

## Article

# Lithological Controls on Chemical Weathering and CO<sub>2</sub> Consumption at Small Watershed Scale: Insights from Hydrochemistry and Stable Carbon Isotope

Yuanzheng Zhang <sup>1,2</sup> , Wenlong Huang <sup>3</sup>, Zhuohan Zhuang <sup>3</sup>, Jing Hua <sup>2</sup>, Litong Bai <sup>1</sup>, Yi Ding <sup>1</sup>, Ling Zheng <sup>1</sup>, Cheng Wang <sup>1</sup>, Chuang Zhao <sup>4</sup> and Yunde Liu <sup>1,\*</sup>

<sup>1</sup> MOE Key Laboratory of Groundwater Quality and Health & Hubei Key Laboratory of Yangtze River Basin Environmental Aquatic Science, School of Environmental Studies, China University of Geosciences, Wuhan 430078, China; zhangyuanzheng@nies.org (Y.Z.); litong.bai@cug.edu.cn (L.B.); dy0357@cug.edu.cn (Y.D.); zl24@cug.edu.cn (L.Z.); wc0109@cug.edu.cn (C.W.)

<sup>2</sup> Nanjing Institute of Environmental Sciences, Ministry of Ecology and Environment of China, Nanjing 210042, China; huaqing@nies.org

<sup>3</sup> Guangdong Geologic Survey Institute, Guangzhou 510080, China; ddyhwlong@163.com (W.H.); zhuangzhuohan1991@163.com (Z.Z.)

<sup>4</sup> Shandong Institute of Geophysical and Geochemical Exploration, Jinan 250013, China; zccug0918@163.com

\* Correspondence: liuyunde@cug.edu.cn

## Abstract

Previous investigations into lithology-driven weathering processes have largely emphasized large-scale spatial assessments, while studies targeting small watershed scales remain scarce. This study investigated two adjacent watersheds (Chengjia: CJ; Datan: DT) under comparable climatic conditions in Guangdong, China, using hydrochemistry and stable carbon isotopes. The CJ watershed exhibited low-TDS (20–66 mg/L) HCO<sub>3</sub>-Na-Ca-type waters dominated by silicate weathering, whereas the DT watershed displayed high-TDS (70–278 mg/L) HCO<sub>3</sub>-Ca-type waters, indicative of mixed carbonate–silicate weathering. Results of carbon isotope composition of dissolved inorganic carbon confirmed that H<sub>2</sub>CO<sub>3</sub>-driven weathering was the dominant mechanism in both watersheds. In the CJ watershed, 79.5% of dissolved cations in surface water originated from silicate weathering, yielding a CO<sub>2</sub> consumption rate (CCR) of  $0.28 \times 10^6$  mol/km<sup>2</sup>/yr, while carbonate weathering was negligible. Conversely, in the DT watershed, 86.4% of dissolved cations were derived from carbonate weathering, yielding a CCR of  $1.94 \times 10^6$  mol/km<sup>2</sup>/yr, whereas silicate weathering contributed only 10.3% of cations with a CCR of  $0.23 \times 10^6$  mol/km<sup>2</sup>/yr. The chemical weathering rate of carbonate can be up to 10 times that of silicate, resulting in a larger CCR. This study demonstrated the key impact of lithology on hydrochemical characteristics and CO<sub>2</sub> consumption at small watershed scales.

**Keywords:** chemical weathering; CO<sub>2</sub> consumption; hydrogeochemistry; stable carbon isotope; lithological control



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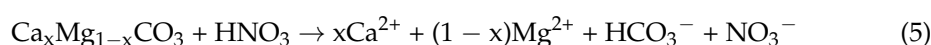
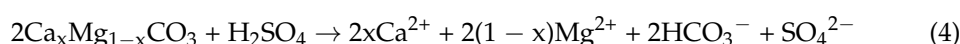
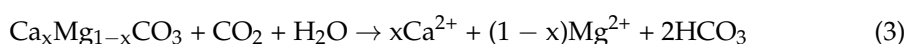
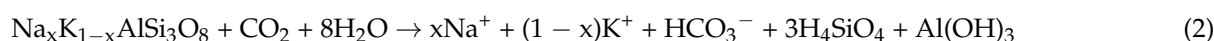
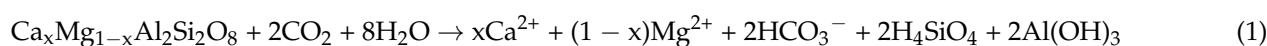
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## 1. Introduction

Chemical weathering, involving the dissolution of silicate and carbonate rocks, plays a critical role in the global carbon cycle [1–3]. The dissolution of silicate minerals (Equations (1) and (2)) and carbonate minerals (Equation (3)) by carbonic acid (H<sub>2</sub>CO<sub>3</sub>) facilitates the transfer of atmospheric/soil CO<sub>2</sub> to aquatic systems, where it is converted to dissolved inorganic carbon (DIC) and ultimately transported to the ocean for long-term

storage [4,5]. However, dissolution of silicate and carbonate minerals (Equation (3)) by  $\text{H}_2\text{SO}_4$  (Equation (4)) and  $\text{HNO}_3$  (Equation (5)) does not capture  $\text{CO}_2$  [6,7]. A fundamental distinction exists between silicate and carbonate weathering in terms of their carbon cycle impacts. Silicate weathering represents a permanent carbon sink, as the subsequent deposition processes do not release  $\text{CO}_2$  back to the atmosphere [8,9]. In contrast, carbonate weathering results in no net effect on atmospheric  $\text{CO}_2$  over geological timescales, as the carbon initially consumed during dissolution is subsequently released during carbonate precipitation in marine environments [10,11].



In addition to reaction mechanisms, the weathering rate of silicate is significantly slower than that of carbonate [12,13]. Therefore, lithology is a key factor controlling chemical weathering and  $\text{CO}_2$  consumption [3,14]. Understanding the role of lithology in regulating rock weathering processes and  $\text{CO}_2$  consumption is crucial for accurately assessing the global carbon cycle and carbon sink potential.

The distinct weathering behaviors of silicate and carbonate lithologies yield characteristic solute signatures [15–17]. Silicate weathering continuously releases  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  into water, whereas carbonate weathering primarily releases  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [5,7]. These two processes lead to distinct hydrochemical compositions in natural waters [18,19]. Consequently, hydrochemical composition serves as a robust proxy for identifying dominant weathering processes and quantifying consequent  $\text{CO}_2$  consumption [20–22].

In addition to hydrochemical analysis, carbon isotope fractionation of dissolved inorganic carbon (DIC) can provide supplementary evidence for chemical weathering and  $\text{CO}_2$  consumption [23,24]. Under closed-system conditions, chemical weathering of silicate and carbonate consumes limited  $\text{CO}_2$ , and the carbon isotope composition of DIC ( $\delta^{13}\text{C}\text{-DIC}$ ) depends on the following endmembers [7,23–25]:

- (1) Silicate weathering by  $\text{H}_2\text{CO}_3$  produces DIC entirely derived from soil  $\text{CO}_2$  (Equations (1) and (2)), preserving the soil  $\text{CO}_2$  isotopic signature. The  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  derived from both root autotrophic respiration and heterotrophic decomposition of soil organic matter closely match those of the parent plant material [7]. For instance, the predominant C3 plants in South China yields  $\delta^{13}\text{C}\text{-DIC}$  values ranging from  $-30.0\text{‰}$  to  $-24.2\text{‰}$ .
- (2) Carbonate weathering by  $\text{H}_2\text{CO}_3$  produces DIC, with half derived from carbonate minerals ( $\delta^{13}\text{C}\text{-DIC} \approx 0\text{‰}$ ) and half from soil  $\text{CO}_2$  ( $\delta^{13}\text{C}\text{-DIC} \approx -30.0\text{‰}$  to  $-24.2\text{‰}$ ) as shown in Equation (3), resulting in  $\delta^{13}\text{C}\text{-DIC}$  values of approximately  $-15.0\text{‰}$  to  $-12.1\text{‰}$ .
- (3) Carbonate weathering by  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  produces DIC entirely sourced from carbonate minerals ( $\delta^{13}\text{C} \approx 0\text{‰}$ ) (Equations (4) and (5)), yielding  $\delta^{13}\text{C}\text{-DIC}$  values near  $0\text{‰}$ .

