

Reply to reviewer comments on “Temporary and net sinks of atmospheric CO₂ due to chemical weathering in subtropical catchment with mixing carbonate and silicate lithology” (bg-2019-310)

Dear Editor and Reviewers,

Thank you very much for your letter and for the reviewers' comments concerning our manuscript entitled “Temporary and net sinks of atmospheric CO₂ due to chemical weathering in subtropical catchment with mixing carbonate and silicate lithology” (bg-2019-310). Those comments are all valuable and very helpful for revising and improving our manuscript, as well as the important guiding significance to our researches. We have checked the manuscript and revised it according to the comments very carefully. **All the changes have been indicated in an annotated version of the revised manuscript (submission item "Revised manuscript ")**. The item-by-item responses to the reviewer comments are followed. Thank you very much for all your help, and we are looking forward to hearing from you.

Please find the following response to the comments of referees:

Responses to handling editor:

Handling editor 's comments: I think that the manuscript has substantially been improved. The reviewer has evaluated it as reached to the acceptance level. Please make a final step for some technical corrections that the reviewer suggested. You are almost there.

Response: Thank you very much for your time and the handling of our manuscript. We greatly

appreciate both your help and that of the referees concerning improvement to our manuscript. The technical corrections that the reviewer suggested have been corrected, the revisions have been marked in the revised manuscript and the responses to reviewers are as follows.

Responses to Reviewer #1:

Question 1: L. 71 Please define "DIC" by spelling it out, as "DIC (dissolved inorganic carbon)".

Answer 1: Thank you very much for your suggestion. The "DIC" has been defined as dissolved inorganic carbon. The corresponding modifications can be seen in [Line 71](#).

Question 2: L. 138-139 "The hydrochemical compositions of rain water were summarized in Table S1 in the supplementary materials." Please delete this sentence. The rain water data should be noted in the result section, NOT in the material and methods. Furthermore, similar arguments were already shown in the result section (L. 307-311).

Answer 2: Thank you very much for your suggestion. The sentence "The hydrochemical compositions of rain water were summarized in Table S1 in the supplementary materials." has been deleted.

Question 3: L. 484 There are garbled characters (or unreferred citation in Chinese?).

Answer 3: Thank you very much for your reminding. The garbled characters are "Fig.2". The corresponding modifications can be seen in [Line 483](#).

1 **Temporary and net sinks of atmospheric CO₂ due to chemical**
2 **weathering in subtropical catchment with mixing carbonate and**
3 **silicate lithology**

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12
13 **Abstract:** The study provided the major ion chemistry, chemical weathering rates and temporary
14 and net CO₂ sinks in the Beijiang River, which was characterized as hyperactive region with high
15 chemical weathering rates, carbonate and silicate mixing lithology and abundant sulfuric acid
16 chemical weathering agent of acid deposition and acid mining drainage (AMD) origins. The total
17 chemical weathering rate of 85.46 t·km⁻²·a⁻¹ was comparable to other rivers in the hyperactive zones
18 between the latitude 0-30°. Carbonate weathering rate of 61.15 t·km⁻²·a⁻¹ contributed to about 70%
19 of the total. The lithology, runoff and geomorphology had significant influence on the chemical
20 weathering rate. The proportion of carbonate outcrops had significant positive correlation with the
21 chemical weathering rate. Due to the interaction between dilution and compensation effect,
22 significant positive linear relationship was detected between runoff and total, carbonate and silicate

23 weathering rates. The geomorphology factors such as catchment area, average slope and
24 hypsometric integral value (HI) had non-linear correlation with chemical weathering rate and
25 showed significant scale effect, which revealed the complexity in chemical weathering processes.
26 DIC-apportionment showed that CCW (Carbonate weathering by CO_2) was the dominant origin of
27 DIC (35%-87%). SCW (Carbonate weathering by H_2SO_4) (3%-15%) and CSW (Silicate weathering
28 by CO_2) (7%-59%) were non-negligible processes. The temporary CO_2 sink was $823.41 \times 10^3 \text{ mol}$
29 $\text{km}^{-2} \text{ a}^{-1}$. Compared with the “temporary” sink, the net sink of CO_2 for the Beijiang River was
30 approximately $23.18 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ of CO_2 and was about 2.82% of the “temporary” CO_2 sink.
31 Human activities (sulfur acid deposition and AMD) dramatically decreased the CO_2 net sink and
32 even make chemical weathering a CO_2 source to the atmosphere.

33 **Keywords:** Chemical weathering, DIC-apportionment, CO_2 temporary sink, CO_2 net sink

34 **1 Introduction**

35 Chemical weathering driven by weak carbonic acid (H_2CO_3) that originates from atmosphere
36 CO_2 or soil respiration under natural conditions is a fundamental geochemical process regulating
37 the atmosphere-land-ocean carbon fluxes and earth’s climate (Guo et al., 2015). Carbonate and
38 silicate weathering define the two typical categories of chemical weathering. From the view of the
39 global carbon cycle, the CO_2 consumption due to carbonate weathering is recognized the “temporary”
40 sink because the flux of CO_2 consumed by carbonate dissolution on the continents is balanced by
41 the flux of CO_2 released into the atmosphere from the oceans by carbonate precipitation on the
42 geological time scale (Cao et al., 2015; Garrels, 1983). While the consumption of CO_2 during the
43 chemical weathering of silicate rocks has been regard as the net sink of CO_2 and regulates the global
44 carbon cycle (Hartmann et al., 2009; Hartmann et al., 2014b; Kempe and Degens, 1985; Lenton and

45 Britton, 2006). Thus in carbonate-silicate mixing catchment, it is essential to distinguish proportions
46 of the two most important lithological groups, i.e., carbonates and silicates, and evaluate the net
47 CO₂ sink due to chemical weathering of silicate (Hartmann et al., 2009).

48 In addition to the chemical weathering induced by H₂CO₃, sulfuric acid (H₂SO₄) of
49 anthropogenic origins produced by sulfide oxidation such as acid deposition caused by fossil fuel
50 burning and acid mining discharge (AMD) also becomes an important chemical weathering agent
51 in the catchment scale. Many studies have shown the importance of sulfide oxidation and subsequent
52 dissolution of other minerals by the resulting sulfuric acid at catchment scale (Hercod et al., 1998;
53 Spence and Telmer, 2005). Depending on the fate of sulfate in the oceans, sulfide oxidation coupled
54 with carbonate dissolution could facilitate a release of CO₂ to the atmosphere (Spence and Telmer,
55 2005), the carbonate weathering by H₂SO₄ plays a very important role in quantifying and validating
56 the ultimate CO₂ consumption rate. Thus, under the influence of human activities, the combination
57 of silicate weathering by H₂CO₃ and carbonate weathering by H₂SO₄ controlled the net sink of
58 atmospheric CO₂.

