

Natural and anthropogenic factors affecting geochemistry of the Jialing and Yangtze Rivers in urban Chongqing, SW China

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ABSTRACT

Owing to the complex relationship between natural factors and anthropogenic activities, rivers passing through urban areas present special challenges to geochemists attempting to understand geochemical conditions and fluxes. Research here on a river impacted by urban development, influenced by both natural and anthropogenic factors, helps to understand the mechanisms of the processes that cause changes in water quality. In this study, we collected water samples weekly at three sampling sites from the Jialing and Yangtze Rivers in the urban area of Chongqing. To explore the evolutionary processes and factors influencing surface water quality, we used stoichiometry and principle component analysis (PCA). Results show that the samples belonged to the $\text{HCO}_3\text{SO}_4\text{--Ca}$ hydrochemical facies. The hydrochemical characteristics of the two rivers were mainly controlled by rock weathering. Carbonate mineral weathering exhibited the largest contribution. Sulfuric acid was involved in carbonate mineral weathering reactions, but gypsum dissolution had little effect on surface water chemistry. PCA revealed that rock weathering, soil erosion, domestic sewage, and agricultural activities contribute to the dissolved chemical load in the Jialing and Yangtze Rivers. The chemical characteristics of the Yangtze River mainstream exhibited changes due to recharge from the Jialing River. Compared with historical data (1959–1990), we found that river water in our study area was more acidic because of coal emissions from industrial activities in Sichuan and Guizhou Provinces. As a result of urbanization and the increase in domestic sewage, the average Cl^-/Na^+ molar ratio at the sampling sites is approximately 50% greater than historical background data. Furthermore, NO_3^- was sensitive to agricultural activities, indicating that agricultural activities have an effect on the Jialing and Yangtze Rivers in the urban Chongqing.

1. Introduction

The major dissolved loads of rivers can yield information about chemical erosion processes, CO_2 consumption, regional climate change, vegetation, soil conditions, and anthropogenic activity (Chen et al., 2005; Martin and Whitfield, 1983; Meybeck, 1987, 1998, 2003). Under the pressure of increasing population, economic development, and changes in land use patterns, the original hydrogeochemical characteristics of many rivers have undergone alterations (Chen et al., 2005; Ometo et al., 2010; Zhang et al., 2015b), especially rivers that are influenced by urban areas (Connor et al., 2014; Kaushal et al., 2017; Merchán et al., 2015; Rose, 2007). Noteworthy examples of such rivers are the Seine, Rhine, Weser, and Elbe Rivers in Europe, the Mississippi and St. Lawrence Rivers in North America, and the Minjiang and Huai Rivers in China (Gaillardet et al., 1999; Qin et al., 2006; Zhang et al.,

2011). The conditions prevalent in such rivers present special challenges to geochemists attempting to understand geochemical conditions and fluxes (Chambers et al., 2016). Thus, identifying the factors and processes through which natural and human activities affect the hydrogeochemistry of large rivers in urban areas is not only useful to calculate the chemical flux of rivers, but also essential to provide a scientific basis for environmental protection, socioeconomic development, and academic exploration.

The Jialing and Yangtze Rivers in urban Chongqing, a city of about 8,000,000 people in southwest China, are particularly well suited to the exploration of the complex factors and processes controlling the hydrochemistry of river water. In terms of discharge and length, the Yangtze River is the third largest river in the world and the largest in China, draining an area of 1.8 million km^2 , accounting for 18.8% of the Chinese landmass (Varis and Vakkilainen, 2001). This basin, with its

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complex climate, geology, soil, and vegetation types, plays an important role in the global biogeochemical cycle and in China's economic development, and has been significantly affected by large scale anthropogenic activity (Chen et al., 2002; Chetelat et al., 2008). The Jialing River, the largest tributary of the Yangtze River, meets the main channel of the Yangtze River in the urban center of Chongqing. Furthermore, the population density and the level of urbanization, industry and agriculture in this basin are relatively high. The water of the Jialing and Yangtze Rivers is used for drinking as well as for agricultural, industrial, and domestic purposes. Therefore, it is essential to understand the mechanisms and processes by which the interacting natural and anthropogenic activities in the urban center of Chongqing impact the Jialing and Yangtze Rivers.

Previous studies have shown that the geochemistry of the source region of the Yangtze River is mainly controlled by evaporite mineral dissolution, while the other sections in the Yangtze River basin are dominated by carbonate mineral weathering. The weathering of silicate minerals plays a less important role in determining the major element chemistry of the Yangtze River basin (Chen et al., 2002; Chetelat et al., 2008; Jiang et al., 2015; Noh et al., 2009; Qu et al., 2015). The surface water of the Yangtze River in Sichuan and Guizhou Provinces has become increasingly acidic, a process that has been exacerbated by anthropogenic activity (Chen et al., 2002). Analysis of sulfate isotopes of the Jialing River (Li et al., 2011) and the Wuhan section of Yangtze River (Li et al., 2015) has shown that SO_4^{2-} mainly comes from high sulfur coal combustion and oxidation of sulfide minerals. Chetelat et al. (2008) used mass balance methods to determine the contribution rates of different sources (including natural and anthropogenic activities) to dissolution loads and calculated the different rock weathering rates and the CO_2 consumption flux in the Yangtze River basin. They found that the Chongqing section of the Yangtze River was significantly affected by anthropogenic activities.

The aforementioned studies have made substantial progress in hydrogeochemical investigations of the Yangtze River basin. However, due to increased anthropogenic influence on the geochemical characteristics of this basin (Guo et al., 2015), data from before the 1990s, such as that used by Hu et al. (1982), and Chen et al. (2002), cannot be used to reflect the current state of water geochemistry of the Yangtze River. Data obtained after the 1990s (Chetelat et al., 2008; Jiang et al., 2015; Noh et al., 2009; Qu et al., 2015) may have a low sampling density, potentially leading to erroneous hydrochemical information for the Yangtze River. Moreover, few studies have been conducted on the influence of water input from the Jialing River on the geochemical characteristics of the Yangtze River mainstream, and none of them are sufficiently systematic. For these reasons, we propose two hypotheses: (1) after its confluence with the Jialing River, the geochemical characteristics of the main channel of the Yangtze River change; (2) industrial and agricultural activities and urbanization have a deep impact on the hydrochemistry of the Yangtze and Jialing Rivers in the Chongqing urban area. In order to verify our hypotheses, in this study, we undertook weekly sampling and monitoring of the main channels of the Jialing and Yangtze Rivers in the Chongqing urban area, with the aim of further understanding their temporal and spatial dynamics and the factors influencing water chemistry in the study area. Thus, the goals of this study were to (1) quantitatively analyze the contribution rates of different impact factors and processes of hydrochemical composition using principle component analysis (PCA), and compare the different impact factors and hydrochemical processes of the Jialing and Yangtze Rivers in the Chongqing urban area, (2) explore the effects of industrial and agricultural activities and urbanization on the geochemistry of the same part of the Jialing and Yangtze Rivers. This study will also provide a scientific basis for the rational development and protection of water resources in the urban area of Chongqing. From a broader perspective, this study illustrates the characteristics of riverine environments impacted by natural factors and anthropogenic activities throughout the world, because of the proliferation of cities near rivers

and the wastewater they generate.

