

Chemical weathering and CO₂ consumption of a high-erosion-rate karstic river: a case study of the Sanchahe River, southwest China

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Abstract The Sanchahe River in southwest China is a tributary of the Wujiang River and experiences high erosion rates. Geochemical analysis was conducted on Sanchahe River basin samples collected in the wet and dry seasons of 2014 in order to better understand local chemical weathering processes, anthropogenic influences, and associated CO₂ consumption. The samples' total dissolved solid concentrations were found to be significantly higher than that of the global river average. Ca²⁺ was the dominant cation in the samples and accounted for 64 % and 73 % of the total cations in the dry and wet seasons, respectively. HCO₃⁻ and SO₄²⁻ were the dominant anions, accounting for 92 % of the total anions. Stoichiometry analyses of the river waters suggested that the water chemistry is controlled by carbonate dissolution by both carbonic and sulfuric acid. The chemical weathering rates of carbonate and silicate evaporites in the Sanchahe River basin were estimated to be approximately 109.2 and 11.0 t/(km² a), respectively, much higher than both the global mean values and the Wujiang River, a typical karstic river. The CO₂ consumption by carbonate and silicate weathering

are estimated to be 597.4×10^3 and 325.5×10^3 mol/(km² a), which are much higher than corresponding values in the Wujiang River, indicating a high erosion rate in the Sanchahe River basin.

Keywords Sanchahe River · Water chemistry · Carbonate and silicate weathering · CO₂ consumption

1 Introduction

Chemical characteristics of water can be used to trace the sources of solutes in rivers, and they also help understand chemical weathering rates, geologic background, and CO₂ consumption of watersheds (Hu et al. 1982; Gaillardet et al. 1999; Han and Liu 2004; Hren et al. 2007; Chetelat et al. 2008; Liu et al. 2008a; Raymond and Oh 2009; Moosdorf et al. 2011). Carbon sinks associated with the processes of rock weathering (including carbonates and silicates) can affect the global carbon cycle (Meybeck 1987; Liu et al. 2011; Moosdorf et al. 2011). On a geologic time scale, only silicate weathering produces a net impact on atmospheric CO₂ content (silicates: $\text{CaSiO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2 + \text{H}_2\text{O}$; carbonates: $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$) (White et al. 1999). In the shorter term, however, from several decades to thousands of years, the influence of carbonate weathering can be more significant than the impact of silicate weathering due to carbonates' much higher weathering rate (Blum et al. 1998; Kump et al. 2000; Jacobson et al. 2002; Liu et al. 2010). Chemical weathering rate is affected by several factors, such as geologic background, tectonism, weather, and land use (Gibbs 1970; Raymond and Cole 2003; Das et al. 2005; von Blanckenburg 2005; Williams et al. 2005). This study contributes to a more complete understanding of regional

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weathering processes and to the broader knowledge base around the theory and mechanism of carbon sinks in the context of rock weathering.

With about 500,000 km² of karst terrain, southwest China is one of the largest karst-covered areas in the world (Han and Liu 2004). Due to the fragile ecological environment of the area, weathering is very intense and water and soil loss are significant. The Sanchahe River is the headwaters river of the Wujiang River, which is the largest river of Southwest China. The Sanchahe River catchment has one of the highest rates of soil erosion in the Wujiang River watershed (Liu et al. 2015). There are a number of coal mining enterprises in the Sanchahe River catchment as it is the thermal power base of Guizhou Province, and SO₂ deposition is significant. The Sanchahe River is a high-erosion karst river watershed, and is strongly influenced by human activities.

2 Study area

The Sanchahe River (104°18'–106°18'E and 26°10'–27°00'N) originates in Weining County, at the east side of Wumeng Mountain, western Guizhou (Jiao et al. 2013). The total length of the river is 325.6 km. The watershed area is about 7264 km², including 80 % in mountainous regions, 15 % plateau and hilly land, and 5 % flat ground. The vertical drop of the Sanchahe basin is more than 1300 m from west to east, and the average gradient is approximately 4 %. The Sanchahe basin consists of various parent rocks, such as carbonatite and coal-bearing rock strata, as well as basalt (Han and Liu 2004). The western portion of the watershed has a temperate climate, with the remainder falling in the subtropical monsoon climate zone. According to meteorological data from the past 3 years, the annual average temperature in the catchment varies between 12 and 16 °C, with annual average precipitation of 546.9 mm. More than 75 % of the precipitation falls between May and October. Precipitation is at a minimum in winter (December to February), which accounts for less than 5 % of annual precipitation. The mean runoff volume of the Sanchahe basin is about 49.5 × 10⁸ m³. Being related to precipitation, the runoff is distributed unevenly during the hydrologic year, with 80 % of the annual runoff occurring in the wet season.