59 Numerous studies on chemical weathering of larger rivers have been carried out to examine
60 hydrochemical characteristics, chemical erosion and CO₂ consumption rates, and long-term climatic
61 evolution of the Earth, such as the Changjiang River (Chen et al., 2002; Ran et al., 2010), the
62 Huanghe River (Zhang et al., 1995), the Pearl River (Gao et al., 2009; Xu and Liu, 2010; Zhang et
63 al., 2007), the Huai River (Zhang et al., 2011), the rivers of the Qinghai-Tibet Plateau (Jiang et al.,
64 2018; Li et al., 2011; Wu et al., 2008), the Mekong River (Li et al., 2014), the rivers of the Alpine
65 region (Donnini et al., 2016), the Sorocabá River (Fernandes et al., 2016), the rivers of Baltic Sea
66 catchment (Sun et al., 2017), the Amazon River (Gibbs, 1972; Mortatti and Probst, 2003; Stallard

67 and Edmond, 1981; Stallard and Edmond, 1983; Stallard and Edmond, 1987), the Lena River (Huh
68 and Edmond, 1999) and the Orinoco River (Mora et al., 2010). For simplicity of calculation
69 procedure, most of the researches have ignored the sulfuric acid induced chemical weathering and
70 resulted in an overestimation of CO₂ sink. To overcome this shortcoming of traditional mass-balance
71 method, we applied a **dissolved inorganic carbon source (DIC)** apportionment procedure to
72 discriminate the contribution of sulfuric acid induced chemical weathering to validate the temporary
73 and net sink of CO₂ in a typical hyperactive region with carbonate-silicate mixing lithology to give
74 a further understanding of basin scale chemical weathering estimation.

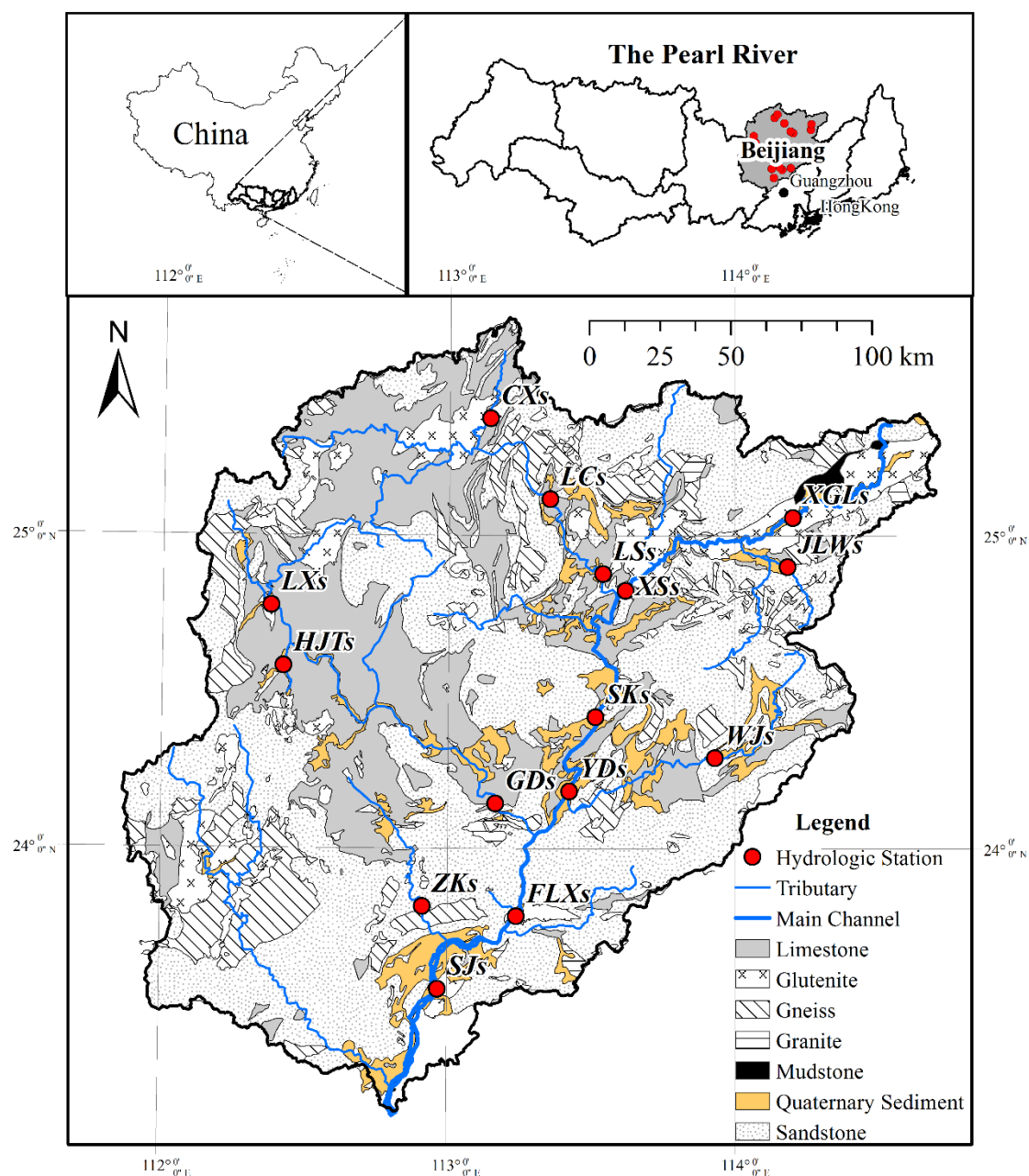
75 About half of the global CO₂ sequestration due to chemical weathering occurs in warm and
76 high runoff regions (Ludwig et al., 1998), so called the hyperactive regions and hotspots (Meybeck
77 et al., 2006). The Pearl River located in the subtropical area in South China includes three principal
78 rivers: the Xijiang, Beijiang, and Dongjiang Rivers. The warm and wet climatic conditions make
79 the Pearl River a hyperactive region in China. The three river basins have distinct geological
80 conditions. The Xijiang River is characterized as the carbonate-dominated area and the Dongjiang
81 River has silicate as the main rock type. While the Beijiang River, which is the second largest
82 tributary of the Pearl River, is characterized as a typical carbonate-silicate mixing basin. In addition,
83 as the serve acid deposition (Larssen et al., 2006) and active mining area (Li et al., 2019), chemical
84 weathering induced by sulfuric acid make the temporary and net sink of atmospheric CO₂ to be
85 reevaluated. So that, in this study, the Beijiang River in Southeast China with a typical subtropical
86 monsoon climate and carbonate-silicate mixing geologic settings was selected as the study area.
87 Three main objectives were summarized as follows: (1) revealed spatial-temporal variations of
88 major element chemistry of the river water, (2) calculated the chemical weathering rate and

89 unraveled the controlling factors on chemical weathering processes, and (3) determined the
90 temporary sink of CO₂ and evaluated the influence of sulfide oxidation on net sink of CO₂ by DIC
91 apportionment procedure.

92 **2 Study area**

93 The Beijiang River Basin, which is the second largest tributary of the Pearl River Basin, is
94 located in the southeast of China (Fig. 1). It covers an area of 52 068 km² and has a total length of
95 573 km. The river basin is located in subtropical monsoon climate zone, with the mean annual
96 temperature across the drainage basin ranging from 14°C to 22°C, the mean annual precipitation
97 ranging from 1390 mm to 2475 mm. The average annual runoff is 51 billion m³, with 70%-80% of
98 the flux occurring from April to September. This can be attributed to the fact that more than 70% of
99 the annual precipitation (about 1800 mm year⁻¹) is concentrated in the wet season (April to
100 September).