Under open system conditions, atmospheric precipitation is a significant factor influencing the  $\delta^{13}\text{C}\text{-DIC}$  in aquatic systems [26]. The  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  ranges from  $-8$  to  $-6\text{‰}$ , with an average of  $-7\text{‰}$  [27].

Previous studies have employed hydrogeochemistry and  $\delta^{13}\text{C}\text{-DIC}$  to investigate chemical weathering and  $\text{CO}_2$  consumption [5,7,10,12,21,23,24,28]. However, most research has focused on large-scale basins, where chemical weathering processes are influenced by

multiple factors, including climate, lithology, soil, vegetation, and human activities [5,7,21]. The complexity of these interactions makes it difficult to isolate the impact of individual factors on CO<sub>2</sub> consumption. In comparison, small watersheds with homogeneous environmental conditions offer ideal natural laboratories for controlled comparative studies, allowing clearer attribution of observed variations to specific weathering processes. Therefore, studies at small watershed scale can provide critical insights into chemical weathering and its influence on hydrogeochemical dynamics and CO<sub>2</sub> consumption.

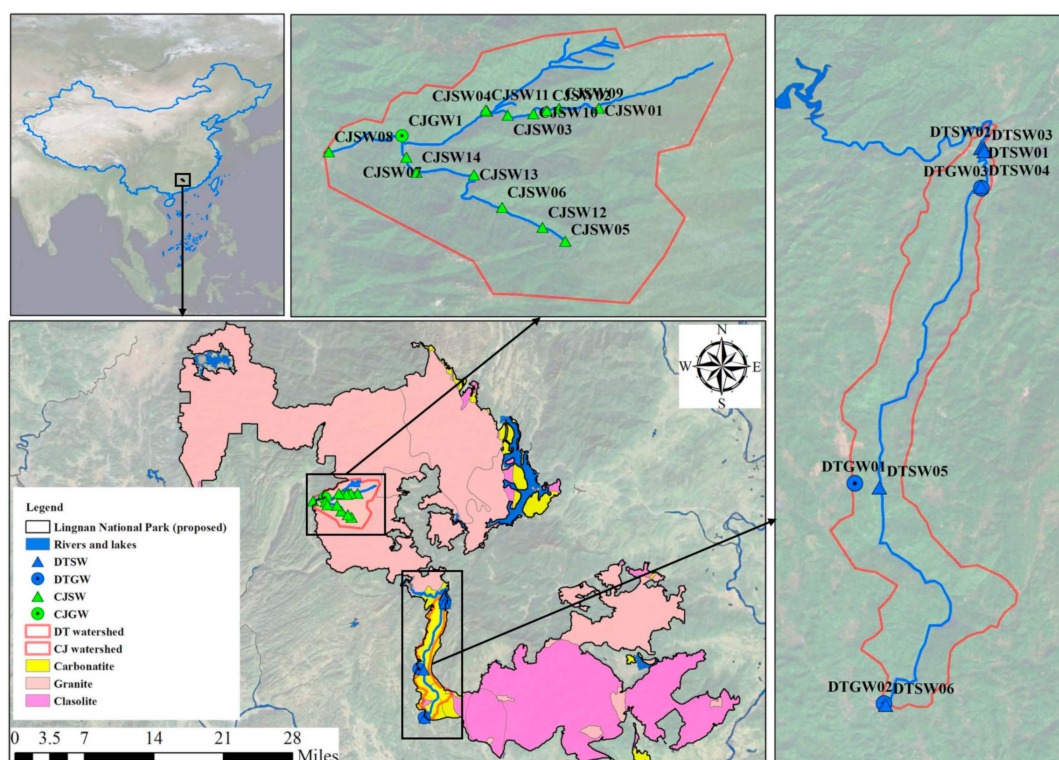
To elucidate the influence of lithology as a dominant variable on chemical weathering and hydrochemical processes at small watershed scale, this study selected two watersheds characterized by consistent climatic conditions, similar vegetation types, and minimal anthropogenic disturbance, but distinct lithologies. By analyzing seasonal variations in hydrochemical characteristics and  $\delta^{13}\text{C}$ -DIC in surface water and groundwater, this study aims to (1) investigate the hydrogeochemical characteristics of surface water and groundwater in these two watersheds; (2) identify the dominant chemical weathering processes in these two watersheds; and (3) assess the CO<sub>2</sub> consumption induced by chemical weathering in these two watersheds.

## 2. Materials and Methods

### 2.1. Study Area

The Chengjia (CJ) and Datan (DT) watersheds are located within the boundary of Lingnan National Park (proposed) in northern Guangdong Province, representing an ecologically significant region of China (Figure 1). The study area is predominantly forested with no residential/industrial area. These adjacent watersheds encompass drainage areas of 55.68 km<sup>2</sup> (CJ) and 48.86 km<sup>2</sup> (DT), with mean annual runoff volumes of 0.067 km<sup>3</sup> and 0.057 km<sup>3</sup>, respectively. The surface water in the DT watershed flows predominantly in a north-to-south direction, whereas in the CJ watershed, the flow direction is oriented from east to west. Both watersheds maintain dense forest cover and experience minimal anthropogenic disturbance. The study area experiences a subtropical monsoon climate, characterized by an average temperature of 8.6 °C in the coldest month (January) and 27.0 °C in the warmest month (July), with a multi-year mean annual temperature of 19.0 °C. Annual precipitation ranges from 1400 to 2400 mm, with distinct wet (March–August) and dry (September–February) seasons. Rivers and streams are primarily precipitation-fed.

These two watersheds exhibit distinct geological characteristics. The CJ watershed is predominantly underlain by Jurassic monzogranite formations, where groundwater occurs principally as bedrock fissure water. In contrast, the DT watershed features extensive outcrops of Carboniferous carbonate rocks, including limestone, dolomitic limestone, and dolomite, with groundwater systems developing as characteristic karst fissure water. The terrain of the CJ watershed is steep, with a stream gradient (the ratio of drop in elevation of a stream per unit horizontal distance) of 0.068, while that of the DT watershed is gentle, with a stream gradient of 0.005.



**Figure 1.** Location of the study area and spatial distribution of sampling sites.

## 2.2. Sampling and Analysis

Field investigations and water sampling were conducted in the CJ and DT watersheds (Figure 1) in July (wet season) and December (dry season) 2023. CJSW-July and CJGW-December represent surface water and groundwater collected from the CJ watershed in July and December, respectively. DTSW-July and DTGW-December represent surface water and groundwater collected from the DT watershed in July and December, respectively. The same applies to other samples. In 2023, a total of 29 and 18 water samples were collected in the CJ and DT watersheds, respectively.