3 Sampling and analytical methods

30 wet season water samples and 28 dry season samples were collected from the main river and the tributaries of the Sanchahe (Fig. 1). Temperature (*T*), pH, dissolved oxygen (DO), and electrical conductivity (EC) were determined

in situ using multi-parameter water probe meters (WTW-3420). HCO₃[−] was measured on site by acid titration using hydrochloric acid. The HCO₃[−] of each sample was measured at least twice, and the titration error was controlled within 5 %. All the water samples were filtered with 0.45 μm mixed cellulose membrane filters (Millipore) on the day they were sampled. After filtration, a fraction of the samples were stored in clean High Density Polyethylene (HDPE) bottles. All the bottles were pre-washed with ultra-purified (double-distilled) HCl and rinsed with Milli-Q 18.2 MΩ water. The samples for cation determination were acidized (pH <2) with HCl. All cations and anions were measured on an ion chromatograph (DIONEX, ICS-1100), with IonPac CS-12A column and IonPac AG-19 column separately, and SiO₂ was measured by colorimetry.

4 Results and discussion

4.1 Composition and temporal variation of the major ions

Table 1 shows the results of water sample analyses from the Sanchahe River basin in both dry and wet seasons. Samples were generally alkaline. The pH ranged from 7.9 to 10.2 in the dry period, averaging 8.3; while pH values ranged from 6.9 to 7.9 in the wet period, with an average of 7.4. The high pH values might have been impacted by the dissolution of limestone and dolomite in river waters. The pH values in the wet season were lower than those in the dry season, which could be due to the concentrated and heavy acid rainfall in the wet seasons, which would tend to lower pH. The total soluble cations (TZ⁺ = 2Ca²⁺ + 2Mg²⁺ + Na⁺ + K⁺) in river waters during the dry period ranged from 3.2 to 9.3 meq/L, averaging 5.2 meq/L, while those in the wet period ranged between 3.3 and 6.6 meq/L, with an average of 4.4 meq/L—all much higher than the global average value (1.25 meq/L) (Meybeck 1981). The average inorganic charge balance (NICB = (TZ⁺ − TZ[−])/TZ⁺) of river water samples was 6 % and 8 % in the dry and wet seasons, respectively.

The total dissolved solid (TDS = Ca²⁺ + Mg²⁺ Na⁺ + K⁺ + HCO₃[−] + SO₄^{2−} + Cl[−] + NO₃[−] + SiO₂) range in the dry season was 247.8–628.4 mg/L, averaging 367.5 mg/L; while the variation in the wet seasons was 241.3–427.5 mg/L, with an average of 311.4 mg/L. These values are much higher than the global average TDS (100 mg/L) (Gaillardet et al. 1999). In comparison with the famous rivers of the world, the Sanchahe River basin displayed higher TDS than the Amazon and Mississippi, but lower than the Nile and Rhine (Table 2). Furthermore, compared with large rivers in China, the Sanchahe River exhibited higher TDS than the Yangtze River

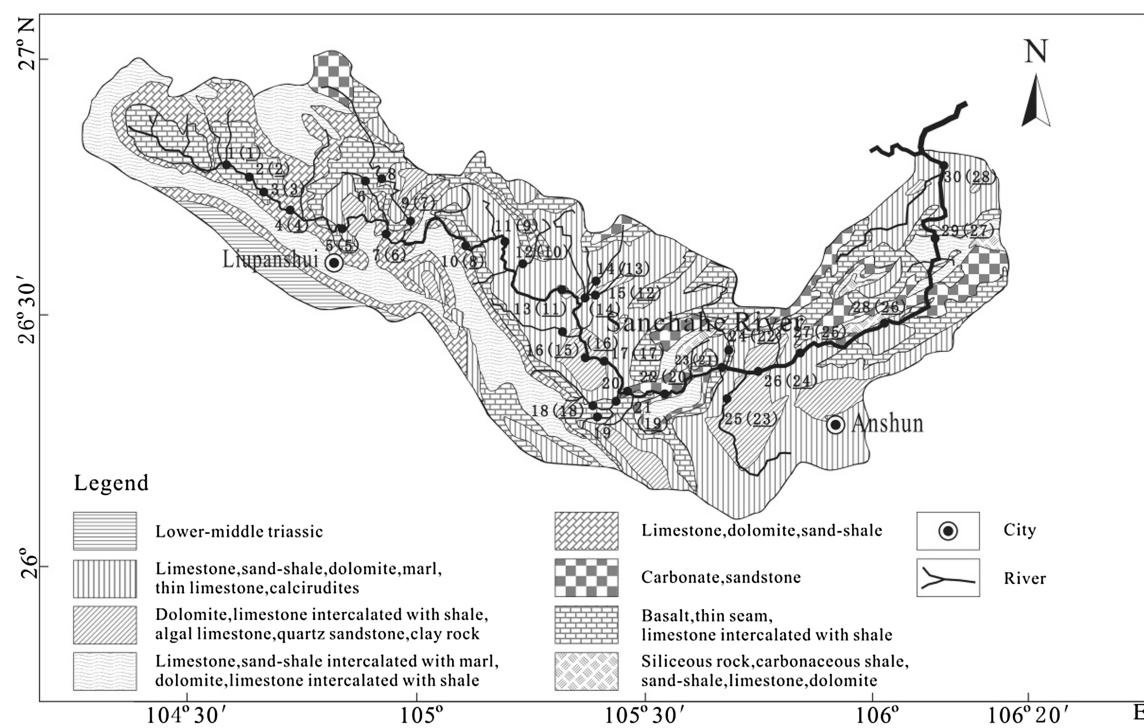


Fig. 1 Sample locations in the Sanchahe River Basin of dry season and rain season (in the brackets)