101 Lithology in the river basin is composed of limestone, sandstone, gneiss and glutenite. In the
102 upper basin, carbonate rock (mainly of limestone) outcrops in the west and center, while sandstone
103 of Devonian era and mudstone of Paleogene era outcrop in the east of upper stream. In the middle
104 of basin, limestone and sandstone cover most of the area, and Cretaceous volcanic rocks are found
105 in the tributary (Lianjiang River), mainly granite. In the lower basin, Achaen metamorphic rocks
106 outcrop in the west, and are composed of gneiss and schist, sandstone covers rest of area of the
107 lower basin. Quaternary sediments scatter along the main stream of the river. The carbonate and
108 silicate rock outcrops in the Beijiang River Basin was 10737 km² (28%) and 24687 km² (65%),
109 respectively.



110
111 **Fig. 1** Geology map and sampling point in the Beiji River basin (produced by Arcgis)

112 **3 Materials and methods**

113 **3.1 Sampling procedure and laboratory analysis**

114 Water samples were collected monthly at 15 hydrologic stations from January to December in
115 2015 (Fig. 1). The river waters were sampled by a portable organic class water sampler along the
116 middle thread of channel in the first day of each month. In addition, to discriminate the contribution
117 of rain inputs, the daily rainwater was also sampled in five stations (SJs, FLXs, YDs, XSs and XGLs)

118 along the main stream. The rainwater collector is consisted of a funnel with diameter of 20 cm and
119 a 5 L plastic bottle. A rubber ball is setup in the funnel to prevent evaporation. All the river and rain
120 water were filtered through 0.45 μm glass fiber filter and stored in 100 ml tubes and stored below
121 4°C until analysis.

122 Electric conductivity (EC), pH and temperature (T) were measured by a multi-parameter water
123 quality meter (HACH-HQ40Q), and alkalinity (HCO_3^-) was measured in filtered water samples by
124 titration in situ. The dissolved SiO_2 was measured by molybdenum yellow method and was analyzed
125 by ultraviolet spectrophotometer (Shimadzu UV-2600). The cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and
126 anions (Cl^- , SO_4^{2-}) were analyzed by ion chromatography (ThermoFisher ICS-900) with limit of
127 detection (L.O.D) of 0.01 mg/L. Reference, blank and replicate samples were employed to check
128 the accuracy of all the analysis and the relative standard deviations of all the analysis were within
129 $\pm 5\%$. The electrical balance (E.B.) defined by the equation of $\text{E.B.} =$
130 $\frac{\text{meq}(\text{sum of cations}) - \text{meq}(\text{sum of anions})}{\text{meq}(\text{sum of cations and anions})} \times 100$ of the water samples was less than 5%.

131 3.2 Calculation procedure

132 3.2.1 Chemical weathering rates

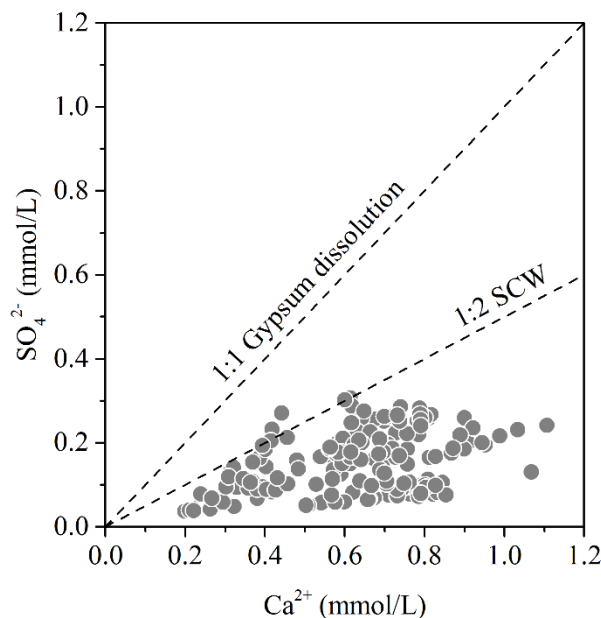
133 The mass balance equation for element X in the dissolved load can be expressed as (Galy and
134 France-Lanord, 1999):

$$135 [X]_{\text{riv}} = [X]_{\text{pre}} + [X]_{\text{eva}} + [X]_{\text{sil}} + [X]_{\text{car}} + [X]_{\text{anth}} \quad (1)$$

136 Where $[X]$ denotes the elements of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- in $\text{mmol}\cdot\text{L}^{-1}$. The
137 subscripts riv, pre, eva, sil, car and anth denote the river, precipitation source, evaporite source,
138 silicate source, carbonate source and anthropogenic source.

139 In the study area, the anthropogenic source of major ions except for SO_4^{2-} was ignored due to

140 the following two reasons. (1) Two main characteristics of much polluted rivers are that TDS is
 141 greater than 500 mg/L and the Cl⁻/Na⁺ molar ratio is greater than that of sea salts (about 1.16) (Cao
 142 et al., 2016a; Gaillardet et al., 1999). The TDS in the study area ranged from 73.79 to 230.16 mg·L⁻
 143 ¹ and the low TDS implied that the anthropogenic origins of major ions could be ignored in the study.
 144 However, the Beijiang River is characterized as a typical region suffered from serve acid deposition
 145 (Larssen et al., 2006) and active mining area (Li et al., 2019). The acid deposition and acid mining
 146 discharge contribute to the highest concentration of SO₄²⁻. (2) Natural origin of SO₄²⁻ is the
 147 dissolution of evaporite, such as gypsum, while no evaporite was found in the study area. If SO₄²⁻
 148 comes from the gypsum dissolution, the ratios of Ca²⁺ and SO₄²⁻ should be close to 1:1. The
 149 stoichiometric analysis (Fig.2) showed that the ratio of Ca²⁺ and SO₄²⁻ deviated from 1:1 and also
 150 proved this point.



151
 152 **Fig. 2 Stoichiometric relationship between Ca²⁺ and SO₄²⁻. The “SCW” means carbonate**
 153 **weathering induced by sulfuric acid**

154 So that, on the basis of the theory of rock chemical weathering and ignoring the anthropogenic
 155 origins of major ions (except for SO₄²⁻), the major elements of river water can be simplified as

156 followed:

$$157 \quad [\text{Cl}^-]_{\text{riv}} = [\text{Cl}^-]_{\text{pre}} + [\text{Cl}^-]_{\text{eva}} \quad (2)$$

$$158 \quad [\text{K}^+]_{\text{riv}} = [\text{K}^+]_{\text{pre}} + [\text{K}^+]_{\text{sil}} \quad (3)$$

$$159 \quad [\text{Na}^+]_{\text{riv}} = [\text{Na}^+]_{\text{pre}} + [\text{Na}^+]_{\text{eva}} + [\text{Na}^+]_{\text{sil}} \quad (4)$$

$$160 \quad [\text{Ca}^{2+}]_{\text{riv}} = [\text{Ca}^{2+}]_{\text{pre}} + [\text{Ca}^{2+}]_{\text{sil}} + [\text{Ca}^{2+}]_{\text{car}} \quad (5)$$

$$161 \quad [\text{Mg}^{2+}]_{\text{riv}} = [\text{Mg}^{2+}]_{\text{pre}} + [\text{Mg}^{2+}]_{\text{sil}} + [\text{Mg}^{2+}]_{\text{car}} \quad (6)$$

$$162 \quad [\text{HCO}_3^-]_{\text{sil}} = [\text{K}^+]_{\text{sil}} + [\text{Na}^+]_{\text{sil}} + 2[\text{Mg}^{2+}]_{\text{sil}} + 2[\text{Ca}^{2+}]_{\text{sil}} \quad (7)$$

$$163 \quad [\text{HCO}_3^-]_{\text{car}} = [\text{HCO}_3^-]_{\text{riv}} - [\text{HCO}_3^-]_{\text{sil}} \quad (8)$$

$$164 \quad [\text{SO}_4^{2-}]_{\text{riv}} = [\text{SO}_4^{2-}]_{\text{pre}} + [\text{SO}_4^{2-}]_{\text{anth}} \quad (9)$$