In situ measurements of water, pH, and electrical conductivity (EC) were performed using a portable multiparameter water quality analyzer (Orion VM-01, Thermo Fisher Scientific, Waltham, MA, USA). Within 24 h of collection, alkalinity titration was conducted using standard hydrochloric acid solution to determine  $\text{HCO}_3^-$  concentration. For anion analysis, water samples were filtered through  $0.45\ \mu\text{m}$  PTFE membranes and stored in sealed 50 mL PET bottles. Cation samples were similarly filtered and then acidified with ultrapure  $\text{HNO}_3$  to  $\text{pH} < 2$  before sealing. Samples for  $\delta^{13}\text{C}$ -DIC were collected in 40 mL brown glass vials without headspace, then vials were sealed immediately with airtight caps and preserved with  $\text{HgCl}_2$  to inhibit microbial activity. All samples were refrigerated at  $4\ ^\circ\text{C}$  prior to laboratory analysis.

Major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ) were analyzed using ion chromatography (ICS-1100, Thermo Fisher Scientific, Waltham, MA, USA) with  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  as the eluent [29]. Major cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) were analyzed using inductively coupled plasma–optical emission spectrometry (iCAP7400+, Thermo Fisher Scientific, Waltham, MA, USA) [30] according to a Chinese standard (water quality—determination of 32 elements—inductively coupled plasma optical emission spectrometry). Total dissolved solids (TDSs) were determined using gravimetric analysis (the difference in weight between the water before and after drying at  $105\ ^\circ\text{C}$  [31]. DIC was converted to  $\text{CO}_2$  through acidification with phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The liberated  $\text{CO}_2$  was then extracted under



vacuum and passed through an ethanol trap cooled with liquid N<sub>2</sub> to remove residual water vapor. Finally, the purified CO<sub>2</sub> was cryogenically transferred to a sample tube for isotopic analysis. The  $\delta^{13}\text{C}$ -DIC were analyzed with isotope ratio mass spectrometry (MAT 253, Thermo Fisher Scientific, United States), and are reported as per mille (‰) relative to Vienna Pee Dee Belemnite (VPDB) [7]. A statistical summary of hydrogeochemical and isotopic parameters is exhibited in Table 1.

**Table 1.** Statistical summary of hydrogeochemical and isotopic parameters of samples.

| Sample Number     |    |     | TDS   | pH  | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Cl <sup>−</sup> | SO <sub>4</sub> <sup>2−</sup> | HCO <sub>3</sub> <sup>−</sup> | NO <sub>3</sub> <sup>−</sup> | SiO <sub>2</sub> | $\delta^{13}\text{C}$ |
|-------------------|----|-----|-------|-----|------------------|------------------|-----------------|----------------|-----------------|-------------------------------|-------------------------------|------------------------------|------------------|-----------------------|
|                   |    |     | mg/L  | /   | mg/L             | mg/L             | mg/L            | mg/L           | mg/L            | mg/L                          | mg/L                          | mg/L                         | mg/L             | ‰                     |
| CJSW<br>-July     | 14 | Max | 64.4  | 7.7 | 10.5             | 0.6              | 5.7             | 1.5            | 0.8             | 1.9                           | 45.0                          | 2.2                          | 14.5             | −10.4                 |
|                   |    | Min | 20.5  | 6.4 | 0.4              | 0.0              | 1.7             | 0.3            | 0.2             | 0.7                           | 5.1                           | 0.2                          | 5.1              | −14.9                 |
|                   |    | Ave | 32.7  | 7.1 | 1.9              | 0.1              | 2.9             | 0.9            | 0.4             | 1.1                           | 13.3                          | 0.9                          | 8.3              | −12.2                 |
| CJSW<br>-December | 14 | Max | 66.1  | 7.5 | 9.2              | 0.6              | 6.0             | 2.4            | 2.0             | 3.2                           | 38.0                          | 3.3                          | 16.2             | −6.1                  |
|                   |    | Min | 23.0  | 6.7 | 0.2              | 0.0              | 1.9             | 0.5            | 0.2             | 0.8                           | 5.4                           | 0.0                          | 6.1              | −12.7                 |
|                   |    | Ave | 36.7  | 7.0 | 1.7              | 0.1              | 3.4             | 1.3            | 0.6             | 1.4                           | 13.6                          | 0.9                          | 9.5              | −9.4                  |
| CJGW<br>-December | 1  | Max |       |     |                  |                  |                 |                |                 | /                             |                               |                              |                  |                       |
|                   |    | Min |       |     |                  |                  |                 |                |                 | /                             |                               |                              |                  |                       |
|                   |    | Ave | 114.3 | 7.2 | 14.3             | 0.7              | 15.4            | 2.4            | 7.2             | 7.8                           | 62.1                          | 2.6                          | 15.4             | −17.7                 |
| DTSW<br>-July     | 6  | Max | 95.3  | 7.7 | 26.1             | 4.1              | 2.5             | 1.5            | 1.3             | 3.8                           | 89.0                          | 2.3                          | 6.1              | −12.1                 |
|                   |    | Min | 69.6  | 6.5 | 16.9             | 1.6              | 2.3             | 0.9            | 0.6             | 2.1                           | 59.5                          | 2.1                          | 5.6              | −12.6                 |
|                   |    | Ave | 80.6  | 7.1 | 20.1             | 2.5              | 2.4             | 1.0            | 0.8             | 2.6                           | 72.9                          | 2.2                          | 5.9              | −12.3                 |
| DTSW<br>-December | 6  | Max | 147.4 | 8.0 | 48.8             | 7.7              | 3.0             | 1.6            | 1.2             | 5.8                           | 141.1                         | 2.4                          | 7.5              | −10.4                 |
|                   |    | Min | 101.3 | 7.5 | 27.3             | 3.2              | 2.1             | 1.1            | 0.8             | 3.5                           | 86.8                          | 1.7                          | 5.4              | −12.8                 |
|                   |    | Ave | 127.4 | 7.8 | 37.5             | 5.0              | 2.7             | 1.4            | 1.0             | 4.5                           | 118.3                         | 2.1                          | 6.6              | −11.5                 |
| DTGW<br>-July     | 3  | Max | 246.9 | 8.2 | 92.0             | 8.5              | 1.7             | 0.9            | 1.1             | 5.7                           | 277.6                         | 2.4                          | 6.1              | −16.6                 |
|                   |    | Min | 181.0 | 7.4 | 50.4             | 2.4              | 0.5             | 0.4            | 0.7             | 4.1                           | 196.0                         | 0.4                          | 3.0              | −16.6                 |
|                   |    | Ave | 215.3 | 7.7 | 72.6             | 4.6              | 1.0             | 0.7            | 0.8             | 4.7                           | 238.9                         | 1.7                          | 4.5              | −16.6                 |
| DTGW<br>-December | 3  | Max | 277.7 | 8.1 | 115.4            | 12.3             | 1.8             | 0.9            | 1.2             | 6.2                           | 284.9                         | 1.8                          | 6.5              | −11.5                 |
|                   |    | Min | 201.8 | 7.6 | 61.7             | 3.5              | 0.8             | 0.5            | 0.5             | 4.3                           | 205.2                         | 0.3                          | 3.7              | −16.5                 |
|                   |    | Ave | 235.1 | 7.8 | 88.9             | 6.5              | 1.2             | 0.8            | 0.8             | 5.1                           | 239.4                         | 1.3                          | 5.0              | −13.2                 |