2. General setting of the study area

According to the data from the Ministry of Water Resources of the People's Republic of China (2016), the region from the source of the Yangtze River (Geladaindong peak) to the Jiangbei District of Chongqing measures approximately 8.67 million km^2 . The average annual runoff at the Cuntan hydrologic station in the Jiangbei District of Chongqing is approximately 343.4 billion m^3 . The water here flows across the Qinghai, Tibet, Yunnan, Sichuan Provinces and Chongqing City. The climate in the study area ranges from a continental plateau climate in the west to a subtropical monsoon climate in the east. The annual mean temperature ranges from -4.2°C to 18°C , and the annual precipitation ranges from 283 mm to 1350 mm. Hydrochemical features differ substantially from the source region to the Cuntan station because of the different geological features, location, altitude effects, topography, and diversity of the monsoon source. The concentration of total dissolved solids (TDS) gradually decreases from 3037 mg/L in the Yangtze source region to 223 mg/L at the Cuntan station (Chen et al., 2002; Noh et al., 2009).

The geology of the Yangtze River basin, from the source region to the Cuntan station, is complex: the river flows over Precambrian to Quaternary rocks (Fig. 1a). Carbonate rocks are typically distributed across the Yunnan–Guizhou Plateau (Chen et al., 2002), almost consistent with the direction of the Yangtze River mainstream (Fig. 1a). Furthermore, the clastic rocks in the watershed are widely distributed in the Sichuan basin area (Yang et al., 2016); igneous rocks are predominantly distributed in Yunnan Province, and metamorphic rocks are mainly scattered in Yunnan and Sichuan (Noh et al., 2009, Fig. 1a).

Apart from the source area of the Yangtze River, which has relatively little impact by human activities, the region from Yunnan Province to Chongqing City is more densely populated and has been affected by intense industrial and agricultural activities. Chongqing is one of the most economically advanced cities in SW China. The automobile, electronics, equipment manufacturing, and materials industries are the primary industries here, whereas agricultural activities consist of the cultivation of rice, citrus, and oil crops. Due to its topographic features, industrial development is distributed along the rivers and railways, forming a zonal distribution pattern, and has resulted in a corresponding pattern of pollution. With accelerating urbanization, the population in the main urban area increased from 6.6 million in 2007 to 8.52 million in 2016 (CSB and NBSCST, 2008; 2017). Urban land use requirements also increased consistently, along with a corresponding increase in the discharge of domestic sewage from 6,523.8 million tons in 2007 to 17,602.1 million tons in 2016 (PRCNBS, 2008; 2016).

3. Materials and methods

In order to capture the spatial and temporal dynamics of the hydrogeochemistry of the Jialing and Yangtze Rivers in the main Chongqing urban area, three sampling sites (JLJ, CJ1, and CJ2) were selected. JLJ is located on the Jialing River in the Beibei District ($\text{N}29^\circ50'0.85''$, $\text{E}106^\circ26'32.69''$). CJ1 is in the Yangtze River in the Yuzhong District, the central business district (CBD) of Chongqing ($\text{N}26^\circ35'00''$, $\text{E}106^\circ34'21.59''$), where there is no water recharging from the Jialing River. CJ2 is situated in the Yangtze River in the Jiangbei District ($\text{N}29^\circ32'41.04''$, $\text{E}106^\circ34'17.7''$), where the water of the Jialing River mixes with the water of the Yangtze River (Fig. 1b). Sampling was conducted at a weekly interval from January 11 to December 25, 2016, except for two instances in February. Pre-cleaned 555-mL and 80-mL high-density polyethylene bottles were used for anion and cation sample collection, respectively. The cation samples were filtered with a $0.45\text{-}\mu\text{m}$ membrane filter before adding 3 drops of HNO_3 to ensure the pH value was < 2 . 147 water samples were collected in all. The samples were taken to the laboratory on the day of sampling and refrigerated at

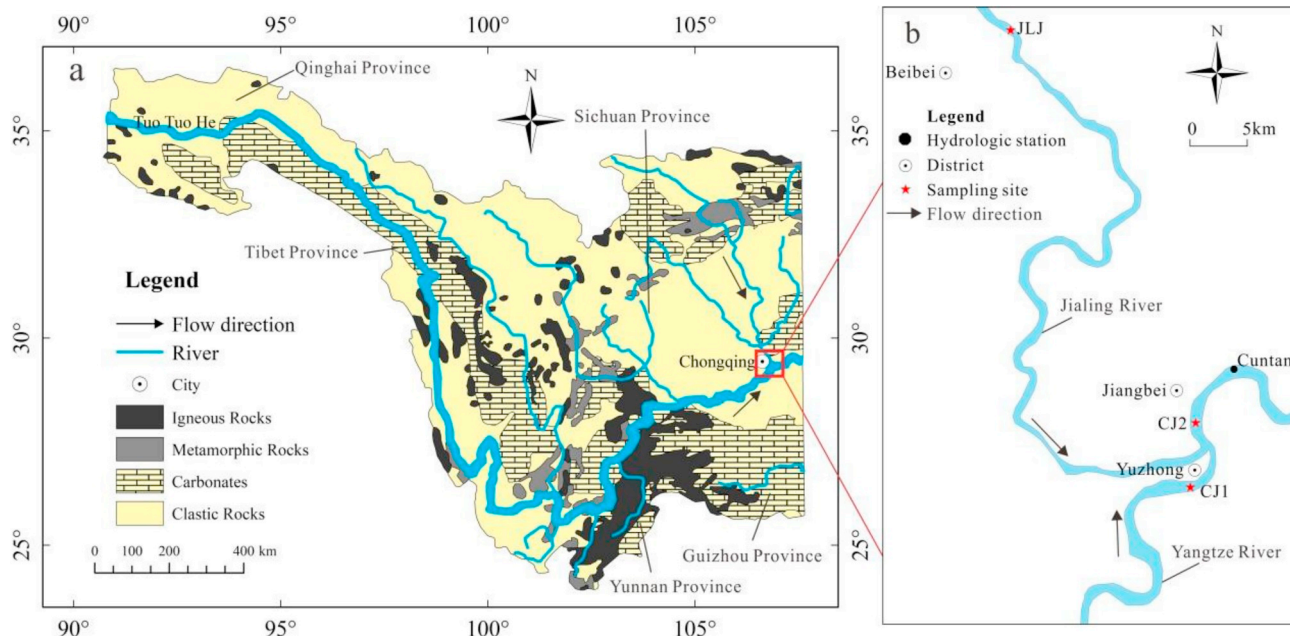


Fig. 1. a: Hydrogeological map of the source region of the Yangtze River in SW China (modified from Chetelat et al. (2008)), b: sampling sites within the urban Chongqing.

4 °C until analysis.

The pH, water temperature (t), and electrical conductivity (EC) of the samples were measured *in situ* using a Multi3430 portable multi-parameter water quality analyzer (WTW, Germany) with a precision of 0.001 pH units, 0.01 °C, and 1 $\mu\text{S}/\text{cm}$. HCO_3^- concentrations were determined using an alkalinity kit (Merck) with an accuracy of 0.1 mmol/L. SO_4^{2-} and NO_3^- concentrations were measured by a UV spectrophotometer with an accuracy of 0.01 mg/L. Cl^- concentrations were measured by AgNO_3 titration with a relative standard deviation of 2.1%. Concentrations of cations including K^+ , Na^+ , Ca^{2+} and Mg^{2+} , and those of elements such as Si, Fe, Al, and Mn were measured by ICP-OES Optima 2100 DV (PerkinElmer, USA) with a relative standard deviation of less than 0.5% in an hour. The determination of anions and cations was performed in the Chongqing Key Laboratory of Karst Environment at Southwest University in Beibei, Chongqing, China.

Along with the collection of the water samples, discharge data taken at 08:00 a.m. on the sampling days at the Cuntan station were obtained from the Yangtze River Waterway Information Network (www.cjsw.com) and used as real-time runoff data for CJ2. The TDS value was calculated using the geological software package Aquachem 5.1 (Schlumberger). A charge balance check (< 5%) was carried out to verify that the measured data were credible.