165 Firstly, the measured ion concentrations of the rain water are rectified by evaporation

166 coefficient $\alpha=0.63=P/R$ (with P the precipitation and R the runoff) and calculated the contributions

167 of atmospheric precipitation. Secondly, the molar ratios of $\text{Ca}^{2+}/\text{Na}^+$ (0.4) and $\text{Mg}^{2+}/\text{Na}^+$ (0.2) for

168 silicate end-member (Zhang et al., 2007) are used to calculate the contribution of Ca^{2+} and Mg^{2+}

169 from silicate weathering, and then, residual Ca^{2+} and Mg^{2+} were attributed to carbonate weathering.

170 For monthly data, the contributions of different sources can be calculated as followed:

$$171 \quad R_{\text{car}} = ([\text{Ca}^{2+}]_{\text{car}} + [\text{Mg}^{2+}]_{\text{car}}) / S \times 100\% \quad (10)$$

$$172 \quad R_{\text{sil}} = ([\text{K}^+]_{\text{sil}} + [\text{Na}^+]_{\text{sil}} + [\text{Ca}^{2+}]_{\text{sil}} + [\text{Mg}^{2+}]_{\text{sil}}) / S \times 100\% \quad (11)$$

$$173 \quad R_{\text{eva}} = [\text{Na}^+]_{\text{eva}} / S \times 100\% \quad (12)$$

$$174 \quad R_{\text{pre}} = ([\text{K}^+]_{\text{pre}} + [\text{Na}^+]_{\text{pre}} + [\text{Ca}^{2+}]_{\text{pre}} + [\text{Mg}^{2+}]_{\text{pre}}) / S \times 100\% \quad (13)$$

$$175 \quad S = [\text{Ca}^{2+}]_{\text{car}} + [\text{Mg}^{2+}]_{\text{car}} + [\text{Ca}^{2+}]_{\text{sil}} + [\text{Mg}^{2+}]_{\text{sil}} + [\text{Na}^+]_{\text{sil}} + [\text{K}^+]_{\text{sil}} + [\text{Na}^+]_{\text{eva}} +$$

$$176 \quad [\text{Ca}^{2+}]_{\text{pre}} + [\text{Mg}^{2+}]_{\text{pre}} + [\text{Na}^+]_{\text{pre}} + [\text{K}^+]_{\text{pre}} \quad (14)$$

177 Where R denotes the proportions of dissolved cations from different sources. S denotes the total

178 concentrations of cations for river water in $\text{mmol}\cdot\text{L}^{-1}$.

179 The total, carbonate and silicate chemical weathering rates (TWR, CWR and SWR) of a year
180 can be estimated as followed:

$$181 \quad \text{CWR} = \sum_{i=1}^{n=12} \left[\left(24 \times [\text{Mg}^{2+}]_{\text{car}} + 40 \times [\text{Ca}^{2+}]_{\text{car}} + 61 \times [\text{HCO}_3^-]_{\text{car}} \times 0.5 \right)_i \times Q_i / (10^6 \text{A}) \right] \quad (15)$$

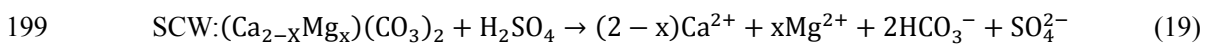
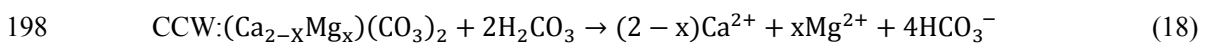
$$182 \quad \text{SWR} = \sum_{i=1}^{n=12} \left[\left(39 \times [\text{K}^+]_{\text{sil}} + 23 \times [\text{Na}^+]_{\text{sil}} + 24 \times [\text{Mg}^{2+}]_{\text{sil}} + 40 \times [\text{Ca}^{2+}]_{\text{sil}} + 96 \times [\text{SiO}_2]_{\text{sil}} \right)_i \times \right. \\ 183 \quad \left. Q_i / (10^6 \text{A}) \right] \quad (16)$$

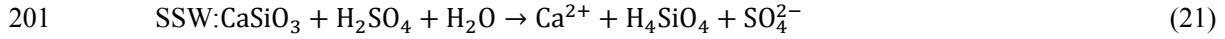
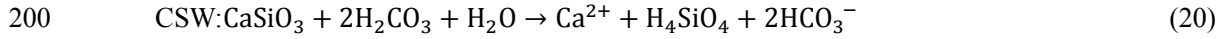
$$184 \quad \text{TWR} = \text{CWR} + \text{SWR} \quad (17)$$

185 Where TWR, CWR and SWR have the unit of $\text{t km}^{-2} \text{a}^{-1}$, Q_i denotes discharge in $\text{m}^3 \cdot \text{month}^{-1}$, and A
186 denotes the catchment area in km^2 .

187 3.2.2 DIC apportionments

188 In the Beijiing River, the pH values of water samples ranged from 7.5 to 8.5 with an average
189 of 8.05. Under this pH conditions, the major species of DIC is HCO_3^- . In addition, HCO_3^- accounted
190 for more than 95% in all sampling sites based on calculation, thus the concentration of HCO_3^-
191 (mmol/L) was used to represent the DIC concentration in this study. The riverine DIC originates
192 from several sources including carbonate minerals, respired soil CO_2 and atmospheric CO_2 , and it
193 could be affected by processes occurring along the water pathways (Khadka et al., 2014; Li et al.,
194 2008). Four dominant weathering processes, including (1) carbonate weathering by carbonic acid
195 (CCW), (2) carbonate weathering by sulfuric acid (SCW), (3) silicate weathering by carbonic acid
196 (CSW), (4) and silicate weathering by sulfuric acid (SSW), can be described by the following
197 reaction equations:





202 Where CaSiO_3 represents an arbitrary silicate.

203 According to the study of Galy and France-Lanord (1999) and Spence and Telmer (2005),

204 carbonate and silicate weathering by carbonic acid in the same ratio as carbonate and silicate

205 weathering by sulfuric acid, for monthly data the mass balance equations are followed:

206 $[\text{SO}_4^{2-}]_{\text{riv}} - [\text{SO}_4^{2-}]_{\text{pre}} = [\text{SO}_4^{2-}]_{\text{SCW}} + [\text{SO}_4^{2-}]_{\text{SSW}}$ (22)

207 $[\text{SO}_4^{2-}]_{\text{riv}} - [\text{SO}_4^{2-}]_{\text{pre}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \frac{\alpha_{\text{CSW}} \times \alpha_{\text{SCW}}}{\alpha_{\text{CCW}}} \times [\text{HCO}_3^-]_{\text{riv}}$ (23)

208 Where the subscripts CCW, SCW, CSW and SSW denotes the four end-members defined by

209 carbonate weathering by carbonic acid, carbonate weathering by sulfuric acid, silicate weathering

210 by carbonic acid and silicate weathering by sulfuric acid, respectively. The parameter α denotes the

211 proportion of DIC derived from each end-member processes.