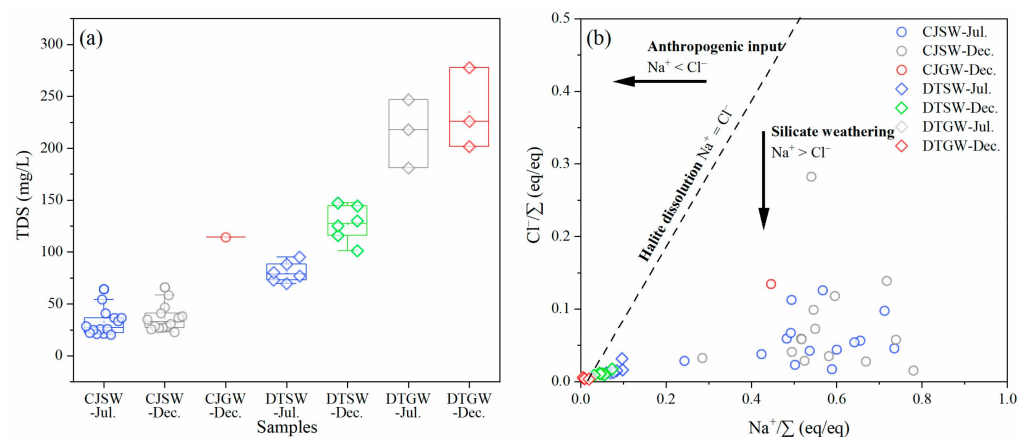
### 3. Results and Discussion

#### 3.1. Hydrochemical Characteristics

As shown in Figure 2a, the TDS of surface water in the CJ watershed ranged from 20.5 to 64.4 mg/L (average: 32.7 mg/L) in the wet season (July) and from 23.0 to 66.1 mg/L (average: 36.7 mg/L) in the dry season (December). The TDS of surface water in CJ watershed is close to the global average TDS value for granite watersheds (23 mg/L) [32]. The TDS of groundwater in the CJ watershed was 114.3 mg/L in the dry season. In contrast, the TDS of surface water in the DT watershed ranged from 69.6 to 95.3 mg/L (average: 80.6 mg/L) in the wet season and from 101.3 to 147.4 mg/L (average: 127.4 mg/L) in the dry season. The TDS of groundwater in the DT watershed varied between 181 and 246.9 mg/L (average: 215.3 mg/L) in the wet season and 201.8–277.7 mg/L (average: 235.1 mg/L) in the dry season. The marked differences in TDS between the CJ and DT watersheds implied distinct hydrochemical characteristics and underlying formation mechanisms.

The atmospheric input is considered as a potential source for solutes in aquatic systems [33,34]. In both watersheds, the TDS content of surface water and groundwater is lower in the wet season than that in the dry season. This may be attributed to abundant rainfall and faster water cycling in the wet season, which enhances dilution effects and weakens water–rock interactions. The TDS content in local rainwater is approximately 15.0 mg/L [18]. The TDS of rainfall in the study area is relatively close to that of surface

water in the CJ watershed but significantly lower than that in the DT watershed, indicating that the hydrochemical composition of surface water in the CJ watershed is more influenced by rainfall than that in the DT watershed. The difference in TDS of surface water between the wet and dry seasons is much greater in the DT watershed ( $\Delta = 46.8$  mg/L) than in the CJ watershed ( $\Delta = 4.0$  mg/L). This suggested a stronger influence of discharge from groundwater to surface water in the DT watershed in the dry season.



**Figure 2.** (a) TDS contents in different water samples, (b) correlation between  $\text{Cl}^-/\Sigma^+$  and  $\text{Na}^+/\Sigma^+$  ( $\Sigma^+ = \text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ ; in units of charge equivalents).

Human activities are also a potential factor influencing the hydrochemical composition [18,34]. As shown in Figure 2b,  $\text{Cl}^-/\text{Na}^+$  ratios observed in both the CJ and DT watersheds were lower than 1, indicating that the influence of anthropogenic input was negligible [34]. Therefore, the chemical composition of water bodies in the study area was primarily influenced by natural processes, consistent with the region's undisturbed forest ecosystems. Furthermore, Figure 2b shows that the milliequivalent concentrations of  $\text{Na}^+$  are generally higher than those of  $\text{Cl}^-$  in both watersheds, indicating the influence of silicate weathering [7].

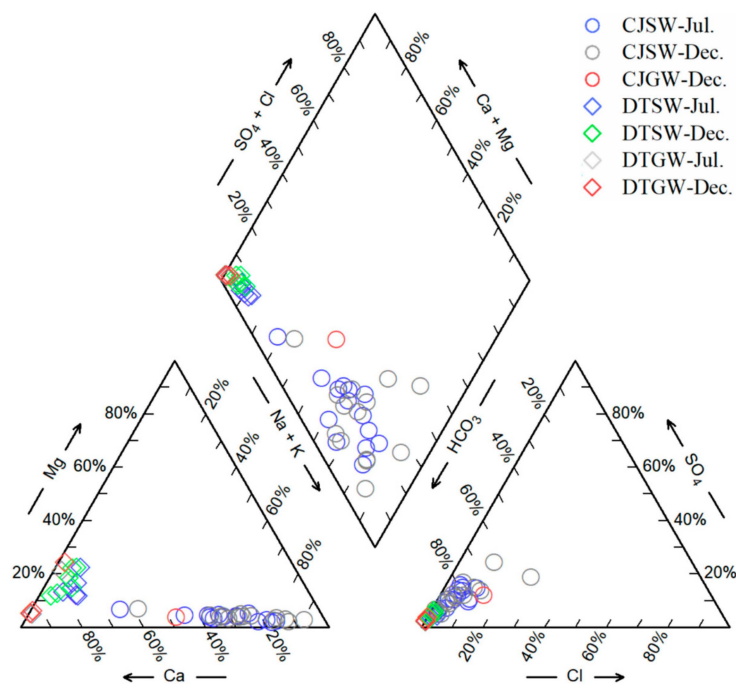
Piper trilinear diagrams were used to further investigate the formation mechanisms of hydrochemical characteristics in the two watersheds (Figure 3) [35]. In the CJ watershed, the relative abundance of major cations followed the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ , while  $\text{HCO}_3^-$  was the predominant anion, far exceeding those of other anions. Both surface water and groundwater in the CJ watershed were classified as  $\text{HCO}_3^- \text{Na} \cdot \text{Ca}$  type. In contrast, in the DT watershed, surface water and groundwater exhibited significantly higher  $\text{Ca}^{2+}$  concentrations than other cations, while maintaining  $\text{HCO}_3^-$  as the principal anion. Thus, the surface water and groundwater in the DT watershed were classified as  $\text{HCO}_3^- \text{Ca}$  type.

The differences in hydrochemical composition and TDS content between the CJ and DT watersheds suggested distinct formation mechanisms. Gibbs diagrams can distinguish the dominant controls on hydrochemical composition, including atmospheric precipitation, rock weathering, and evaporation–crystallization [36,37]. As shown in Figure 4, both surface water and groundwater samples from the CJ watershed in wet season (July) and dry season (December) exhibited low TDS and high  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  values, indicating a mixed influence of atmospheric precipitation and rock weathering on hydrochemical characteristics. In contrast, DT watershed samples exhibited significantly higher TDS and lower  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  ratios compared to CJ watershed samples (Figure 4), demonstrating rock weathering as the predominant control with negligible contributions from rainfall or evaporation. Notably, dry-season (December) surface water in the DT watershed showed TDS and  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  values approaching those of local groundwater, providing

further evidence for substantial groundwater discharge into surface water systems in the dry season.