Principal component analysis (PCA) is a method that uses the idea of dimensionality reduction to transform multiple indicators into a few comprehensive indicators that can reflect most of the information of the original variables without information overlap. This method has been widely used in geochemistry research (e.g. Cloutier et al., 2008; Xue et al., 2011; Yang et al., 2013). The PCA was conducted with SPSS 19 software (IBM).

4. Results

4.1. Hydrochemical data characteristics

The concentrations of major elements and pH, t , and EC of samples from JLJ, CJ1 and CJ2 are shown in Fig. 3. Statistics of the physical and chemical indices of water in the Yangtze and Jialing Rivers are presented in Table 1. The pH of samples from the three sampling sites ranged from 6.29 to 9.20. The mean pH values at JLJ, CJ1, and CJ2

were 8.12, 8.00, and 7.92, respectively, indicating alkaline water. The t values ranged from 9.23 to 33.3 °C. The average t values at JLJ, CJ1, and CJ2 were 21.4, 19.7, and 20.2 °C, respectively. The coefficient of variation (CV) value of t at JLJ was higher than that in the Yangtze River, indicating that the Jialing River is more sensitive to air temperature. The EC values varied from 264 to 462 $\mu\text{S}/\text{cm}$. The mean EC values at JLJ, CJ1, and CJ2 were 370, 341, and 351 $\mu\text{S}/\text{cm}$, respectively. The maximum CV value of EC was observed at JLJ. The order of cation mass concentration at JLJ, CJ1, and CJ2 was $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, with $\text{Ca}^{2+} + \text{Mg}^{2+}$ accounting for more than 74% of the total cation concentration. The order of anion mass concentration was $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$, with $\text{HCO}_3^- + \text{SO}_4^{2-}$ accounting for more than 75% of the total anion concentration. The Si concentrations ranged from 0.77 to 11.73 mg/L; the mean values at CJ1, CJ2, JLJ were 6.87, 6.65, and 5.82 mg/L, respectively. The order of the other element concentrations was $\text{Fe} > \text{Al} > \text{Mn}$ at the three sampling sites. TDS values ranged from 239 to 356 mg/L, which are much higher than the global river average (65 mg/L; Meybeck, 2003). The hydrochemical facies of the three sampling points correspond to the $\text{HCO}_3\text{SO}_4\text{-Ca}$ facies throughout the year (Fig. 2).

4.2. Spatial and temporal variation of runoff, t , and major ions

Fig. 3 shows the monthly trend of the physiochemical indices of water samples from the three sampling sites and the discharge at the Cuntan station. Discharge during the summer flood period was approximately twice that during the winter dry period, showing that river flow at the station was characterized by clear seasonal variations. This corresponds well to the monsoon climate in the study area. The discharge and concentration of chemical ions in the water samples of JLJ, CJ1, and CJ2 show opposite trends (Fig. 3), indicating that most of the chemical ions are highly influenced by flow dilution (Pasquini and Sacchi, 2012).

At CJ1 and CJ2, the values of t and the major ions showed obvious variation, and their variation trends were consistent. Temperature values were affected by air temperature, which increased from the start of the monitoring period until August, and gradually decreased from August to the end of December. The concentrations of Ca^{2+} , Mg^{2+} , K^+ ,

Table 1
Statistics of physiochemical parameters of water from the Yangtze and Jialing Rivers in the urban Chongqing, SW China.

Sampling site	Eigenvalue	pH	t (°C)	EC (µS/cm)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Si (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	TDS (mg/L)	
JLJ	Min	7.08	9.9	264	36.4	7.03	6.14	1.92	110	29.4	9.93	0.53	0.77	0.005	0.001	0	246	
	Max	9.20	33.3	462	61.6	14.1	15.8	4.08	177	60.2	26.2	12.5	9.85	0.651	0.534	0.046	356	
	Mean	8.12	21.4	370	50.5	10.3	10.9	2.77	150	46.3	16	7.27	5.82	0.12	0.096	0.011	315	
	Std	0.491	7.08	46.0	5.67	1.73	2.57	0.557	15.4	8.59	3.74	2.5	2.32	0.15	1.11	0.011	30.8	
CJ1	Min	0.06	0.331	0.124	0.112	0.167	0.237	0.201	0.103	0.185	0.234	0.344	0.399	1.25	11.6	1	0.097	
	Max	6.49	9.23	275	34.7	8.02	7.92	1.66	110	28.5	10.6	0.09	2.25	0.003	0.008	0	239	
	Mean	8.38	26	401	53.2	13.2	21.3	2.93	153	57.6	33.3	11.2	11.1	2.341	1.91	0.124	334	
	Std	8.01	19.7	340	43	10.2	13	2.33	131	42.2	19.2	6.12	6.9	0.312	0.269	0.021	290	
CJ2	Min	0.033	0.219	0.098	0.113	0.116	0.284	0.146	0.083	0.19	0.253	0.366	0.307	1.42	1.3	1.19	0.077	
	Max	6.29	9.25	279	35.8	7.96	8.56	4.12	110	28.1	10.6	0.04	2.22	0.007	0.014	0.001	242	
	Mean	8.36	27.8	427	53.9	14.7	19.6	1.77	177	58.6	33.3	10.7	11.7	0.813	1.12	0.109	344	
	Std	7.92	20.3	352	44.7	10.4	13	2.55	136	43.8	19.0	6.26	6.62	0.206	0.188	0.018	297	
CV	Min	0.31	4.87	37	4.93	1.59	3.17	0.457	14.9	8.26	4.15	2.54	2.17	0.221	0.207	0.019	26.2	
	Max	0.04	0.24	0.105	0.11	0.153	0.244	0.179	0.11	0.189	0.218	0.406	0.328	1.07	1.10	1.06	0.09	
	Mean																	
	Std																	

Std: standard deviation.
CV: coefficient of variation.

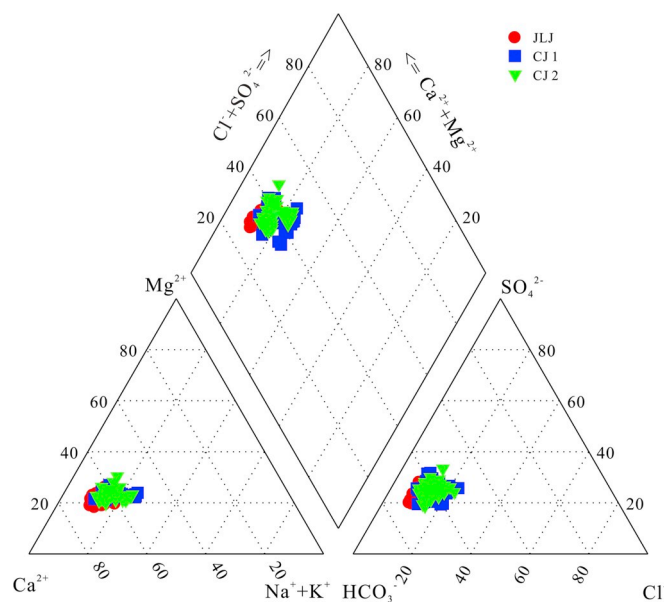


Fig. 2. Piper plot of Jialing and Yangtze Rivers in the urban Chongqing, SW China, indicating the hydrochemical facies of HCO₃:SO₄-Ca.