212 According to the above description, the ion balance equations are followed:

213 $[\text{Ca}^{2+}]_{\text{car}} + [\text{Mg}^{2+}]_{\text{car}} = \alpha_{\text{CCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}}$ (24)

214 $[\text{SO}_4^{2-}]_{\text{SCW}} + [\text{SO}_4^{2-}]_{\text{SSW}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \frac{\alpha_{\text{CSW}} \times \alpha_{\text{SCW}}}{\alpha_{\text{CCW}}} \times [\text{HCO}_3^-]_{\text{riv}}$ (25)

215 $\alpha_{\text{CCW}} + \alpha_{\text{SCW}} + \alpha_{\text{CSW}} = 1$ (26)

216 Combing the above equations, the proportions of HCO_3^- derived from three end-members

217 (CCW, SCW and CSW) can be calculated, and the DIC (equivalent to HCO_3^-) fluxes by different

218 chemical weathering processes are calculated by following equations.

219 $[\text{HCO}_3^-]_{\text{CCW}} = \alpha_{\text{CCW}} \times [\text{HCO}_3^-]_{\text{riv}}$ (27)

220 $[\text{HCO}_3^-]_{\text{SCW}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}}$ (28)

221 $[\text{HCO}_3^-]_{\text{CSW}} = \alpha_{\text{CSW}} \times [\text{HCO}_3^-]_{\text{riv}}$ (29)

222 3.2.3 CO₂ consumption rate and CO₂ net sink

223 According to the equations (17)~(20), only the processes of CCW and CSW can consume the
224 CO₂ from atmosphere or soil and only half of the HCO₃⁻ in the water due to carbonate weathering
225 by carbonic acid come from atmospheric CO₂. Thus, the CO₂ consumption rates (CCR) for CCW
226 and CSW can be calculated as followed (Zeng et al., 2016):

$$227 \quad CCR_{CCW} = \sum_{i=1}^{n=12} \{ [0.5 \times (Q/A) \times [HCO_3^-]_{CCW}] / 1000 \}_i \quad (30)$$

$$228 \quad CCR_{CSW} = \sum_{i=1}^{n=12} \{ [(Q/A) \times [HCO_3^-]_{CSW}] / 1000 \}_i \quad (31)$$

229 Where Q is discharge in m³·a⁻¹, [HCO₃⁻] is concentration of HCO₃⁻ in mmol·L⁻¹, A is catchment area
230 in km², so that the CCR has the unit of 10³ mol km⁻²·a⁻¹.

231 According to the classical view of the global carbon cycling (Berner and Kothavala, 2001),
232 the CCW is not a mechanism that can participate to the amount of CO₂ in the atmosphere because
233 all of the atmospheric fixed through CCW is returned to the atmosphere during carbonate
234 precipitation in the ocean. However, when sulfuric acid is involved as a proton donor in carbonate
235 weathering, half of the dissolved carbon re-release to the atmospheric during carbonate precipitation.
236 Thus, SCW leads to a net release of CO₂ in ocean-atmosphere system over timescale typical of
237 residence time of HCO₃⁻ in the ocean (10⁵ years). Meanwhile, in case of CSW, followed by
238 carbonate deposition, one of the two moles of CO₂ involved is transferred from the atmosphere to
239 the lithosphere in the form of carbonate rocks, while the other one returns to the atmosphere,
240 resulting a net sink of CO₂. Therefore, the net CO₂ consumption rate (CCR_{Net}) due to chemical
241 weathering can be concluded as followed:

$$242 \quad CCR_{Net} = \sum_{i=1}^{n=12} \{ [(0.5 \times [HCO_3^-]_{CSW} - 0.5 \times [HCO_3^-]_{SCW}) \times (Q/A)] / 1000 \}_i \quad (32)$$

243 3.3 Spatial and statistical analysis

244 The hypsometric integral value (HI) (PIKE and WILSON, 1971) was employed in this study
245 to evaluate the influence of terrain on the chemical weathering. HI is an important index to reveal
246 the relationship between morphology and development of landforms and can be used to establish
247 the quantitative relationship between the stage of geomorphological development and the material
248 migration in the basin (PIKE and WILSON, 1971; Singh et al., 2008; STRAHLER, 1952). The HI
249 value of each watershed is calculated by the elevation-relief ratio method and can be obtained by
250 the following equation (PIKE and WILSON, 1971):

$$251 \quad HI = \frac{\text{Mean.elevation} - \text{Min.elevation}}{\text{Max.elevation} - \text{Min.elevation}} \quad (33)$$

252 Where HI is the hypsometric integral; Mean.elevation is the mean elevation of the watershed;
253 Min.elevation is the minimum elevation within the watershed; Max.elevation is the maximum
254 elevation within the watershed. According to the hypsometric integral value (HI), the
255 geomorphological development can be divided into three stages: inequilibrium or young stage (HI >
256 0.6), equilibrium or mature stage (0.35 < HI ≤ 0.6), and monadnock or old age (HI ≤ 0.35),
257 which can reflect the erodible degree and erosion trend of the geomorphology (Xiong et al., 2014).

258 The watershed of the study area was divided by using hydrological analysis module of ArcGIS.
259 The average slope and HI was conducted by spatial analysis module of ArcGIS. The area of
260 silicate/carbonate outcrops was calculated by hydrological module of ArcGIS based on geology map
261 from provided by China Geological Survey. The data of river water discharge was provided by the
262 local hydrology bureau.

263 All statistical tests were conducted using SPSS version 22.0. One-way analysis of variance
264 (ANOVA) was performed to check the differences of monthly major ion concentrations and

265 dissolved inorganic carbonate isotopes with significance at $p < 0.05$. Principal component analysis
266 (PCA) was employed to unravel the underlying data set through the reduced new variables, analyzed
267 the significant factors affecting the characteristics of water chemistry.

268 4 Results

269 4.1 Chemical compositions

270 The major physical-chemical parameters of river water samples were presented in Table 1. In
271 Table 1, the chemical parameters of river water were the flow-weighted average over 12 months.
272 For every sampling station, the flow-weighted average of ion concentration can be expressed
273 followed the equation $[X]_{average} = \frac{\sum_{i=1}^{n=12} [X]_i \times Q_i}{\sum_{i=1}^{n=12} Q_i}$, where $[X]$ denotes the elements of Ca^{2+} , Mg^{2+} ,
274 Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- in $\text{mmol} \cdot \text{L}^{-1}$. Q denotes average monthly discharge in $\text{m}^3 \cdot \text{s}^{-1}$. The
275 subscripts i denotes 12 months from January to December. For all the monthly samples, the pH
276 values ranged from 7.5 to 8.5 with an average of 8.05. Average EC was $213 \mu\text{s} \cdot \text{cm}^{-1}$, ranging from
277 81 to $330 \mu\text{s} \cdot \text{cm}^{-1}$. The TDS of river water samples varied from 73.8 to $230.2 \text{ mg} \cdot \text{L}^{-1}$, with an average
278 of $157.3 \text{ mg} \cdot \text{L}^{-1}$, which was comparable with the global average of $100 \text{ mg} \cdot \text{L}^{-1}$ (Gaillardet et al.,
279 1999). Compared with the major rivers in China, the average TDS was significantly lower than the
280 Changjiang (Chen et al., 2002), the Huanghe (He Jiangyi, 2017) the Zhujiang (Zhang et al., 2007),
281 the Huaihe (Zhang et al., 2011) and the Liaohe (Ding et al., 2017). However, the average TDS was
282 higher than the rivers draining silicate-rock-dominated areas, e.g., Dojiang River ($59.9 \text{ mg} \cdot \text{L}^{-1}$) in
283 Southern China (Xie Chenji, 2013), North Han River ($75.5 \text{ mg} \cdot \text{L}^{-1}$) in South Korea, (Ryu et al.,
284 2008), the Amazon ($41 \text{ mg} \cdot \text{L}^{-1}$) and the Orinoco ($82 \text{ mg} \cdot \text{L}^{-1}$) draining the Andes (Dosseto et al.,
285 2006; Edmond et al., 1996).