Table 1 Major ionic compositions of the river water samples from Sanchahe River

Item	Unit	Dry season		Wet season	
		Variation	Average	Variation	Average
pH	–	7.9–10.2	8.3	6.9–7.9	7.4
T	°C	9.1–15.5	11.4	16.2–24.7	20.2
TDS	mg/L	247.8–628.4	367.5	241.3–427.5	311.4
SiO ₂	mmol/L	0.02–0.14	0.08	0.09–0.17	0.11
Ca ²⁺	meq/L	2.16–5.21	3.35	2.63–4.08	3.20
Mg ²⁺	meq/L	0.42–2.01	0.87	0.34–1.41	0.66
Na ⁺	meq/L	0.12–3.33	0.92	0.22–1.62	0.47
K ⁺	meq/L	0.02–0.21	0.06	0.03–0.08	0.04
HCO ₃ [–]	meq/L	1.69–2.89	2.31	1.08–3.00	2.02
SO ₄ ^{2–}	meq/L	0.76–5.61	2.13	0.87–4.39	1.72
NO ₃ [–]	meq/L	0.06–0.25	0.14	0.08–0.22	0.16
Cl [–]	meq/L	0.06–1.19	0.27	0.05–0.24	0.12

(TDS = 220 mg/L) (Chetelat et al. 2008) and the Xijiang River (TDS = 241 mg/L) (Xu and Liu 2010), and lower than the Yellow River (TDS = 460 mg/L) (Gaillardet et al. 1999).

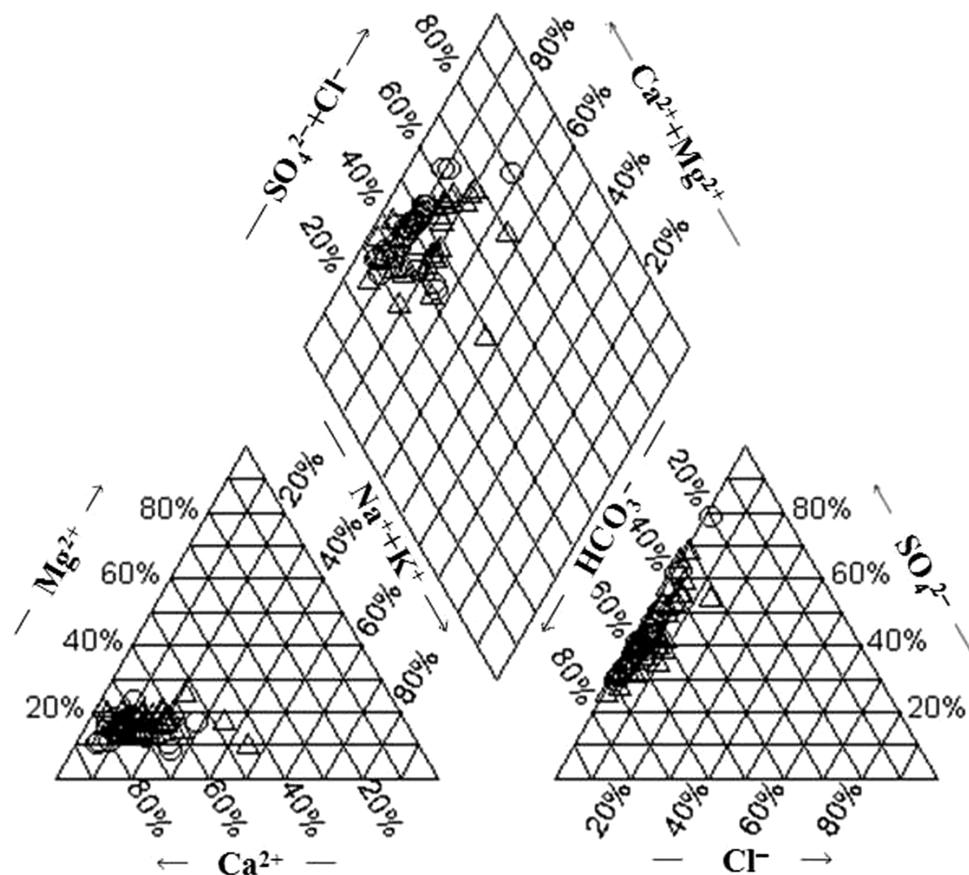
The main cation in river waters during the sampling campaign was Ca²⁺ (Fig. 2). For the dry season samples, Ca²⁺ accounted for 64 % of all the cations, with

