the effects of anthropogenic acids on the carbon cycle of the earth’s surface have been widely reported worldwide [24,25,31,74,75]. Considering that the karst area occupies 15% of the world’s total land area [76], the effects of anthropogenic acids on the chemical weathering of carbonate rocks in karst systems should not be ignored, especially in the karst areas with the extensive use of fertilizers, the large discharge of sewage and severe acid precipitation, otherwise the actual karst carbon sink budget will be overestimated.

5. Conclusions

In this study, data about hydrogeochemical compositions and δ$^{13}$C$_{DIC}$ of spring water samples were collected monthly in two typical karst catchments with distinct carbonate lithology (Yaji limestone catchment, Beidiping mixed limestone–dolomite catchment) in Southwest China. The average contribution rates of atmospheric inputs and carbonate weathering to the total cationic load in spring water were 2.24% and 97.8% in Yaji, and 3.09% and 96.9% in Beidiping, respectively. Carbonate weathering was caused not only by carbonic acid but also by sulfuric acid from acid precipitation. The participation of sulfuric acid in carbonate weathering increased the weathering rate and decreased the karst carbon sink by 14% and 7% in Yaji (composed of limestone) and by 19% and 11% in Beidiping (composed of limestone–dolomite), respectively. Thus, simply replacing carbonate rocks with a type of carbonate rock can increase uncertainty in the assessment of the chemical weathering rate and karst carbon sink budget induced by sulfuric acid. The participation of anthropogenic sulfuric acid can increase the rate of carbonate weathering...
by 14–19% and decrease the karst carbon sink flux by 7–11% in Southwest China. Therefore, anthropogenic acids influence the global carbon cycle and climate change by carbonate weathering due to the large karst areas in the world. On the one hand, when accurately calculating the karst carbon sink flux, the contribution of anthropogenic acids to carbonate weathering should be reasonably deducted; otherwise, the actual karst carbon sink budget will be overestimated. On the other hand, understanding more comprehensively the impact process and mechanism of anthropogenic acids on karst carbon sinks from the perspective of carbonate lithology can further improve the accuracy of the assessment of karst carbon sink budget in karst catchments.

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