The Gibbs diagram revealed distinct hydrochemical controls between the two watersheds (Figure 4). Hydrochemical composition of the CJ watershed showed dual influences from both rock weathering and atmospheric precipitation, whereas that of the DT watershed was predominantly controlled by rock weathering. Geological investigations demonstrated contrasting lithologies between the watersheds. The CJ watershed is underlain by granite formations, while carbonate rocks dominate the DT watershed. This lithological contrast drives fundamentally different weathering regimes. In the carbonate-rich DT watershed, extensive dissolution of carbonate minerals, such as calcite and dolomite, produced  $\text{Ca}^{2+}$ -enriched waters ( $\text{HCO}_3\text{-Ca}$  type). Conversely, weathering of silicate minerals (such as albite and potassium feldspar) in the granitic CJ watershed generated waters with elevated  $\text{Na}^+$  concentrations ( $\text{HCO}_3\text{-Na-Ca}$  type).

The weathering types controlling hydrochemical composition can be further verified using molar ratios such as  $\text{Ca}^{2+}/\text{Na}^+$  vs.  $\text{HCO}_3^-/\text{Na}^+$  [38,39]. As shown in Figure 5, groundwater samples from the DT watershed clustered near the carbonate endmember, confirming the dominant role of carbonate weathering. Surface water samples from the DT watershed distributed between the silicate and carbonate endmembers, suggesting a combined influence of silicate and carbonate weathering. As shown in Figure 1, the upper reaches of the DT watershed border the northern granitic terrain, potentially imparting granitic weathering signatures to the hydrochemical composition of the surface water. In contrast, both groundwater and surface water from the CJ watershed were located close to the silicate endmember, indicating silicate weathering as the main control. All water samples from both watersheds were far from the evaporite endmember, implying negligible influence of evaporite dissolution. These hydrochemical findings align well with the actual lithology of the two watersheds, demonstrating the critical role of lithology in shaping their hydrochemical characteristics.



**Figure 3.** Piper trilinear diagram for water samples.

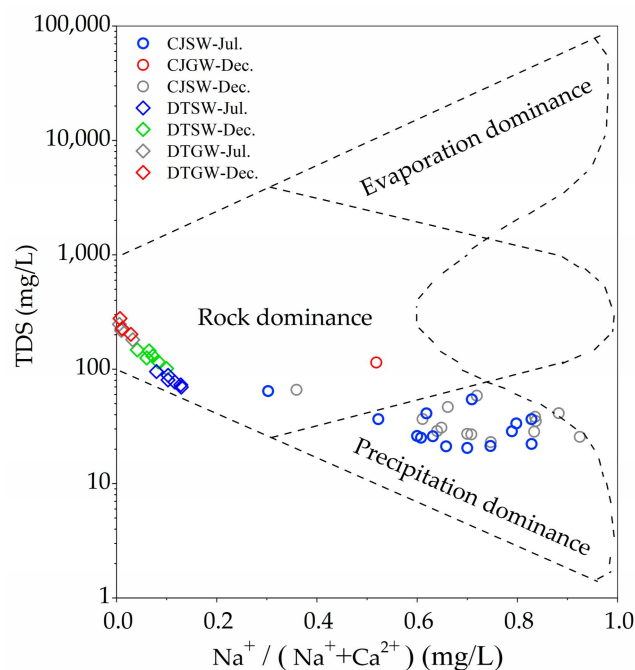


Figure 4. Gibbs diagram for water samples.

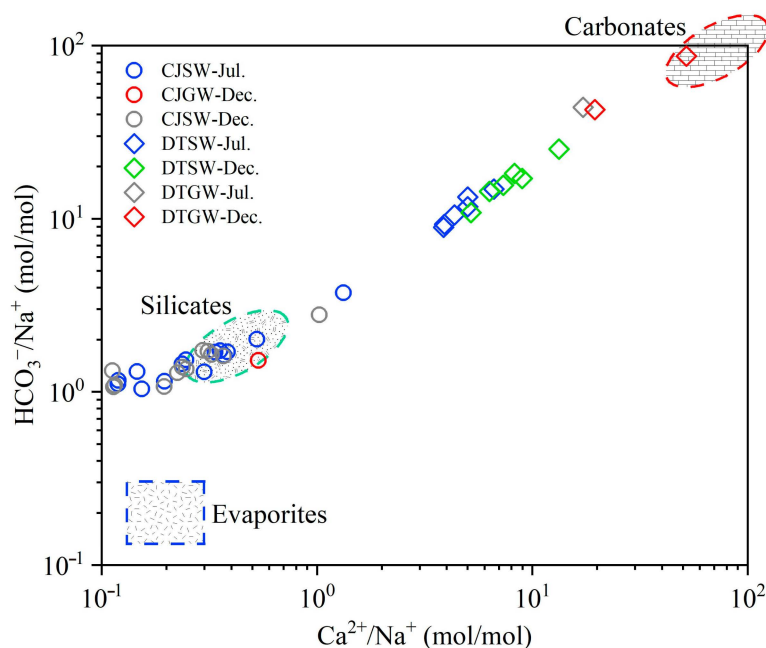
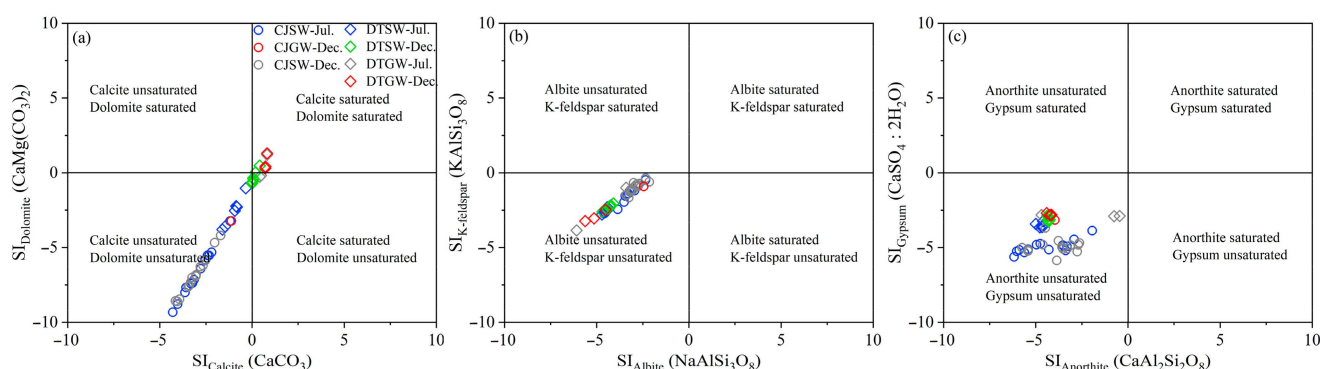


Figure 5. Correlation between  $\text{HCO}_3^-/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$ .

To further elucidate chemical weathering processes and their impacts on hydrochemical compositions in both surface and groundwater across the two watersheds, saturation indices (SI) were calculated for representative water samples using PHREEQC (3.6.3 version). As illustrated in Figure 6a, groundwater in the DT watershed reached saturation states for both calcite and dolomite during July and December ( $\text{SI} > 0$ ), indicating dominant carbonate weathering influences. This result, that hydrochemical compositions of waters in the DT watershed were dominated by rock weathering, was consistent with Figure 4. While surface waters in DT showed lower SI values than groundwater, they approached near-saturation conditions. Notably, DT's surface waters exhibited significantly higher SI values in December (dry season) compared to July (wet season), suggesting enhanced



groundwater contributions to surface water during low-flow periods. In contrast, waters in the CJ watershed remained markedly undersaturated with respect to both calcite and dolomite ( $SI < 0$ ), confirming limited carbonate weathering effects.