concentrations varying between 2.2 and 5.2 meq/L, averaging 3.4 meq/L; while for the wet period samples, Ca²⁺ comprised 73 % of all the cations, with concentrations ranging from 2.4 to 4.1 meq/L, and averaging 3.2 meq/L. The second most prevalent cations were Mg²⁺ and Na⁺, with less Mg²⁺ than Na⁺ in the dry season and more Mg²⁺ than Na⁺ in the wet season. Mg²⁺ and Na⁺ together comprised 15 % of the total cations. K⁺ accounted for only about 5 % of all cations. During the sampling period, HCO₃[–] and SO₄^{2–} were the major anions in river water samples, accounting for 48 % and 44 % of the total anions, respectively. Their concentration variations in the dry season were 1.7–2.9 and 0.8–5.6 meq/L, respectively, with average values of 2.3 and 2.1 meq/L. In the wet season, HCO₃[–] and SO₄^{2–} comprised 50 % and 42 % of the total anions, respectively, with concentration ranges 1.1–3.0 and 0.9–4.4 meq/L, and average values of 2.0 and 1.7 meq/L. NO₃[–] and Cl[–], together accounted for 7 % of the total anions, with higher Cl[–] than NO₃[–] in the dry period and lower Cl[–] than NO₃[–] in the wet period.

Across the basin, all the equivalent concentration ratio data points of (Ca²⁺ + Mg²⁺)/HCO₃[–] fall beneath the slope of 1, while the equivalent concentration ratio data points of (Ca²⁺ + Mg²⁺)/(HCO₃[–] + SO₄^{2–}) are on either side of the slope 1. Most points plot along the line of 1:1, indicating a good balance of (Ca²⁺ + Mg²⁺) and (HCO₃[–] + SO₄^{2–}). This may be caused by watershed erosion and rock weathering combined with SO₄^{2–} input

Table 2 Major ionic compositions of Sanchahe River Basin and other rivers

Basin	TDS (mg/L)	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	Cl^- (meq/L)	SO_4^{2-} (meq/L)	HCO_3^- (meq/L)	SiO_2 (mmol/L)
Sanchahe River (annual average)	339	0.70	0.05	3.28	0.77	0.20	1.93	2.17	0.10
Wujiang River (Han and Liu 2004)	317	0.18	0.04	3.08	1.07	0.11	1.16	2.79	0.10
Changjiang River (Chetelat et al. 2008)	220	0.45	0.06	1.72	0.66	0.30	0.61	1.83	0.16
Huanghe River (Gaillardet et al. 1999)	460	2.37	0.11	2.35	1.70	1.56	1.39	3.36	0.13
Xijiang River (Xu and Liu 2010)	241	0.14	0.05	2.27	0.64	0.08	0.34	2.53	0.10
Amazon (Gaillardet et al. 1999)	44	0.08	0.02	0.30	0.07	0.06	0.09	0.34	0.12
River Nile (Gaillardet et al. 1999)	388	2.26	0.20	1.55	1.15	1.26	1.08	2.85	0.21
Mississippi river (Gaillardet et al. 1999)	216	0.48	0.07	1.70	0.73	0.29	0.53	1.90	0.13
River Rhine (Gaillardet et al. 1999)	600	3.96	0.16	4.03	0.94	4.94	1.54	2.59	0.09

Fig. 2 Piper diagram of the river water samples from Sanchahe River Basin

from oxidation of sulfide minerals and acid precipitation. Previous studies suggest that sulfuric acid in watershed erosion and rock weathering processes of the southwest karst rivers (Li et al. 2008) contributes significantly to the chemical composition of river water. The Sanchahe River basin possesses abundant coal resources. Large-scale mining of high-sulfur coal and numerous coal-fired power plants in this area produce and emit SO_2 into the atmosphere, which could then form sulfuric acid in

precipitation, contributing to rock weathering and erosion in the watershed (Fig. 3).

4.2 Source of dissolved load

4.2.1 Atmospheric input

Chloride is the most useful reference to evaluate atmospheric inputs to rivers in many studies because it is conservative and

is not involved in biogeochemical cycling (Gaillardet et al. 1997; Viers et al. 2001; Liu et al. 2013). The concentration of Cl^- in river water is assumed to be entirely derived from the atmosphere; the contribution of evaporites is negligible (Negrel et al. 1993). By using the Cl^- -normalized ratios of rainwater, concentrations of other elements can be corrected with regard to the contribution of atmospheric deposition. According to Larssen et al. (1999), the average level of Cl^- is 0.01 meq/L in rural Guizhou, and about 0.021 meq/L in Guiyang City (Xiao et al. 2013). We did not analyze rainwater during the period of study. Consequently, values of atmospheric $[\text{Cl}]$ concentrations calculated with evapo-transpiration factors were used in the correction of atmospheric inputs for the mainstem.

The atmospheric contribution of element X ($X = \text{Ca}^{2+}$, Mg^{2+} , Na^+ , K^+ , and SO_4^{2-}) to river water can be derived from the following equation:

$$X_r = \left(\frac{X}{\text{Cl}^-} \right)_{\text{rain}} \times (\text{Cl}^-)_{\text{rain}} / f_{\text{et}} \quad (1)$$

where X_r is the contribution of element X from rain to rivers; f_{et} is the evapo-transpiration factor; and $(X/\text{Cl}^-)_{\text{rain}}$ is the molar ratio of element X over Cl^- in rainwater. $F_{\text{et}} = P/(P - E)$, where P is annual precipitation (mm) and E is annual mean evaporation (mm). The X/Cl^- ratios of volume-weighted mean concentrations of rainwater in Puding reported by Wu et al. (2012) were used as $(X/\text{Cl})_{\text{rain}}$ in the calculation; $\text{Cl}^- = 0.014 \text{ meq/L}$, $\text{Ca}^{2+} = 0.16 \text{ meq/L}$, $\text{Mg}^{2+} = 0.004 \text{ meq/L}$, $\text{Na}^+ = 0.011 \text{ meq/L}$, $\text{K}^+ = 0.009 \text{ meq/L}$, and $\text{SO}_4^{2-} = 0.15 \text{ meq/L}$.