HCO₃⁻ and SO₄²⁻ reached maximum values in spring, and the lowest value appeared during the summer flood period due to dilution effect. Na⁺ and Cl⁻ concentrations fluctuated upwards from January to December with the highest value being noted in December. Furthermore, Si concentrations increased from January to July before decreasing until December (except for individual extremes). The change in NO₃⁻ concentration was complex and fluctuating; the concentration in February, March, and August to December was relatively stable, and that from April to July was highly variable (Fig. 3), indicating the influence of multiple factors in the rainy season.

At JLJ, the *t* values and concentrations of Ca²⁺, Mg²⁺, K⁺, HCO₃⁻, and SO₄²⁻ were similar to those of CJ1 and CJ2. However, the changes in Na⁺, Cl⁻, and NO₃⁻ concentrations were different; the highest values of Na⁺ and Cl⁻ appeared in spring and autumn and the lowest values appeared in spring. NO₃⁻ concentrations in January to August were consistent with changes in the Yangtze River, but the trend from September to December was not stable, first increasing and then decreasing. The mixing of the Jialing River water with the Yangtze River had some effect on the hydrochemistry of samples from CJ2, causing their ionic concentrations to slightly increase and decrease compared with that from CJ1. However, it did not cause the ionic concentrations of the samples at CJ2 to deviate considerably from those at CJ1 (Fig. 3).

5. Discussion

5.1. Hydrochemical controlling factors

The Gibbs diagram (Gibbs, 1972) is a useful tool for identifying river information related to the relative importance of three factors controlling water chemistry, including evaporation and crystallization, rock weathering, and precipitation. According to the TDS versus Na⁺/(Na⁺ + Ca²⁺) or Cl⁻/(Cl⁻ + HCO₃⁻) weight ratio plot, when the TDS value is low (10 mg/L) and the value of Na⁺/(Na⁺ + Ca²⁺) or Cl⁻/(Cl⁻ + HCO₃⁻) is approximately 1, the water is dominated by atmospheric precipitation and its points are distributed in the lower right corner of the Gibbs diagram. When the TDS value is medium (70–300 mg/L) and the value of Na⁺/(Na⁺ + Ca²⁺) or Cl⁻/(Cl⁻ + HCO₃⁻) is lower than 0.5, the water is dominated by rock weathering and its points are distributed on the left side of the middle of the diagram. When the TDS value is high and the value of Na⁺/(Na⁺ + Ca²⁺) or Cl⁻/(Cl⁻ + HCO₃⁻) is approximately 1, the water is

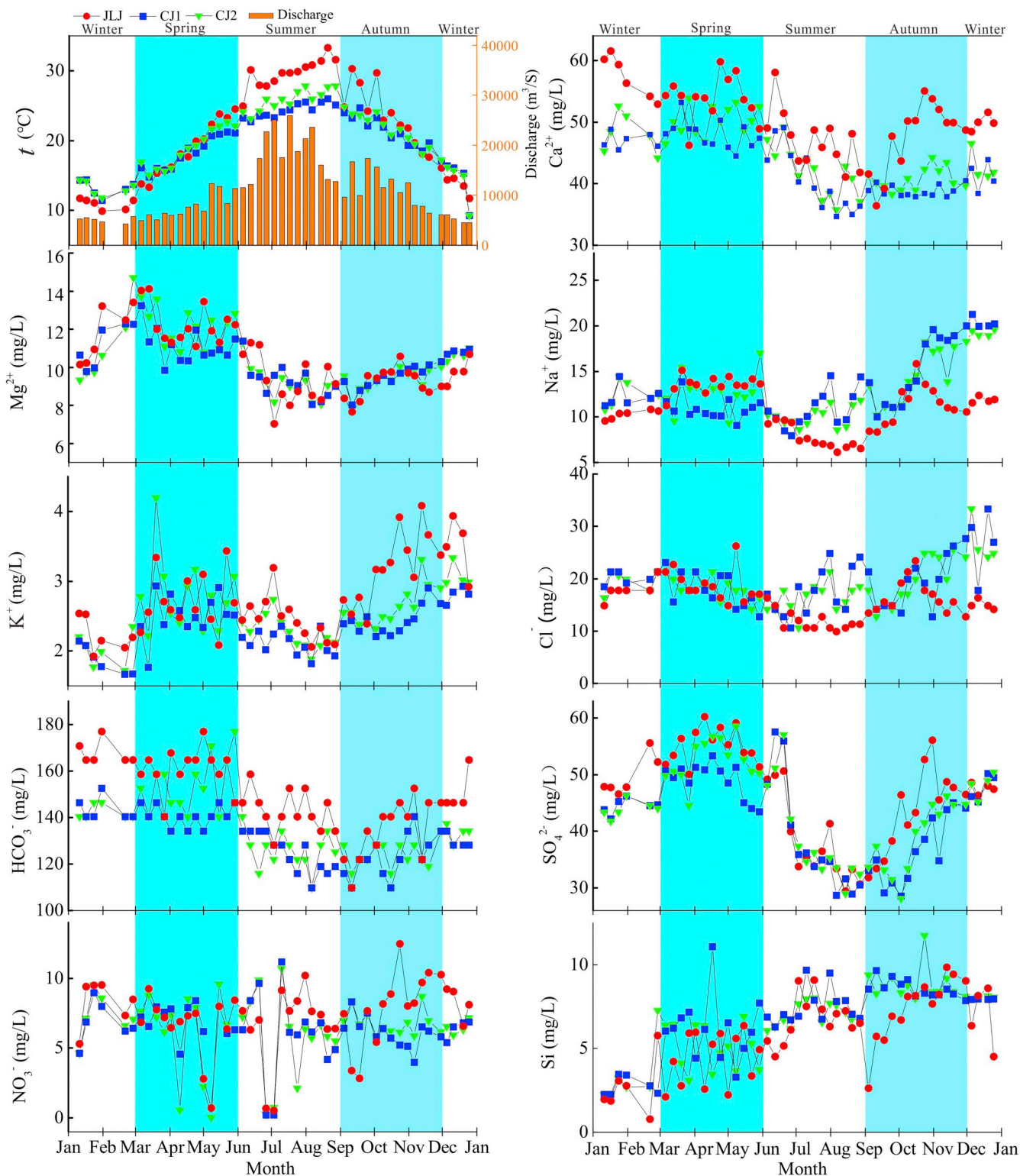


Fig. 3. Variation in discharge, physiochemical indices of the Jialing and Yangtze Rivers in the urban Chongqing, SW China. Discharge data were measured at the Cuntan hydrologic station.

dominated by evaporation and fractional crystallization and its points are distributed in the upper right corner (Fig. 4). The TDS values at JLJ, CJ1, and CJ2 ranged from 239 to 356 mg/L, the equivalent weight ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ranged from 0.11 to 0.36 and the weight ratio of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ranged from 0.11 to 0.31. Plotting the above sample parameters on the Gibbs diagram showed that the waters of JLJ, CJ1 and CJ2 were dominated by rock weathering (Fig. 4). The mean

values of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ at JLJ, CJ1, and CJ2 were 0.156, 0.208, and 0.202, and those for $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ were 0.155, 0.2, 0.195, respectively. This may indicate that the water at JLJ is more intensely dominated by rock weathering, and that CJ1 was slightly affected by evaporation crystallization relative to the samples at JLJ and CJ2. This is because the intense evaporation and dominant ions (Cl^- , Na^+) in the source region of the Yangtze River, and the discharge in the source