286

Table 1 The major physical-chemical parameters of river water samples at 15 hydrological station in the Beijiang River (mean \pm SD). The total dissolved solid

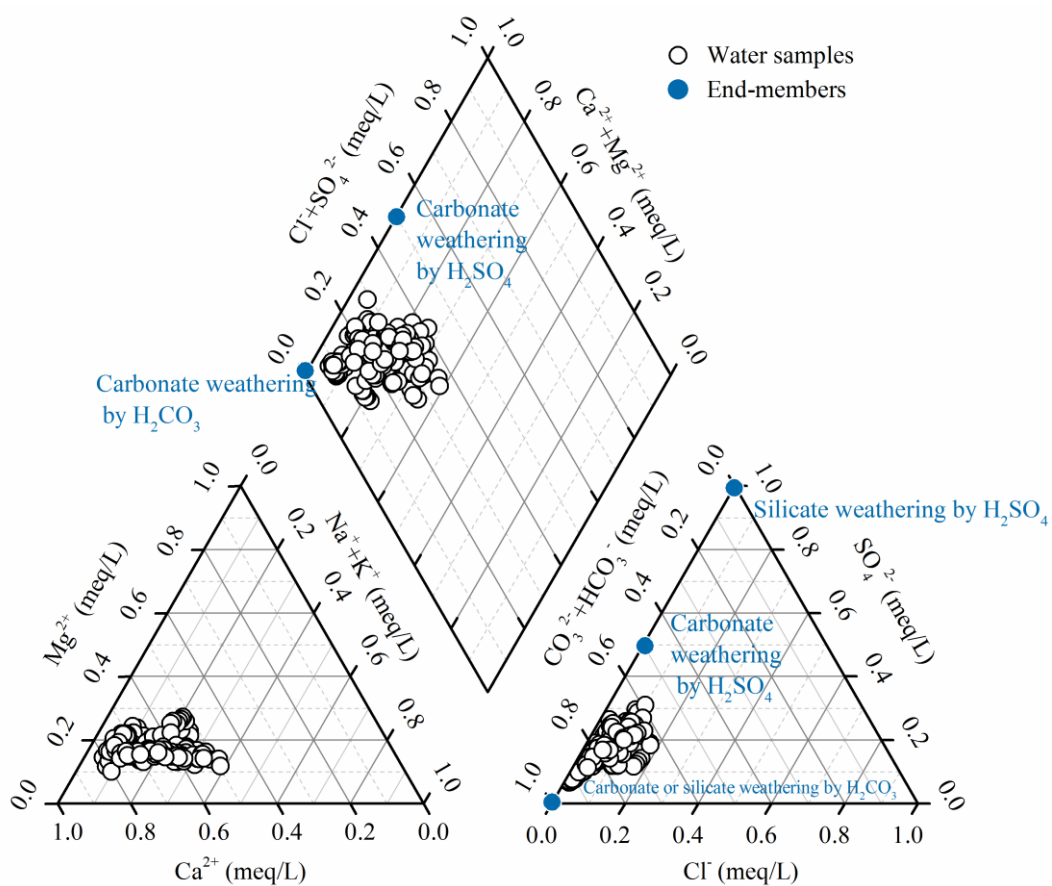
287

(TDS, mg·L⁻¹) expressed as the sum of major inorganic species concentration (Na⁺+K⁺+Ca²⁺+Mg²⁺+HCO₃⁻+Cl⁻+SO₄²⁻+NO₃⁻+SiO₂)

Hydrological stations	pH	EC (μs/cm)	TDS (mg/L)	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	HCO ₃ ⁻ (μmol/L)	Cl ⁻ (μmol/L)	SO ₄ ²⁻ (μmol/L)	SiO ₂ (μmol/L)	HI
JLWs	7.9±0.2	95±40	81.1±25.6	111.4	51.9	223.5	103.9	701.9	28.3	44.5	225.2	0.34
CXs	8.2±0.2	219±50	163.7±20.9	118.1	40.1	793.3	187.1	1593.6	60.5	199.4	106.3	0.29
HJTs	8.1±0.2	203±34	151.8±21.9	100.2	29.9	686.7	203.9	1708.7	29.5	72.2	156.6	0.30
ZKs	8.1±0.1	218±45	161.3±21.1	426.4	66.2	560.3	134.1	1276.9	134.7	161.4	151.9	0.22
XGLs	7.8±0.2	168±16	117.9±8.9	315.4	112.4	422.4	101.0	992.2	213.9	112.6	178.9	0.18
WJs	8.1±0.1	260±27	172.9±16.7	197.8	59.0	767.3	122.6	1467.1	99.1	162.8	183.4	0.25
LXs	8.1±0.2	236±33	171.8±19.6	122.1	38.1	813.5	176.0	1829.4	51.5	89.2	145.7	0.21
LCs	8.2±0.1	253±26	196.1±20.0	287.4	46.8	862.6	234.4	1845.7	115.7	232.4	130.7	0.27
LSs	8.3±0.1	220±46	184.2±18.3	258.9	58.2	793.5	202.9	1740.6	109.0	191.9	121.4	0.25
XSs	7.9±0.1	156±30	123.9±17.6	305.0	86.1	366.8	110.9	966.6	103.8	166.5	218.7	0.24
GDs	8.1±0.1	232±11	169.4±8.3	112.6	40.5	781.6	172.1	1798.5	44.0	90.3	141.2	0.24
SKs	8.1±0.2	238±22	161.1±17.4	345.3	73.6	641.0	162.5	1304.1	174.4	223.5	160.1	0.21
Yds	7.8±0.2	241±54	165.9±34.0	296.4	59.3	674.8	160.9	1515.0	118.7	175.9	144.4	0.21
FLXs	8.0±0.2	232±37	161.4±22.8	187.6	95.1	577.0	135.0	1262.4	111.9	159.6	169.5	0.21
SJs	8.1±0.1	230±27	176.4±18.9	355.0	83.4	663.5	156.2	1367.7	182.4	190.5	180.5	0.21

288

289 Major ion compositions were shown in the Piper plot (Fig. 3). Ca^{2+} was the dominant cation
 290 with concentration ranging from 199 to 1107 $\mu\text{mol}\cdot\text{L}^{-1}$, accounting for approximately 49% to 81%,
 291 with an average of 66% (in μEq) of the total cation composition in the river water samples. HCO_3^-
 292 was the dominant anion, with concentration ranging from 640 to 2289 $\mu\text{mol}\cdot\text{L}^{-1}$. On average, it
 293 comprised 77% (59%~92%) of total anions, followed by SO_4^{2-} (16%) and Cl^- (6%). The major ionic
 294 composition indicated that the water chemistry of the Beijiang River Basin was controlled by both
 295 carbonate and silicate weathering.