The calculation results show the respective contributions of Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and SO_4^{2-} from rain to rivers to be 0.042, 0.47, 0.012, 0.033, 0.028, and 0.46 meq/L, explaining only a fraction of the water chemistry of river water.

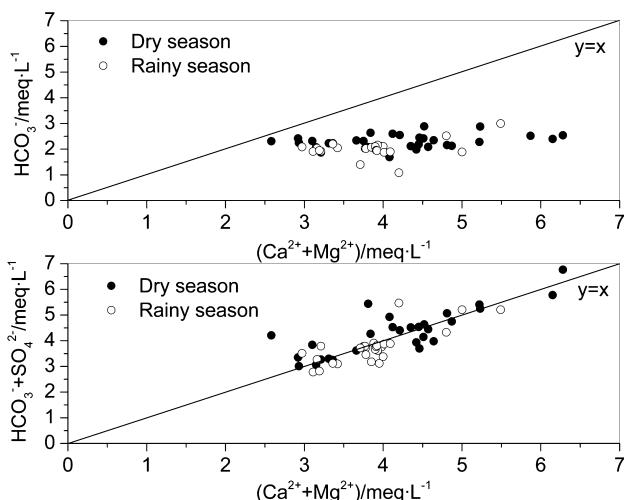


Fig. 3 Equivalent charge balance of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus HCO_3^- and versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ of the Sanchahe River Basin

4.2.2 Anthropogenic input

The Sanchahe River basin is characterized by high SO_4^{2-} content, with the $\text{SO}_4^{2-}/\text{Na}^+$ value much larger than in other rivers globally. SO_4^{2-} in the river originates from several sources, such as hydrotrogenic rock (e.g., gypsum) dissolution, sulfide oxidation, and atmospheric acid deposition. The molar ratios of $\text{SO}_4^{2-}/\text{Na}^+$ and $\text{NO}_3^-/\text{Na}^+$ can also be used to track the sources of SO_4^{2-} (Fig. 4). SO_4^{2-} and NO_3^- of the Sanchahe River basin display a linear relationship, indicating that SO_4^{2-} and NO_3^- may have derived from the same source; this source is likely to be anthropogenic, as NO_3^- is generally considered an anthropogenic emission.

Rainwater at Guiyang and Puding contains a high concentration of SO_4^{2-} (Wu et al. 2012; Han et al. 2011). Therefore, the high content of SO_4^{2-} in the rainwater of the Sanchahe River basin implies that the influence of acid rain on water chemistry in the study area is significant. At least some of the SO_4^{2-} in the river waters is likely due to acid rain input related to extensive and intensive use of S-enriched coal and power production via coal combustion in the research area, one of the most heavily acid rain-polluted areas in China for many years (Larsen et al. 1999, 2006; Aas et al. 2007).

Concentrations of SO_4^{2-} and NO_3^- increased from upstream to downstream (Fig. 5), which is consistent with the fact that human activity increases upstream to downstream. The headwaters of the Sanchahe River basin are dominated by agricultural activities, while the lower portions contain the significant industrial base of Liupanshui.

In addition, $\delta^{34}\text{S}$ values in river waters and in industrial emissions, coal, and soil in Guizhou Province were reported to be from 2‰ to 8‰ by Hong et al. (1993), while Jiang et al. (2007) reported $\delta^{34}\text{S}$ of dissolved SO_4^{2-} from the Sanchahe River at about −7.3‰, indicating SO_4^{2-} was mainly derived from the oxidation of sulfide. It is therefore suggested that the dissolved SO_4^{2-} in the Sanchahe River is primarily derived from sulfide oxidation and acid rain deposition.

4.3 Chemical budget and chemical weathering rate estimation

4.3.1 Chemical budget

As was discussed in Sect. 4.2, the solutes in river water have several sources, expressed as the following:

$$[X]_{\text{river}} = [X]_{\text{atmosphere}} + [X]_{\text{anthropogenic}} + [X]_{\text{carbonaterock}} + [X]_{\text{silicate}} + [X]_{\text{sulfide}} \quad (2)$$

Some hypotheses were needed to calculate the exact sources of each element. First, we assumed that the