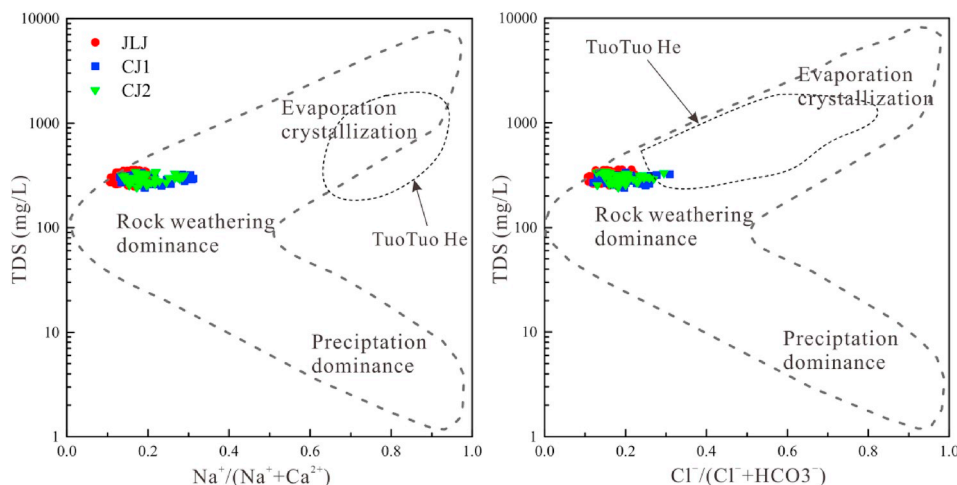


Fig. 4. Gibbs diagram of Jialing and Yangtze Rivers in the urban Chongqing, SW China. The data of Tuo Tuo He are from Jiang et al. (2015). The water chemistry at JLJ, CJ1, and CJ2 was controlled by rock weathering.

region contributes nearly 25% of the total flow of the Yangtze River (Jiang et al., 2015), and that CJ2 was affected by a combination of JLJ and CJ1. However, the chemical characteristics of the water at JLJ, CJ1, and CJ2 are the same as those of most rivers in China (Hu et al., 1982) but differ from the source of the Yangtze River, such as at the Tuo Tuo He which is dominated by evaporation and crystallization (Jiang et al., 2015; Fig. 4).

5.2. Rock weathering analysis

Ternary diagrams are employed to develop an overall understanding of the rock–water reactions that control the major chemical compositions of river water (Stallard and Edmond, 1983). Generally, in the cation ternary diagram, the dissolution of evaporite minerals should be at the $Na^+ + K^+$ side, limestone dissolution should fall on the $Mg^{2+}-Ca^{2+}$ line, and silicate mineral dissolution should lie at the $Mg^{2+}-Ca^{2+}$ to $Na^+ + K^+$ side. In an anion and Si ternary diagram, the product of pure carbonate rock weathering should be dominated by HCO_3^- , with almost no Si. In this study, the data points fall in a relatively high HCO_3^- position and the product of evaporite mineral

weathering falls at one end of a relatively high proportion of $Cl^- + SO_4^{2-}$ (Fig. 5). Thus, silicate weathering causes the water to have both HCO_3^- and Si, and as a result, the data points fall in the middle of a triangular plot. After triangulating the water sample parameters (Fig. 5), we observe that Ca^{2+} was the most abundant cation in the water samples of JLJ, CJ1, and CJ2, $Na^+ + K^+$ was the second most abundant, and Mg^{2+} was the least abundant. On the anion and Si ternary plot, HCO_3^- exhibited the highest contribution, followed by $Cl^- + SO_4^{2-}$, and Si exhibited the lowest contribution. These results indicate that the geochemistry of the water samples was mainly dominated by carbonate weathering, followed by evaporite weathering, and then by weathering of silicate rocks. These results are consistent with the rock type distribution in the study area (Fig. 1). However, the proportion of $Cl^- + SO_4^{2-}$ and $Na^+ + K^+$ in the two ternary diagrams vary widely, which corresponds with their CV values in Table 1. This indicates that the dissolution of evaporites fluctuated within the study period. Spatially, water samples from JLJ exhibited a slightly higher proportion of Ca^{2+} and HCO_3^- , illustrating more intense weathering of carbonate rocks in the Jialing River.

Compared with some large rivers in the world, the anion

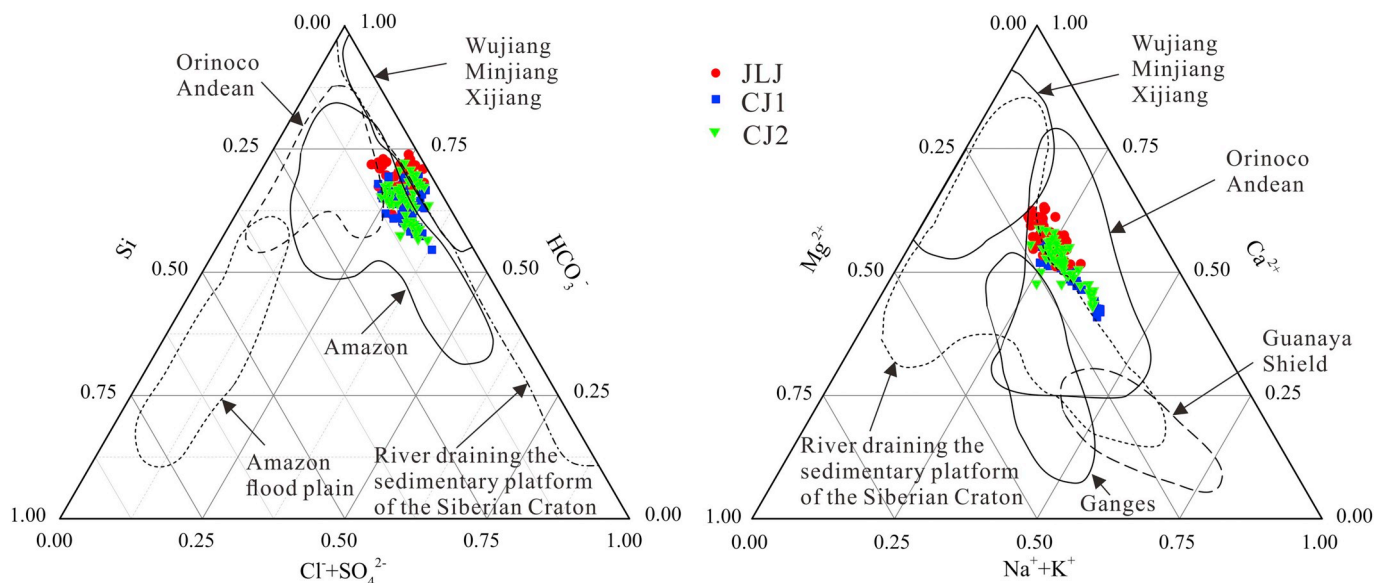


Fig. 5. Ternary diagrams showing anion and Si and cation compositions of JLJ, CJ1, and CJ2 in comparison with other large rivers in the world. Data sources are Han and Liu (2004) for Wujiang, Yoon et al. (2008) for Minjiang, Xu and Liu (2007) for Xijiang, Gibbs (1972) for the Amazon, Huh et al. (1998) for the river draining the sedimentary platform of the Siberian Craton, Stallard and Edmond (1983) for the Amazon flood plain, Edmond et al. (1996) for the Orinoco Andean, Sarin et al. (1989) for the Ganges, and Edmond et al. (1995) for the Guayana Shield.