**Figure 6.** (a–c) Correlations between saturation indices of different minerals in waters.

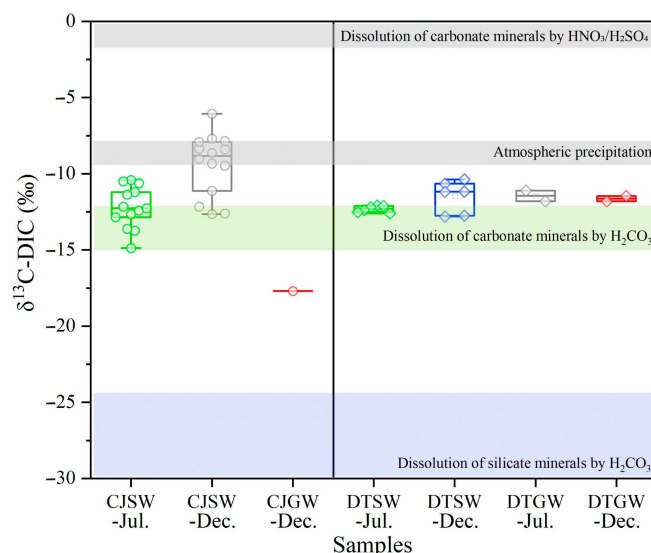
Figure 6b revealed that waters in the CJ watershed had higher saturation states for albite and K-feldspar compared to DT, consistent with more intensive silicate weathering. The seasonal pattern of higher albite and K-feldspar SI values in December surface waters was consistent with the DT watershed's behavior, again indicating stronger groundwater–surface water interactions during dry periods. Figure 6c demonstrated significantly higher gypsum saturation indices in the DT watershed waters compared to that in the CJ watershed, which aligns with the observed  $SO_4^{2-}$  concentration differences between watersheds (Table 1). The consistently negative saturation indices for both silicate and carbonate minerals in waters of the CJ watershed (Figure 6) indicated limited rock weathering activity, which aligns with the patterns shown in Figure 4 (precipitation dominance).

### 3.2. Identification of $CO_2$ Consumption During Chemical Weathering Using $\delta^{13}C$ -DIC

Theoretically, increasing contributions of carbonate weathering by  $H_2SO_4$  and  $HNO_3$  to  $CO_2$  consumption should elevate  $SO_4^{2-}/HCO_3^-$  and  $NO_3^-/HCO_3^-$  molar ratios, consequently driving  $\delta^{13}C$ -DIC values toward more positive signatures [7]. However, our data revealed no significant positive correlation between  $\delta^{13}C$ -DIC and either  $SO_4^{2-}/HCO_3^-$  or  $NO_3^-/HCO_3^-$  ratios in both surface and groundwater samples from the studied watersheds ( $p > 0.05$ ). This absence of correlation indicated that carbonate weathering by  $H_2SO_4$  and  $HNO_3$  played a negligible role in  $CO_2$  consumption in the studied watersheds.

The  $\delta^{13}C$ -DIC values of groundwater in the CJ watershed were significantly more negative than the end-member of carbonate weathering by  $H_2CO_3$  ( $-30.0\text{‰}$  to  $-24.2\text{‰}$ ), indicating substantial silicate weathering influences (Figure 7). Surface waters in the CJ watershed exhibited intermediate  $\delta^{13}C$ -DIC values ( $-14.9\text{‰}$  to  $-6.1\text{‰}$ ) between end-member of atmospheric precipitation ( $-6\text{‰}$  to  $-8\text{‰}$ ) and carbonate weathering by  $H_2CO_3$  ( $-30.0\text{‰}$  to  $-24.2\text{‰}$ ) during both July and December sampling campaigns. Field geological surveys confirmed the absence of carbonate outcrops in the CJ watershed, suggesting that surface water chemistry reflects the mixing of atmospheric inputs and silicate weathering by  $H_2CO_3$ .

In contrast, both groundwater and surface water in the DT watershed showed  $\delta^{13}C$ -DIC values ( $-12.8\text{‰}$  to  $-10.4\text{‰}$ ) intermediate between precipitation and weathering by  $H_2CO_3$  end-members. This pattern corresponds with the watershed's dominant carbonate lithology, confirming mixed atmospheric and carbonate weathering sources. These isotopic patterns were consistent with the analysis of hydrochemical characteristics.



**Figure 7.**  $\delta^{13}\text{C-DIC}$  in different water samples. The end-member values of  $\delta^{13}\text{C-DIC}$  were derived from previous studies [7,23–25].

### 3.3. Quantitative Analysis of Chemical Weathering and $\text{CO}_2$ Consumption

The Straightforward Method is a classical approach used to determine the chemical composition and evolution of surface water by analyzing dissolved ions [18,40]. It involves straightforward calculations based on measured concentrations of major ions to understand hydrogeochemical processes such as rock–water interactions and mixing [18,40]. The Straightforward Method was employed to calculate the contributions of different end-members to the dissolved ions in the surface water. The major ions in surface water originate from atmospheric precipitation, anthropogenic inputs, and the chemical weathering of rocks and minerals, which can be expressed as:

$$[\text{X}]_{\text{river}} = [\text{X}]_{\text{atm}} + [\text{X}]_{\text{anthro}} + [\text{X}]_{\text{carb}} + [\text{X}]_{\text{sil}} + [\text{X}]_{\text{evap}} \quad (6)$$

In Equation (6), the subscripts river, atm, anthro, carb, sil, and evap represent the contributions from the river, atmospheric precipitation, anthropogenic inputs, carbonate rocks, silicate rocks, and evaporites, respectively. The X represents ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ .

Since there is no exposure of evaporites in the study area and the influence of human activities is minimal, the lowest  $\text{Cl}^-$  content in the watershed ( $6 \mu\text{mol/L}$  in July and  $5 \mu\text{mol/L}$  in December) was used as the atmospheric input. The concentrations of other atmospheric input ions X ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) were estimated by correcting the molar concentration ratios of these ions to  $\text{Cl}^-$  in precipitation [41], as follows:

$$[\text{X}]_{\text{atm}} = [\text{Cl}^-]_{\text{atm}} \times (\text{X}/\text{Cl})_{\text{atm}} \quad (7)$$

By integrating actual rainwater samples collected in this study with the average values from previous rainwater data in the Nanling region [42], the average molar concentration ratios of ions from precipitation input were calculated as follows:  $\text{Na}^+/\text{Cl}^- = 0.83$ ,  $\text{K}^+/\text{Cl}^- = 1.21$ ,  $\text{Ca}^{2+}/\text{Cl}^- = 3.06$ , and  $\text{Mg}^{2+}/\text{Cl}^- = 0.22$ .