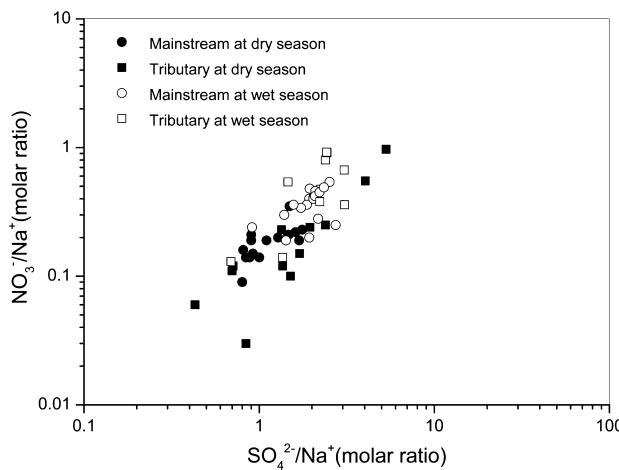


Fig. 4 Variations of $\text{SO}_4^{2-}/\text{Na}^+$ with $\text{NO}_3^-/\text{Na}^+$ molar ratios of the Sanchahe River waters

atmosphere and human activities are the main Cl^- contributors. According to the analysis in Sect. 4.2.1, Cl^- derived from the atmosphere is about 0.042 meq/L; additional Cl^- originates from human activities, and the balance with Na^+ . Second, that SO_4^{2-} may stem from precipitation and oxidation of sulfide minerals, with all of the additional SO_4^{2-} (more than $[\text{SO}_4^{2-}]_{\text{atmospheric}}$) derived from sulfide mineral oxidation. Third, that the cation (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) contribution from human activities to river water is negligible. Based on the above assumptions, we reduced the equations as below:

$$[\text{Cl}^-]_{\text{atmosphere}} = 0.042 \text{ meq/L} \quad (3)$$

$$[\text{Cl}^-]_{\text{river}} = [\text{Cl}^-]_{\text{atmosphere}} + [\text{Cl}^-]_{\text{anthropogenic}} \quad (4)$$

$$[\text{Na}^+]_{\text{river}} = [\text{Na}^+]_{\text{atmosphere}} + [\text{Cl}^-]_{\text{anthropogenic}} + [\text{Na}^+]_{\text{silicate rock}} \quad (5)$$

$$[\text{SO}_4^{2-}]_{\text{river}} = [\text{SO}_4^{2-}]_{\text{atmosphere}} + [\text{SO}_4^{2-}]_{\text{sulfide}} \quad (6)$$

$$[\text{K}^+]_{\text{river}} = [\text{K}^+]_{\text{silicate}} + [\text{K}^+]_{\text{atmosphere}} \quad (7)$$

$$[\text{Ca}^{2+}]_{\text{river}} = [\text{Ca}^{2+}]_{\text{carbonate}} + [\text{Ca}^{2+}]_{\text{silicate}} + [\text{Ca}^{2+}]_{\text{atmosphere}} \quad (8)$$

$$[\text{Mg}^{2+}]_{\text{river}} = [\text{Mg}^{2+}]_{\text{carbonate}} + [\text{Mg}^{2+}]_{\text{silicate}} + [\text{Mg}^{2+}]_{\text{atmosphere}} \quad (9)$$

Previous studies (Galy and France-Lanord 1999; Han and Liu 2004; Liu et al. 2013) demonstrate that it's difficult to distinguish Ca^{2+} and Mg^{2+} produced by carbonate weathering from that produced by silicate weathering. Generally, K^+ originates from the atmosphere and silicate weathering, and it's challenging to estimate the $\text{Mg}^{2+}/\text{K}^+$ value of silicate weathering because carbonate rock is the bedrock of Sanchahe River region. Galy and France-

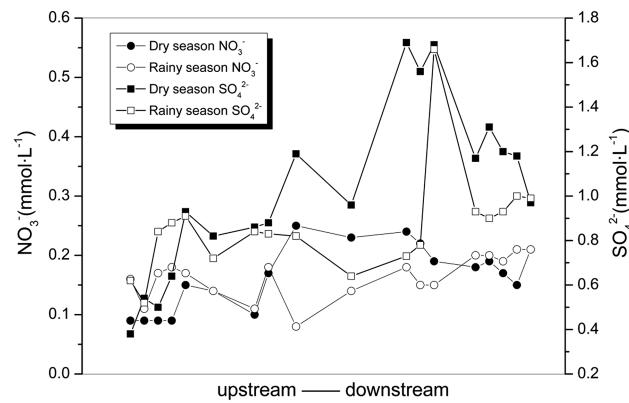


Fig. 5 Spatial distribution of NO_3^- and SO_4^{2-} of the Sanchahe River mainstream