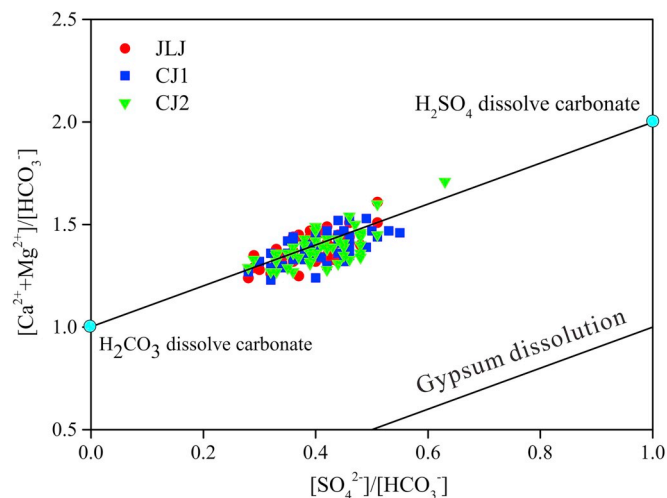
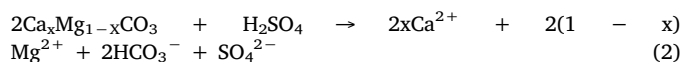
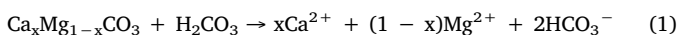


Fig. 6. Relationship between $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ and $[\text{SO}_4^{2-}]/[\text{HCO}_3^-]$, indicating that H_2CO_3 and H_2SO_4 participate in carbonate weathering, and that gypsum dissolution has little effect on the hydrochemistry of JLJ, CJ1, and CJ2 in the urban Chongqing, SW China.

composition of the water of the Jialing and Yangtze Rivers in the Chongqing main urban area lies between that of Wujiang (Han and Liu, 2004), Minjiang (Yoon et al., 2008), Xijiang (Xu and Liu, 2007), the Amazon (Gibbs, 1972), and the sedimentary platform of the Siberian Craton (Huh et al., 1998), and far from that of the Amazon flood plain (Stallard and Edmond, 1983). Furthermore, the cation composition lies between that of the sedimentary platform of the Siberian Craton, Orinoco, and the Andean (Edmond et al., 1996), and far from that of the Ganges (Sarin et al., 1989) and Guayana Shield Rivers (Edmond et al., 1995). This suggests that the differences in distribution of rock types between the regions lead to the unique characteristics of the Jialing and Yangtze Rivers in the Chongqing urban area.

5.3. Effect of H_2CO_3 and H_2SO_4 on carbonate weathering and gypsum dissolution

Identifying the agents causing carbonate weathering is important to understand the factors that may contribute to the water characteristics in a region (Han and Liu, 2004). Naturally, if only H_2CO_3 is involved in carbonate weathering, the chemical reaction is given by Eq. (1) and the equivalent ratio of $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ is 1. If the equivalent ratio is more than 1, then HCO_3^- cannot be balanced by $[\text{Ca}^{2+} + \text{Mg}^{2+}]$ and additional H_2SO_4 is required for carbonate weathering; the chemical reaction in this case is given by Eq. (2) (Li et al., 2010). According to Eq. (2), if the equivalent ratio of $[\text{SO}_4^{2-}]/[\text{HCO}_3^-]$ is 1, then the equivalent ratio of $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ is 2. In this study, the equivalent ratio of $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ at JLJ, CJ1, and CJ2 were both noted to be more than 1 (Fig. 6). This indicates that H_2CO_3 alone is not responsible for carbonate rock dissolution, and other acids such as H_2SO_4 may participate in the weathering of these rocks. This finding agrees with the findings of Zhang and Zhao (2017) in the carbonate dominated rivers of China. Although gypsum strata are distributed throughout the study area, such as gypsum of the Middle Cambrian, the Early and Middle Permian and the Early Cretaceous which have been observed in the Tibet and Sichuan Provinces (Liu et al., 2017; Xue, 1986). The equivalent ratios of $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ and $[\text{SO}_4^{2-}]/[\text{HCO}_3^-]$ are far from the gypsum dissolution line (Fig. 6), indicating that the contribution of H_2CO_3 and H_2SO_4 during carbonate weathering had a greater effect on the sampled waters than that of gypsum dissolution.



5.4. Principal component analysis (PCA)

The qualitative methods described above can only estimate the contribution of the three rock types. However, because the study area is densely populated, and the three sampling sites are within the urban Chongqing, the impact of human activities on water quality is inevitable. Hence, PCA is used to analyze the water samples from the JLJ, CJ1 and CJ2 to determine the impact of human activities on the associated rivers. The results of the Kaiser–Meyer–Olkin (0.738, 0.697, 0.63 for JLJ, CJ1, and CJ2, respectively) and Bartlett's tests (0 for JLJ, CJ1, and CJ2) imply that PCA may support the decision to significantly reduce the dimensions of the original dataset. The number of factors, called principal components (PCs), are defined according to criteria whereby only PCs with eigenvalues > 1 were selected. In this study, four PCs (PC1, PC2, PC3, and PC4) were extracted for each of the JLJ, CJ1, CJ2 and the results are listed in Table 2.

At JLJ, the total variance contribution rate is 86.2% and the contribution rate of PC1 is 42.4%. Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , and EC have high component loads, representing the dissolution of carbonate (Eq. (1) and Eq. (2)), evaporite dissolution and human activities also contribute to Na^+ and Cl^- inputs (Panno et al., 2006). The contribution rate of PC2 is 21.1%, with high component loads of Fe, Al, and Mn. Vesper and White (2003) proved that in addition to soil erosion, Fe, Al, Mn concentrations rise during storm events. Yang et al. (2013) suggested that elevated Fe, Al, and Mn concentrations in karst groundwater reflect soil erosion by surface flow. Thus, the PC2 result indicates soil erosion in the region. The contribution rate of PC3 is 14.0%, and K^+ and Si have high component loads, representing the dissolution of potassium feldspar (Nédeltcheva et al., 2006), which proves that granite exists in the upper reaches of the Jialing River basin (Li et al., 2011). The contribution rate of PC4 is 8.71%; NO_3^- has a high component load, indicating the inputs may from agricultural activities and domestic sewage (Cao et al., 2015; Ding et al., 2014).

At CJ1, the total variance contribution rate is 82.3%. The contribution rate of PC1 is 33.7% with high component loads of Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , and EC, representing the weathering of dolomite and limestone during rock–water interactions. The contribution rate of PC2 is 22.0%, and Fe, Al, and Mn have high component loads, consistent with the soil erosion components noted at JLJ. The contribution rate of PC3 is 17.8%, and Na^+ and Cl^- have high component loads, representing the product of evaporite weathering or anthropogenic inputs. The contribution of PC4 is 9.0% with a high component load of K^+ , which may be related to input from anthropogenic activities.

CJ2 represents the water PC after the confluence of the Jialing and Yangtze Rivers. The total contribution rate at this site is 82.5%. The contribution rate of PC1 is 32.6% with high component loads of Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and EC, consistent with PC1 at CJ1, which is indicative of carbonate weathering. The contribution rate of PC2 is 22.3%, and Fe, Al, and Mn have high component loads, equivalent to PC2 at JLJ and CJ1, which represents soil erosion. The contribution rate of PC3 is 18.2%, and Na^+ , K^+ , and Cl^- have high component loads, representing the weathering of evaporite and human activity input. The contribution rate of PC4 is 9.4% with a high component load of NO_3^- , which is in accordance with the agricultural activities represented by PC4 at JLJ.

Combining the PCA information for the JLJ, CJ1 and CJ2 reveals that rock weathering, including carbonate, silicate, and evaporite weathering, accounts for the highest contribution to the geochemistry of the Jialing and Yangtze Rivers. This finding is in good agreement with the inferences drawn from the Gibbs and ternary diagrams (Figs. 4 and 5). Furthermore, the three sampling sites were influenced by soil erosion, i.e., Fe, Al, and Mn produced as a result of erosional processes

Table 2
Principal component analysis of water chemistry in the Jialing and Yangtze Rivers in the urban Chongqing, SW China.