296

297

Fig. 3 Piper plot of river water samples in the Beijiang River

298

299

300

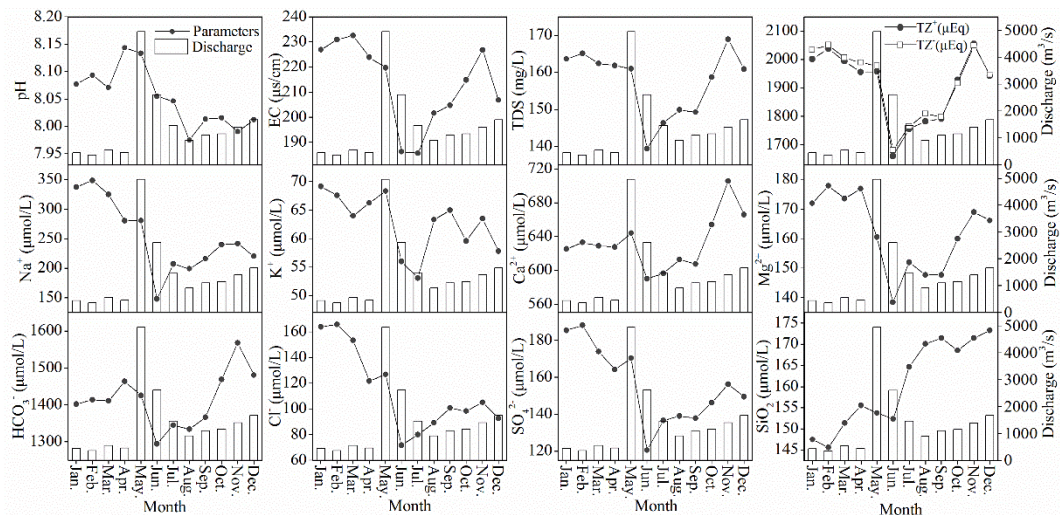
The PCA was used to extract the factors controlling the chemical compositions. The varimax rotation was used to reduce the number of variables to two principal components (PCs), which together explain 76.88% of the total variance in the data. The first PC (PC1) explained

301 approximately 50.02% of the total variations, and was considered to represent “carbonate
302 weathering factor” because of the high loadings of EC, TDS, Ca^{2+} , Mg^{2+} and HCO_3^- concentrations.
303 The second PC (PC2) explained 26.85% of the total variance and presented high loadings for Na^+
304 and K^+ concentrations. Thus, the PC2 represented a “silicate weathering factor”. These two PCs
305 were considered to be two important sources of major ions in the Beijiang River Basin.

306 The hydrochemical compositions of rain water were presented in Table S1. Ca^{2+} was the
307 dominant cation with concentration ranging from 6.9 to 282.6 $\mu\text{mol}\cdot\text{L}^{-1}$, accounting for
308 approximately 65% of the total cation composition in the rain water samples. SO_4^{2-} was the
309 dominant anion, with concentration ranging from 21.9 to 1462 $\mu\text{mol}\cdot\text{L}^{-1}$, accounting for
310 approximately 67% of the total anion composition in the rain water samples.

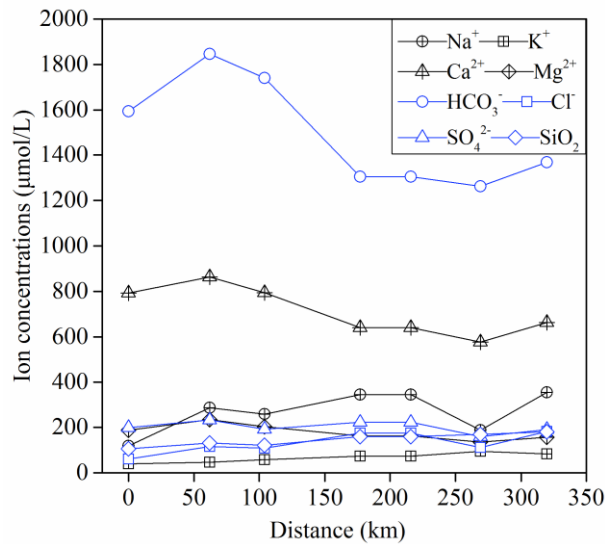
311 **4.2 Seasonal and spatial variations**

312 There were significant seasonal variations in the major ion concentrations (Fig. 4). Two basic
313 patterns of temporal variations could be observed. The first one was related to the carbonate
314 weathering derived ions such as Ca^{2+} and HCO_3^- , which showed high values in November and low
315 values in June. The second one was for the silicate weathering derived ions such as Na^+ and K^+ ,
316 which showed high values in February and low values in June. The minimums occurred in Jun for
317 all the ions showed a significant dilution effect during the high-flow periods.



318
 319 **Fig. 4 Monthly variations of environmental parameters and major ion concentrations in the**
 320 **Beijing River Basin (SJs station). The columns denoted the monthly discharge**

321 It was clear that the Ca^{2+} and HCO_3^- concentrations had a decreasing trend from upstream to
 322 downstream (Fig. 5), this characteristic agrees with the trends observed in the Changjiang River and
 323 the Huai River, where the major elements or TDS concentrations of the main channel showed a
 324 general decreasing trend, and the tributaries display the dilution effect to the main channel. For other
 325 silicate weathering derived ions such as Na^+ , there was a slight increasing trend implying the
 326 chemical inputs from the tributaries. These trends were in accordance with the lithology in the study
 327 area. The carbonate is dominated in the upper stream basin, when river drainages this area, carbonate
 328 weathering contributes to the elevation of Ca^{2+} and HCO_3^- . As the river entered into the downstream
 329 dominated with silicate, the relative low ion concentrations due to silicate weathering contributed
 330 to diluting the Ca^{2+} and introducing extra Na^+ to the main channel.



331
 332 **Fig. 5 Spatial variations of major ion and SiO₂ concentrations in the Beijiang River Basin (From**
 333 **upstream station CXs to the downstream station SJs)**