Lanord (1999) and Han and Liu (2004) propose that for silicate weathering, $\text{Mg}^{2+}/\text{K}^+ = 0.5$ and $\text{Ca}^{2+}/\text{Na}^+ = 0.2$. Based on this, Ca^{2+} and Mg^{2+} from carbonate weathering was estimated, allowing for the further simplification of Eqs. (8) and (9):

$$[\text{Ca}^{2+}]_{\text{river}} = [\text{Ca}^{2+}]_{\text{carbonate}} + 0.2 \times [\text{Na}^+]_{\text{silicate}} + [\text{Ca}^{2+}]_{\text{atmosphere}} \quad (10)$$

$$[\text{Mg}^{2+}]_{\text{river}} = [\text{Mg}^{2+}]_{\text{carbonate}} + 0.5 \times [\text{K}^+]_{\text{silicate}} + [\text{Mg}^{2+}]_{\text{atmosphere}} \quad (11)$$

where the ratio of silicate weathering and the total rock weathering could be represented by the ratio of dissolved cations in silicate weathering and that in the total rock weathering, resulting in:

$$X_{\text{silicate}} = (1.4 \times [\text{Na}^{2+}]_{\text{silicate}} + 2 \times [\text{K}^+]_{\text{silicate}}) / ([\text{Na}^+]_{\text{river}} + [\text{K}^+]_{\text{river}} + 2 \times [\text{Ca}^{2+}]_{\text{river}} + 2 \times [\text{Mg}^{2+}]_{\text{river}}) \quad (12)$$

By calculation, in the dry period, $X_{\text{silicate rock}}$ of the Sanchahe River basin river water samples varied from 0.02 to 0.56, averaging 0.18, and $[X]_{\text{carbonate}}$ ranged between 0.44 and 0.98, with an average value of 0.82; while in the wet seasons, X_{silicate} variation was 0.06–0.37, averaging 0.12, and $[X]_{\text{carbonate}}$ ranged from 0.63 to 0.94, with an average of 0.88.

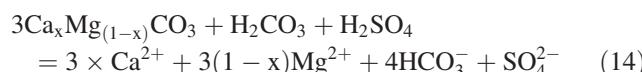
Using X_{silicate} and $X_{\text{carbonate}}$ values and hydrologic data of the watershed, the erosion rates of silicate and carbonate rock were estimated. The chemical weathering rate of silicate rock is represented as:

$$\text{TDS}_{\text{silicate}} = [\text{Na}^+]_{\text{silicate}} + [\text{K}^+]_{\text{silicate}} + [\text{Ca}^{2+}]_{\text{silicate}} + [\text{Mg}^{2+}]_{\text{silicate}} + [\text{SiO}_2]_{\text{river}} \quad (13)$$

where Na^+ , K^+ , Ca^{2+} , and Mg^{2+} stem from silicate weathering and dissolving, and all SiO_2 originates from silicate weathering.

Carbonate weathering is widely distributed, and can occur rapidly. Several sources could be involved in

carbonate weathering, such as H_2CO_3 produced by CO_2 dissolving in the water; SO_4^{2-} input from the atmosphere; and H_2SO_4 formed in sulfide mineral oxidation. In this study, we assumed silicate weathering did not contribute H_2SO_4 as the study area is dominated by carbonate rock, and H_2SO_4 tends to participate in carbonate weathering rather than in silicate weathering. The participation of H_2CO_3 and H_2SO_4 in carbonate weathering can be simplified as follows (Han and Liu 2004):



4.3.2 Chemical weathering and CO_2 consumption rate

As is shown in formula (14), 1 mol of H_2CO_3 and 1 mol of H_2SO_4 are needed to dissolve 3 mol carbonate rock, and the equivalent ratio of SO_4^{2-} and HCO_3^- is 0.9, which suggests that H_2SO_4 plays a significant role in the watershed weathering. Li et al. (2008) applied carbon isotopes to demonstrate a similar weathering process in Beipanjiang, which is an upstream tributary of the Xijiang River. Liu et al. (2008b) used carbon and sulfur isotopes to verify H_2SO_4 participation in watershed weathering processes of the Wujiang River, Nanpanjiang, and Beipanjiang.

The chemical weathering process of carbonate rock in the Sanchahe River basin could be affected by H_2CO_3 and H_2SO_4 . We assumed that Ca^{2+} , Mg^{2+} , and HCO_3^- are not impacted by human activities, and based on Eq. (14), the weathering rate of carbonate rock with the participation of both H_2CO_3 and H_2SO_4 can be expressed as below:

$$\begin{aligned} \text{TDS}_{\text{carbonate}} &= [\text{Ca}^{2+}]_{\text{carbonate}} + [\text{Mg}^{2+}]_{\text{carbonate}} \\ &\quad + 3/4[\text{HCO}_3^-]_{\text{carbonate}} \end{aligned} \quad (15)$$

All HCO_3^- in the solutes (produced by silicate weathering) stem from atmospheric dissolved CO_2 . In the solutes generated from carbonate weathering with H_2CO_3 as the only participant, half of the HCO_3^- was generated from atmospheric dissolved CO_2 ; of the solutes affected by both H_2CO_3 and H_2SO_4 , one-fourth of the HCO_3^- was derived from atmospheric dissolved CO_2 . Thus, CO_2 consumed by silicate and carbonate weathering can be calculated by the following two equations:

$$\begin{aligned} \text{CO}_2_{\text{silicate}} &= [\text{HCO}_3^-]_{\text{silicate}} \\ &= [\text{Na}^+]_{\text{silicate}} + [\text{K}^+]_{\text{silicate}} + 2[\text{Ca}^{2+}]_{\text{silicate}} \\ &\quad + 2[\text{Mg}^{2+}]_{\text{silicate}} \end{aligned} \quad (16)$$

$$\begin{aligned} \text{CO}_2_{\text{carbonate}} &= 1/4[\text{HCO}_3^-]_{\text{carbonate}} \\ &= 1/4(2[\text{Ca}^{2+}]_{\text{carbonate}} + 2[\text{Mg}^{2+}]_{\text{carbonate}}) \\ &= 1/2[\text{Ca}^{2+}]_{\text{carbonate}} + 1/2[\text{Mg}^{2+}]_{\text{carbonate}} \end{aligned} \quad (17)$$