Parameters	JLJ				CJ1				CJ2			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Na ⁺	0.846	-0.169	0.352	-0.176	-0.09	-0.173	0.874	0.298	0.118	-0.199	0.913	0.098
K ⁺	0.111	0.100	0.931	0.053	0.142	0.085	0.278	0.871	0.247	0.207	0.739	-0.324
Ca ²⁺	0.889	0.014	-0.185	0.176	0.907	0.111	-0.247	-0.037	0.901	0.114	-0.114	0.03
Mg ²⁺	0.813	-0.242	-0.397	-0.017	0.855	-0.089	0.213	0.007	0.835	0.046	0.202	-0.007
Cl ⁻	0.768	-0.199	0.073	-0.317	0.055	-0.108	0.842	0.032	0.095	-0.162	0.762	0.395
SO ₄ ²⁻	0.925	-0.114	0.076	-0.020	0.85	0.032	0.081	0.188	0.816	-0.022	0.239	-0.002
HCO ₃ ⁻	0.806	-0.077	-0.422	0.203	0.913	-0.061	-0.134	0.049	0.885	0.041	-0.001	-0.257
NO ₃ ⁻	0.142	-0.128	0.139	0.915	0.116	0.503	0.359	-0.447	-0.067	0.184	0.048	0.826
Si	-0.325	0.399	0.662	0.268	-0.626	0.471	0.189	0.382	-0.636	0.499	0.42	-0.141
Al	-0.174	0.961	0.016	-0.127	-0.162	0.947	-0.158	0.049	-0.083	0.975	-0.049	0.002
Fe	-0.189	0.952	0.036	-0.079	-0.049	0.945	-0.148	0.08	0.043	0.974	-0.022	-0.034
Mn	-0.030	0.877	0.319	0.057	0.021	0.846	-0.113	-0.038	0.042	0.843	-0.137	0.185
EC	0.924	-0.093	-0.093	0.159	0.745	-0.081	0.591	0.016	0.859	-0.162	0.384	0.115
t	-0.783	0.132	-0.119	-0.226	-0.746	0.146	-0.481	0.138	-0.607	0.272	-0.358	-0.478
Variance contribution rate (%)	42.4	21.1	14.0	8.71	33.5	22.0	17.8	9.0	32.6	22.3	18.2	9.4
Total contribution rate (%)	42.4	63.5	77.5	86.2	33.5	55.5	73.3	82.3	32.6	54.9	73.1	82.5

constitute the PC2 at these sites. This finding denotes soil erosion in the upper reaches of the Yangtze River, consistent with the results reported by Fan et al. (2010), He and Jiao (2000), and YRWRC (2017). However, an explanation for the causes of soil erosion by both natural and human factors is not provided in this study.

The water chemistry characteristics at JLJ, CJ1 and CJ2 show some differences due to the regional physical geographical conditions and the differences in human activities around each of these sites. In the PC3 at JLJ, the high contribution of K⁺ and Si indicates that potassium feldspar weathering may be related to granite weathering in the Jialing River basin (Li et al., 2011). However, the components of the Yangtze River water do not indicate granite weathering. This may be due to the more complex geological conditions affecting the Yangtze River mainstream and the different source of Si here, leading to an information overlap. The PC loads of Si at CJ1 and CJ2 are not clear but have a weak positive correlation with t, consistent with the results obtained for Xijiang River (Gao et al., 2009). Comparing the two sampling sites in the Yangtze River, we find that, because CJ2 water is influenced by a mixture of water from the Jialing and Yangtze Rivers, it inherits some of the water chemical information from both rivers. K⁺, Na⁺, and Cl⁻ constitute the PC3 at CJ2, and NO₃⁻, which is the product of agricultural activity and domestic sewage, is the PC4. These findings show that, although the contribution of the Jialing River to the flow of the Yangtze River is only 20% (Yang and Yang, 2011), it influences the geochemical characteristics of the Yangtze River.

5.5. Enhanced anthropogenic effects on Jialing and Yangtze Rivers

5.5.1. Intensified river water acidification

Average concentrations of Ca²⁺, Mg²⁺, Na⁺ + K⁺, HCO₃⁻, SO₄²⁻,

Cl⁻, and TDS as well as pH values at JLJ, CJ1, and CJ2 were selected for comparison with the data for the period 1958–1990 from Chen et al. (2002) for Luoduxi, Zhujiatuo, and Cuntan, which are near our three sampling sites (Table 3). At CJ1 and CJ2, Ca²⁺, Mg²⁺, Na⁺ + K⁺, SO₄²⁻, Cl⁻, and TDS concentrations increased. However, HCO₃⁻ concentrations were equal to the historical mean data and the pH value was lower by 0.23 at CJ2 (Table 3).

SO₄²⁻ predominantly originates from coal seams, gypsum dissolution, atmospheric acid rain, and direct input from industrial activity (Han and Liu, 2004; Montoroi et al., 2002). According to the results discussed in section 5.3, the effect of gypsum dissolution can be neglected. Chongqing is located in an area in SW China that is affected by sulfuric acid rain with atmospheric deposition of SO₄²⁻ and a small amount of NO₃⁻ (Lydersen et al., 2006). Chen et al. (2002) showed that the SO₄²⁻ content at the Cuntan station has increased annually and is positively related to the annual coal consumption in Guizhou Province. Li et al. (2011) applied the sulfur isotope tracer method to estimate SO₄²⁻ content in the Jialing River basin and noted that SO₄²⁻ mainly originates from oxidation of sulfide in coal strata and atmospheric input from coal combustion. Thus, coal emission from human activities in the region is the main reason for the increase in SO₄²⁻ content. Xia et al. (1999) conducted a related simulation, which showed that an increase in SO₄²⁻ content would lead to enhanced dissolution of carbonate rocks, followed by a corresponding increase in Ca²⁺ and Mg²⁺, and a decrease in HCO₃⁻ and pH values. This phenomenon is called water acidification. However, along with the data of pH, Ca²⁺, HCO₃⁻ and SO₄²⁻ for CJ2 in Table 3, it is clear that acidification of water caused by human activities has a stronger influence on the water quality at the study sites at present.

Compared with other rivers within urban areas, such as the

Table 3

Comparison of water chemical data between 2016 and 1958–1990 at the Jialing River, and 1958–1990 at the Yangtze River in the urban Chongqing (historical data from Chen et al. (2002)). Compared with the data of 1958–1990, the average concentration of Ca²⁺, Mg²⁺, Na⁺ + K⁺, SO₄²⁻, Cl⁻, and TDS in 2016 have increased significantly at JLJ, CJ1, and CJ2, whereas pH at CJ2 has decreased. The Cl⁻/(Na⁺ + K⁺) ratios at JLJ, CJ1, and CJ2 were higher than those during the period 1958–1990.

Site	Time	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ + K ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	TDS (mg/L)	pH	Cl ⁻ /(Na ⁺ + K ⁺) (mass ratio)	Cl ⁻ /Na ⁺ (molar ratio)
JLJ	2016	50.5	10.4	13.62	150	46.3	16	315	8.12	1.17	0.97
	1958–1990	37.9	8.5	10.9	134	25.2	7.7	212	-	0.71	-
CJ1	2016	43	10.2	15.3	131	42.1	19.2	290	8.01	1.25	0.98
	1958–1990	37.9	8.5	10.9	134	25.2	7.7	219	-	0.71	-
CJ2	2016	44.7	10.4	15.5	136	43.8	19	297	7.92	1.22	0.97
	1958–1990	37.3	8.6	9.9	136	23.8	7.1	224	8.15	0.72	-

Note: “-” indicates no data available.