Since  $\text{Cl}^-$  primarily originates from atmospheric input, evaporites, and anthropogenic sources, the  $\text{Cl}^-$  concentration corrected for precipitation input can be considered as the con-

tribution from evaporites and anthropogenic sources. Assuming that  $\text{Na}^+$  from evaporites and anthropogenic sources is in equilibrium with  $\text{Cl}^-$ , the following relationship holds:

$$[\text{Cl}^-]_{\text{anthro+evap}} = [\text{Cl}^-]_{\text{river}} - [\text{Cl}^-]_{\text{atm}} \quad (8)$$

$$[\text{Na}^+]_{\text{anthro+evap}} = [\text{Cl}^-]_{\text{anthro+evap}} \quad (9)$$

After correcting for atmospheric precipitation, evaporites, and anthropogenic inputs, the remaining  $\text{Na}^+$  and  $\text{K}^+$  (corrected for precipitation input) can be attributed to silicate rock weathering:

$$[\text{Na}^+]_{\text{sil}} = [\text{Na}^+]_{\text{river}} - [\text{Na}^+]_{\text{atm}} - [\text{Na}^+]_{\text{anthro+evap}} \quad (10)$$

$$[\text{K}^+]_{\text{sil}} = [\text{K}^+]_{\text{river}} - [\text{K}^+]_{\text{atm}} \quad (11)$$

Generally,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  primarily originate from carbonate and silicate rocks. Since the exposed lithology in the CJ watershed is Jurassic monzogranite, the contribution of carbonate rock weathering can be neglected. Therefore, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the CJ watershed, after correcting for precipitation input, can be attributed to silicate rock weathering:

$$[\text{Ca}^{2+}]_{\text{sil}} = [\text{Ca}^{2+}]_{\text{river}} - [\text{Ca}^{2+}]_{\text{atm}} \quad (12)$$

$$[\text{Mg}^{2+}]_{\text{sil}} = [\text{Mg}^{2+}]_{\text{river}} - [\text{Mg}^{2+}]_{\text{atm}} \quad (13)$$

Subsequently, the contributions of silicate rock weathering in the CJ watershed, represented by  $[\text{Na}^+]_{\text{sil}}$ ,  $[\text{K}^+]_{\text{sil}}$ ,  $[\text{Ca}^{2+}]_{\text{sil}}$ , and  $[\text{Mg}^{2+}]_{\text{sil}}$ , were used to calculate the end-member ratios for silicate rock weathering:  $\text{K}^+/\text{Na}^+ = 0.17$ ,  $\text{Mg}^{2+}/\text{Na}^+ = 0.03$ , and  $\text{Ca}^{2+}/\text{Na}^+ = 0.21$ . By incorporating the  $\text{Mg}^{2+}/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  molar ratios of the silicate rock end-member in the CJ watershed, the contributions of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from silicate rock weathering in the DT watershed were calculated as follows:

$$[\text{Ca}^{2+}]_{\text{sil}} = [\text{Na}^+]_{\text{sil}} \times [\text{Ca}^{2+}/\text{Na}^+]_{\text{sil}} \quad (14)$$

$$[\text{Mg}^{2+}]_{\text{sil}} = [\text{Na}^+]_{\text{sil}} \times [\text{Mg}^{2+}/\text{Na}^+]_{\text{sil}} \quad (15)$$

The contributions of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from carbonate rock weathering in the DT watershed were determined by subtracting the atmospheric input and silicate rock input from the total  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in surface water:

$$[\text{Ca}^{2+}]_{\text{carb}} = [\text{Ca}^{2+}]_{\text{river}} - [\text{Ca}^{2+}]_{\text{atm}} - [\text{Ca}^{2+}]_{\text{sil}} \quad (16)$$

$$[\text{Mg}^{2+}]_{\text{carb}} = [\text{Mg}^{2+}]_{\text{river}} - [\text{Mg}^{2+}]_{\text{atm}} - [\text{Mg}^{2+}]_{\text{sil}} \quad (17)$$

By iteratively solving the system of Equations (6)–(17), the molar concentrations of cations originating from atmospheric precipitation, carbonate rocks, silicate rocks, evaporites, and anthropogenic activities were determined. Subsequently, the mass concentrations of cations contributed by each end-member in the watershed and their relative contribution rates were calculated.

For the CJ watershed, the average contributions of silicate weathering and atmospheric precipitation input to cations were 77.9% and 19.6% in July, respectively, while in December, they were 81.1% and 14.8%, respectively (Table 2). For the DT watershed, the average contributions of carbonate weathering, silicate weathering, and atmospheric precipitation input to cations were 82.6%, 12.9%, and 4.5% in July, respectively. In December, they were 90.2%, 7.7%, and 2.1%, respectively (Table 2). These findings suggest a mixed carbonate–silicate weathering signature in the DT watershed. The contributions from anthropogenic

input and evaporite dissolution were negligible in the CJ and DT watersheds, which aligns well with the actual conditions of the study area, where there are no exposed evaporites and human activity is minimal.

**Table 2.** Contribution of different sources to cations of river water in study area during different sampling periods.

| Contribution of Different Sources to Cations of River Water | CJSW-July | CJSW-December | DTSW-July | DTSW-December |
|-------------------------------------------------------------|-----------|---------------|-----------|---------------|
| Carbonate weathering (%)                                    | /         | /             | 82.6      | 90.2          |
| Silicate weathering (%)                                     | 77.9      | 81.1          | 12.9      | 7.7           |
| Atmospheric precipitation (%)                               | 19.6      | 14.8          | 4.5       | 2.1           |
| Anthropogenic input (%)                                     | /         | /             | /         | /             |
| Evaporite dissolution (%)                                   | /         | /             | /         | /             |

Values of major ions concentrations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) incorporated into water by dissolution reactions in two studied watersheds were calculated as shown in Table 3. The silicate weathering-derived fluxes of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  to surface waters were comparable between the CJ and DT watersheds. However, carbonate weathering in the DT watershed contributed substantially higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  inputs than in the CJ watershed, resulting in the formation of high-TDS  $\text{HCO}_3$ -Ca-type waters. In contrast, the CJ watershed received relatively minor cation inputs (predominantly  $\text{Ca}^{2+}$  and  $\text{K}^+$ ) from silicate weathering, ultimately producing low-TDS  $\text{HCO}_3$ -Na-Ca-type waters.

**Table 3.** Contribution of chemical weathering (silicate and carbonate) to cations of river water in study area during different sampling periods.

| Contribution to Cations of River Water  | CJSW-July | CJSW-December | DTSW-July | DTSW-December |
|-----------------------------------------|-----------|---------------|-----------|---------------|
| $[\text{Ca}^{2+}]_{\text{sil}}$ (mg/L)  | 1.2       | 1.1           | 0.9       | 0.9           |
| $[\text{Mg}^{2+}]_{\text{sil}}$ (mg/L)  | 0.1       | 0.1           | 0.1       | 0.1           |
| $[\text{K}^+]_{\text{sil}}$ (mg/L)      | 0.6       | 1.1           | 0.5       | 0.5           |
| $[\text{Na}^+]_{\text{sil}}$ (mg/L)     | 2.7       | 3.1           | 1.9       | 2.1           |
| $[\text{Ca}^{2+}]_{\text{carb}}$ (mg/L) | /         | /             | 18.5      | 36.1          |
| $[\text{Mg}^{2+}]_{\text{carb}}$ (mg/L) | /         | /             | 2.4       | 4.9           |

The respective chemical weathering rates of silicate ( $\text{CWR}_{\text{sil}}$ ) and carbonate ( $\text{CWR}_{\text{carb}}$ ) can be then calculated as follow [5,43]:

$$\text{CWR}_{\text{sil}} = ([\text{Ca}^{2+}]_{\text{sil}} + [\text{Mg}^{2+}]_{\text{sil}} + [\text{K}^+] + [\text{Na}^+]) \times Q/A \quad (18)$$

$$\text{CWR}_{\text{carb}} = ([\text{Ca}^{2+}]_{\text{carb}} + [\text{Mg}^{2+}]_{\text{carb}}) \times Q/A \quad (19)$$

Q and A represent the discharge (mean annual runoff) and drainage area, respectively.