CO_2 consumed by silicate rock weathering in the Sanchahe River basin was about 70.5×10^3 and $255.0 \times 10^3 \text{ mol}/(\text{km}^2 \text{ a})$ in the dry and wet periods, respectively. Approximately $325.5 \times 10^3 \text{ mol}/(\text{km}^2 \text{ a})$ of CO_2 is consumed by silicate rock weathering, which is triple the average rate across the larger Wujiang drainage area (Han and Liu 2004) and far higher than the rate [$128 \times 10^3 \text{ mol}/(\text{km}^2 \text{ a})$] in the Beipanjiang watershed (Xu and Liu 2010) (Table 3). Carbonate rock weathering consumed CO_2 (under both

Table 3 Chemical weathering and CO_2 consumption rate of Sanchahe River Basin and other basins

River	Discharge ($10^8 \text{ m}^3/\text{a}$)	Area (10^3 km^2)	Silicate weathering rate		Carbonate weathering rate		CO_2 cons. $10^3 \text{ mol}/(\text{km}^2 \text{ a})$
			t/ $(\text{km}^2 \text{ a})$	CO_2 cons. $10^3 \text{ mol}/(\text{km}^2 \text{ a})$	t/ $(\text{km}^2 \text{ a})$	CO_2 cons. $10^3 \text{ mol}/(\text{km}^2 \text{ a})$	
Dry season	9.9	7.3	2.0	70.5	23.4	128.2	198.7
Rainy season	39.6		9.0	255.0	85.8	469.2	724.2
Whole year	49.5		11.0	325.5	109.2	597.4	922.9
Wujiang (Han and Liu 2004)	376	66.8	6.0	98	97	581	679
Changjiang, datong (Chetelat et al. 2008)	8650	1705	2.4	112	14	379	491
Beipanjiang (Xu and Liu 2010)	143	26.6	5.5	128.9	94.3	966.6	1095.5
Xijiang (Xu and Liu 2010)	2300	352	7.5	154.3	78.5	806.8	966.1
Upper Hanghe (Wu et al. 2005)	232	146	3	90	26.1	270	360
Songhuajiang (Liu et al. 2013)	733	557	2.2	66.6	5.2	53.4	120
Amazon (Gaillardet et al. 1999)	65,900	6112	13	52.4	11.1	105.4	157.8
Mississippi (Gaillardet et al. 1999)	5800	2980	3.8	66.8	16.1	146.3	213.1
Mekong (Li et al. 2014)	4700	795	10.2	191	27.5	286	477

The dry season and rainy season accounted for 20 % and 80 % of the mean annual discharge, respectively

impact of carbonic acid and sulfuric acid) at rates of 128.2×10^3 and 469.2×10^3 mol/(km² a) in the dry and wet seasons, respectively. The annual CO₂ volume consumed by carbonate rock weathering was found to be about 597.4×10^3 mol/(km²), which is similar to the rate in the Wujiang drainage area (Han and Liu 2004), while lower than that of Beipanjiang [966×10^3 mol/(km² a)] (Xu and Liu 2010) and higher than that of several rivers in non-carbonate rock areas, such as the Yangtze River, the Yellow River, and the Songhuajiang River (Table 3). The silicate rock weathering rates of the Sanchahe basin in the dry and wet seasons are 2.0 and 9.0 t/(km² a), respectively, while the carbonate rock weathering rates are 3.4 and 85.8 t/(km² a). This is consistent with rates of rivers flowing through carbonate rock (Table 3).

5 Conclusions

Ca²⁺ is the main cation of Sanchahe River solute, accounting for 64 % and 73 % of the total cations in the dry and wet periods, respectively; the second most prevalent cations are Mg²⁺ and Na⁺. The main anions are HCO₃⁻ and SO₄²⁻, occupying 48 % and 44 %, respectively, of the total anions in the dry season, and 50 % and 42 % in the wet seasons; the next most common anions are NO₃⁻ and Cl⁻.

The weathering rates of carbonate, silicate, and total rock in the Sanchahe River basin during the hydrologic year were calculated to be about 109.2, 11.0, and 120.2 t/(km² a), respectively, indicating an intense watershed erosion effect. Rates CO₂ consumed by carbonate, silicate, and total rock weathering were 597.4×10^3 , 325.5×10^3 and 922.9×10^3 mol/(km² a), respectively, similar to the regional rivers of the karst area in Southwest China.

According to the chemical calculation of the watershed weathering and CO₂ consumption rates, the Sanchahe River is primarily affected by carbonate weathering, followed by silicate weathering. Sulfuric acid participates in carbonate weathering, and the result suggests a high rate of watershed erosion and rock weathering.

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