Chattahoochee River Basin (Rose, 2007) and the Gwynns Falls watershed (Kaushal et al., 2017), concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} , dissolved inorganic carbon (DIC) and pH simultaneously increased as urbanization progressed. This is because the dissolution of cement and leaching from lime may increase concentrations of Ca^{2+} and DIC in urban streams and sediments (Barnes and Raymond, 2009), and leakage of sewer lines may contribute to SO_4^{2-} (Rose, 2007). This does not agree with our research results. With regard to urbanization, the Jialing and Yangtze Rivers are affected by large scale acid deposition, and the carbonates in our study area are widely distributed.

5.5.2. Influence of domestic sewage

$\text{Na}^+ + \text{K}^+$ and Cl^- concentrations at the three sampling sites increased significantly when compared with their mean concentrations during 1965–1990 (Table 3). In particular, the Cl^- concentration in 2016 was more than twice that during 1965–1990 (Table 3). In addition to the contribution of evaporite, which is discussed in section 5.2, domestic wastewater is recognized as a major source of $\text{Na}^+ + \text{K}^+$ and Cl^- . Due to a lack of detailed concentration data for Na^+ and K^+ reported by Chen et al. (2002), the mass ratios of $\text{Cl}^-/(\text{Na}^+ + \text{K}^+)$ at the three sampling sites during 1958–1990 and 2016 were calculated. The mass ratios of $\text{Cl}^-/(\text{Na}^+ + \text{K}^+)$ at Luoduxi, Zhujiatuo, and Cuntan (1958–1990) were 0.71, 0.71, and 0.72, respectively, whereas those at JLJ, CJ1, and CJ2 were higher, with values of 1.17, 1.25, and 1.22, respectively (Table 3). This indicates that extra Cl^- participated in water chemical reactions in the Jialing and Yangtze Rivers. Therefore, the molar ratio of Cl^-/Na^+ —widely applied to geochemical investigations—was used to estimate the present water quality situation and to identify the source of Cl^- and Na^+ (Chetelat et al., 2008; Kaushal et al., 2017; Long et al., 2015).

In this study, we adopt the Cl^- and Na^+ data for Chongqing City reported by Hu et al. (1982) as historical background data ($\text{Cl}^-/\text{Na}^+ = 0.61$). The mean molar ratios of Cl^-/Na^+ for JLJ, CJ1, and CJ2 are 0.97, 0.98, and 0.97 (Table 3), respectively, which are significantly higher than the historical background data from 1980, the global river average value ($\text{Cl}^-/\text{Na}^+ = 0.68$), and the present value for the polluted Taihu Lake ($\text{Cl}^-/\text{Na}^+ = 0.85$; Dai et al., 2015). Furthermore, the mean molar ratios at the sites were lower than those from atmospheric input ($\text{Cl}^-/\text{Na}^+ = 2.8 \pm 1.1$) and agricultural activity input ($\text{Cl}^-/\text{Na}^+ = 5 \pm 1$; Chetelat et al., 2008). In the upper reaches of the Yangtze River basin, the runoff decreased continuously in recent years (YRWRC, 2017). Therefore, we conjecture that the water yield from the evaporite weathering area (mainly from the source region and tributaries) was also reduced accordingly. Furthermore, Chen and Wang (2006) considered that the evaporite dissolution was in a steady state, and the Cl^- concentration in the Yangtze River basin was not significantly related to the sea salt cycle. The input of wastewater pollution, therefore, may be an important source of Cl^- and Na^+ . There are many sewage pipes on both sides of the Yangtze River in the Chongqing main urban area, as well as many food industry vessels operating on the mainstream, which also contribute to Na^+ , K^+ , and Cl^- . As the permanent population of the urban area of Chongqing is constantly increasing, the domestic sewage input may increase accordingly (Li and Fu, 2016). Therefore, the continuous advancement of urbanization may be the reason for the increase in $\text{Na}^+ + \text{K}^+$, Cl^- , and TDS content.

5.5.3. Impact of agricultural activities

The PCA, described in section 5.4, considered NO_3^- to be an independent component with a unique origin. Chetelat et al. (2008) observed that when water from the source region of the Yangtze River enters the Sichuan basin agricultural zone, the NO_3^- concentration increases substantially. Van et al. (2016) showed that the application of manure during farming periods increases the concentration of NO_3^- in surface water. However, Rozemeijer et al. (2010) noted that the concentration is also affected by rainfall dilution during these periods.

Combining these findings above with the results of this study, we

can see that NO_3^- was affected by discharge dilution from April to July, leading to highly fluctuating concentrations (Fig. 3). In such cases, the reason for elevated NO_3^- concentrations may be because the farming and fertilization period occurs during April to July, and soil erosion is most intense during flood periods (Nearing et al., 2015). But soil erosion also results in N loss (Zhang et al., 2015a). Thus, within the study period, the combination of the application of nitrogen fertilizers during agricultural activities and discharge dilution result in unstable NO_3^- concentrations. During the period from August to December, the runoff gradually decreased and NO_3^- concentrations were generally stable because fertilizers were not applied during this period (Fig. 3). However, compared with CJ1 and CJ2, the NO_3^- concentration at JLJ increased suddenly before decreasing again during this period. This is probably attributed to oil crop fertilization in the Jialing River basin. Therefore, dilution and fertilization are the two main factors controlling the fluctuation in NO_3^- .

6. Conclusion

One hundred and forty-seven water samples collected from the Jialing and Yangtze Rivers in the urban area of Chongqing City of SW China during 2016 were analyzed in this study, using stoichiometry and principle component analysis. The results obtained were compared with historical data. Our results suggest that under the influence of climate and lithology, the geochemical characteristics of the Jialing and Yangtze Rivers in the Chongqing urban area show clear temporal and spatial changes. After the Jialing River flows into the Yangtze River, t and the concentrations of major ions in the mainstream of the Yangtze River change slightly. Most samples taken from the sampling sites fell in the $\text{HCO}_3\text{-SO}_4\text{-Ca}$ hydrochemical facies.

The hydrochemical composition of the Jialing and Yangtze Rivers is mainly controlled by weathering of rock, primarily carbonate rock, followed by that of evaporite dissolution, although this proportion varies widely, and then of silicate rock. This corresponds to the rock type distribution in our study. The chemical compositions at JLJ, CJ1, and CJ2 are similar to those of rivers that drain from carbonate source area. Furthermore, they exhibit differences from river basins with limited carbonate areas. Moreover, besides H_2CO_3 , H_2SO_4 participated in carbonate weathering and gypsum dissolution has little effect on the water chemical composition of these rivers. PCA result shows that, in addition to natural rock weathering, soil erosion and human activities also contribute water composition. Due to different natural conditions, the PCs for the three sampling sites differ, and the input of Jialing River water into the Yangtze River causes changes in the chemical characteristics of the Yangtze River water.

Since the 1950s, the increase in human-induced coal emissions has caused a corresponding increase in SO_4^{2-} in the study area and further intensified water acidification up to the present. The large scale of these natural conditions and acid deposition is the main reason for these phenomena. With accelerated urbanization, the influence of domestic sewage on the geochemistry of the Jialing and Yangtze Rivers has become more severe. Additionally, because of soil erosion, NO_3^- variability is sensitive to agricultural activities in this region, but is also influenced by discharge dilution.

In summary, the geochemistry of the Jialing and Yangtze Rivers has been influenced deeply by the interaction between natural conditions and anthropogenic activities; the influence of the latter is continually being enhanced. Due to its high discharge and large basin area, the macroscale influencing factors take precedence. However, with the increase in the urbanization level, the input from sewage water cannot be ignored.

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