$\text{CO}_2$  consumption rate through chemical weathering of silicate ( $\text{CCR}_{\text{sil}}$ ) and carbonate ( $\text{CCR}_{\text{carb}}$ ) by  $\text{H}_2\text{CO}_3$  can be calculated as follows:

$$\text{CCR}_{\text{sil}} = (2 \times [\text{Ca}^{2+}]_{\text{sil}} + 2 \times [\text{Mg}^{2+}]_{\text{sil}} + [\text{K}^+] + [\text{Na}^+]) \times Q/A \quad (20)$$

$$\text{CCR}_{\text{carb}} = (2 \times [\text{Ca}^{2+}]_{\text{carb}} + 2 \times [\text{Mg}^{2+}]_{\text{carb}}) \times Q/A \quad (21)$$

Results of CWR and CCR of silicate and carbonate in the CJ and DT watersheds are shown in Table 4. The  $\text{CWR}_{\text{sil}}$  in the CJ watershed was calculated to

be  $0.24 \times 10^6$  mol/km<sup>2</sup>/yr, while chemical weathering of carbonate was negligible ( $CWR_{carb} \approx 0$ ). In the DT watershed, the  $CWR_{sil}$  and  $CWR_{carb}$  were calculated to be  $0.20 \times 10^6$  and  $0.97 \times 10^6$  mol/km<sup>2</sup>/yr, respectively. These results indicated that the hydrochemical composition of the CJ watershed is primarily influenced by silicate weathering, whereas the DT watershed's hydrochemistry is jointly affected by both carbonate and silicate weathering. The values of  $CWR_{sil}$  in the two watersheds were similar. The surface water in the DT watershed originated from upstream silicate-rich watersheds (Figure 1). As a result, despite carbonate rocks being the predominant lithology in the DT watershed, its  $CWR_{sil}$  values closely approximated those of the silicate-dominated CJ watershed.

The  $CWR_{carb}$  ( $0.97 \times 10^6$  mol/km<sup>2</sup>/yr) in the DT watershed is significantly higher than  $CWR_{sil}$  ( $0.20 \times 10^6$  mol/km<sup>2</sup>/yr), shaping the hydrochemical characteristics of relatively high TDS and Ca<sup>2+</sup> content. In contrast, the CJ watershed, dominated by slower silicate weathering ( $CWR_{sil} = 0.24 \times 10^6$  mol/km<sup>2</sup>/yr), exhibits relatively low TDS and Ca<sup>2+</sup> levels. The  $CWR_{sum}$  ( $CWR_{carb} + CWR_{sil}$ ) for the CJ watershed in July and December are  $0.22 \times 10^6$  mol/km<sup>2</sup>/yr and  $0.26 \times 10^6$  mol/km<sup>2</sup>/yr, respectively, while those for the DT watershed are  $0.83 \times 10^6$  mol/km<sup>2</sup>/yr and  $1.5 \times 10^6$  mol/km<sup>2</sup>/yr in July and December, respectively. Both watersheds exhibit stronger rock weathering in the dry season compared to the wet season, which might be due to higher rainfall and elevated water levels in the wet season reducing the connectivity between rocks and atmospheric CO<sub>2</sub>.

**Table 4.** CO<sub>2</sub> consumption ( $10^6$  mol/km<sup>2</sup>/yr) through chemical weathering of silicate and carbonate and chemical weathering rates ( $10^6$  mol/km<sup>2</sup>/yr) in the CJ and DT watersheds, respectively.

|             | $CWR_{sil}$ | $CWR_{carb}$ | $CWR_{sum}$ | $CCR_{sil}$ | $CCR_{carb}$ | $CCR_{sum}$ |
|-------------|-------------|--------------|-------------|-------------|--------------|-------------|
| CJ-July     | 0.22        | 0            | 0.22        | 0.26        | 0            | 0.26        |
| CJ-December | 0.26        | 0            | 0.26        | 0.30        | 0            | 0.30        |
| CJ-Ave.     | 0.24        | 0            | 0.24        | 0.28        | 0            | 0.28        |
| DT-July     | 0.18        | 0.65         | 0.83        | 0.21        | 1.30         | 1.51        |
| DT-December | 0.21        | 1.29         | 1.50        | 0.24        | 2.58         | 2.82        |
| DT-Ave.     | 0.20        | 0.97         | 1.17        | 0.23        | 1.94         | 2.17        |

The CJ and DT watersheds showed similar  $CCR_{sil}$  values of  $0.28 \times 10^6$  mol/km<sup>2</sup>/yr and  $0.23 \times 10^6$  mol/km<sup>2</sup>/yr, respectively. The  $CCR_{carb}$  of the DT watershed was  $1.94 \times 10^6$  mol/km<sup>2</sup>/yr, but chemical weathering of carbonate was negligible in the CJ watershed ( $CCR_{carb} \approx 0$ ). Therefore,  $CCR_{sum}$  of the DT watershed ( $2.17 \times 10^6$  mol/km<sup>2</sup>/yr) was significantly larger than that of the CJ watershed ( $0.28 \times 10^6$  mol/km<sup>2</sup>/yr). These results indicated lithological controls on hydrochemical characteristics and CO<sub>2</sub> consumption in the two watersheds. However, silicate weathering constitutes a net carbon sink [11]. Consequently, although the DT watershed exhibits significantly higher  $CCR_{sum}$  compared to the CJ watershed, the CJ watershed exhibited superior long-term carbon sequestration capacity when assessed over extended temporal scales. Both watersheds exhibited higher  $CCR_{sil}$  than the global average for silicate-dominated basins ( $0.1 \times 10^6$  mol/km<sup>2</sup>/yr, [8]), indicating a significant CO<sub>2</sub> sequestration capacity.

#### 4. Conclusions

This study investigated the influence of lithology on rock chemical weathering processes and carbon sequestration in two lithologically contrasting watersheds—CJ (granite) and DT (carbonate rock)—located in the Lingnan region of Guangdong Province, China. By integrating hydrochemical analysis, the Straightforward Method, and stable carbon isotope analysis, we demonstrated the lithological controls in regulating weathering dynamics and associated carbon consumption. In the granite-dominated CJ watershed, silicate



weathering driven by  $\text{H}_2\text{CO}_3$  (CWR:  $0.24 \times 10^6 \text{ mol/km}^2/\text{yr}$ ) governed hydrochemical evolution, yielding low total dissolved solids (TDS)  $\text{HCO}_3\text{-Na}\cdot\text{Ca}$ -type waters. Conversely, the carbonate-rich DT watershed exhibited dual control from both carbonate and silicate weathering ( $\text{CWR}_{\text{carb}} = 0.97 \times 10^6 \text{ mol/km}^2/\text{yr}$ ;  $\text{CWR}_{\text{sil}} = 0.20 \times 10^6 \text{ mol/km}^2/\text{yr}$ ), producing high-TDS  $\text{HCO}_3\text{-Ca}$ -type waters. Chemical weathering of the CJ watershed dominated by silicate consumed  $\text{CO}_2$  at a rate of  $0.28 \times 10^6 \text{ mol/km}^2/\text{yr}$ , whereas the DT watershed with both carbonate and silicate weathering generated a CCR value of  $2.17 \times 10^6 \text{ mol/km}^2/\text{yr}$ . Previous research has often focused on large-scale or climatically distinct basins; our work demonstrated that even localized lithological differences (silicate-dominated vs. carbonate-influenced catchments) can lead to significant variations in weathering pathways and CCR. These findings indicated lithology's fundamental control on hydrochemical signatures and  $\text{CO}_2$  drawdown via weathering processes. Given carbon balance's pivotal role in regional sustainability, this study emphasized that future carbon cycle models and sink quantifications must explicitly incorporate lithological variability to improve accuracy, particularly in complex geological terrains like southern China.

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**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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