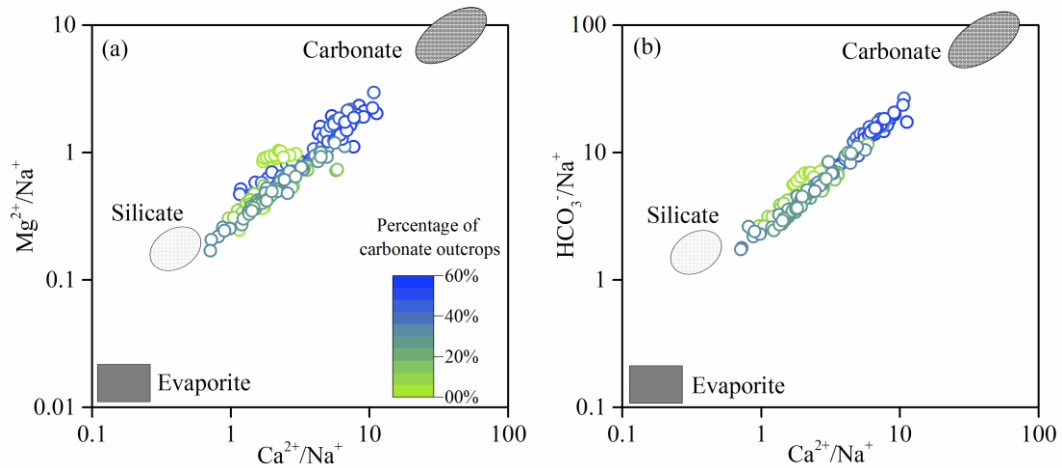
334 **5 Discussion**

335 **5.1 Chemical weathering rates and the controlling factors**

336 **5.1.1 Chemical weathering rates**

337 Atmospheric precipitation inputs, anthropogenic inputs (here refer to the acid deposition and
 338 AMD) and chemical weathering of rocks and minerals as the major sources contributed to the
 339 hydrochemistry in the river basin. Previous studies have shown that rock weathering contributions
 340 to major element composition of the river can be interpreted in terms of mixing among three main
 341 end-members: the weathering products of carbonates, silicates and evaporites (Cao et al., 2016b;
 342 Négrel et al., 1993; Ollivier et al., 2010). The river water samples in the Beijiang River Basin were
 343 displayed on the plots of Na-normalized molar ratios (Fig. 6). In these plots, the contributions from
 344 carbonate weathering correspond to the trend toward high-Ca²⁺ end-member close to the top right
 345 corner, while silicate weathering correspond to the trend toward to high-Na⁺ end-member close to
 346 the low-left corner. It was clear that the samples with high ratio of carbonate outcrop had the highest
 347 molar ratios of Ca²⁺/Na⁺, Mg²⁺/Na⁺ and HCO₃⁻/Na⁺, which made the samples located toward to the

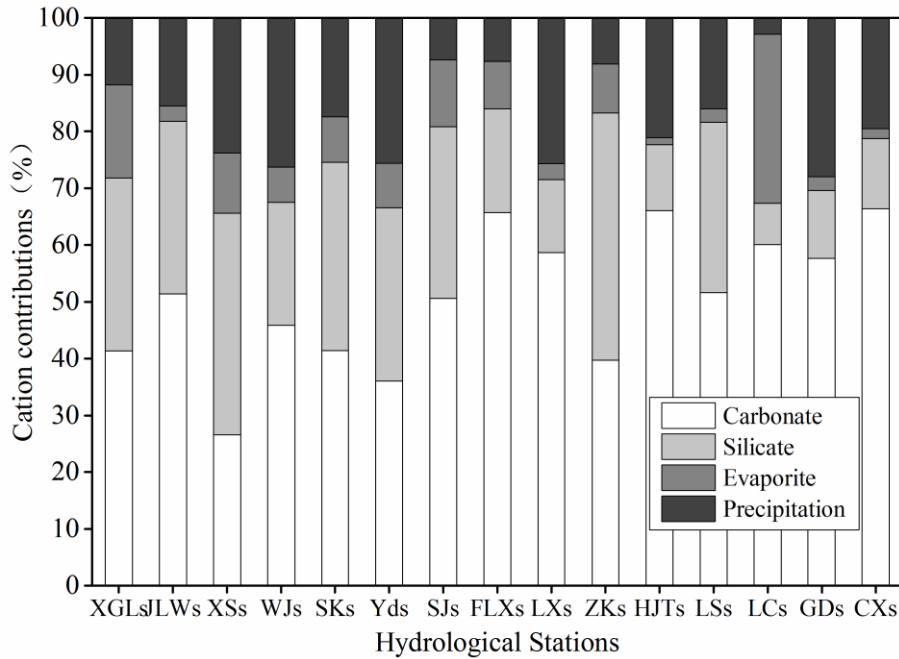
348 carbonate weathering end-member. However, the samples with low $\text{Ca}^{2+}/\text{Na}^+$, $\text{Mg}^{2+}/\text{Na}^+$ and HCO_3^-
 349 $/\text{Na}^+$ ratios showed the influence of silicate weathering. In addition, major ion compositions of the
 350 Beijiang River were mainly contributed by the weathering of carbonates and silicates, and showed
 351 little contribution of evaporite weathering.



352

353 **Fig. 6** Mixing diagrams using Na-normalized molar ratios: (a) $\text{Mg}^{2+}/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ (b) HCO_3^-
 354 $/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ for the Beijiang River Basin. The color ramp showed the percentage of
 355 **carbonate outcrops**

356 Based on the chemical balance method, the calculated contributions of different sources to the
 357 total cationic loads were presented in Fig. 7. The results showed that carbonate weathering was the
 358 most important mechanism controlling the local hydrochemistry, and contributed approximately
 359 50.06% (10.96%~79.96%) of the total cationic loads. Silicate weathering and atmospheric
 360 precipitation inputs accounted for 25.71% (5.55%~70.38%) and 17.92% (0~46.95%), respectively.
 361 Evaporite weathering had the minimum contribution with an average of 6.31% (0~24.36%) to the
 362 total cationic loads.

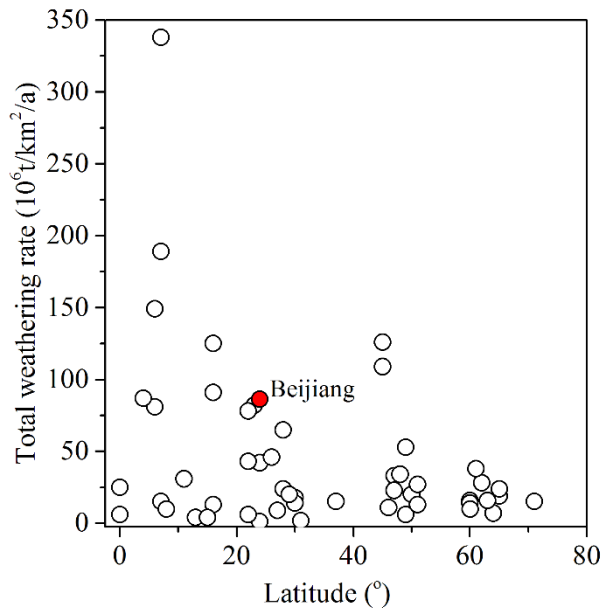


The percentage of carbonate outcrops increases

363

364 **Fig. 7 Calculate contributions (in %) from the different hydrological stations to the total cationic**
 365 **load in the Beijiang River Basin. The cationic loads were the sum of Na⁺, K⁺, Ca²⁺ and Mg²⁺**

366 The result of chemical weathering rates was listed in Table 2. The carbonate weathering
 367 contributes about 70% of the total chemical weathering, and the average of carbonate and silicate
 368 weathering rate in the Beijiang River Basin were 61.15 and 25.31 t·km⁻²·a⁻¹, respectively. In addition,
 369 chemical weathering rates showed significantly seasonal variations with the highest carbonate and
 370 silicate weathering rates in May (16.75 and 5.50 t·km⁻²·month⁻¹, respectively) and the lowest
 371 carbonate and silicate weathering rates in February (0.95 and 0.39 t·km⁻²·month⁻¹, respectively).
 372 Gaillardet et al. (1999) reported the chemical weathering rate of major rivers all over the world and
 373 found that the hyperactive zone with high chemical weathering rate is generally located between the
 374 latitude 0-30° and our study belongs to this area (Fig. 8). The factors influence the balance between
 375 CWR and SWR would be further discussed in the following parts.



376
377 **Fig. 8 Relationship between latitude and total weathering rate (TWR)**

378 **Table 2 The annual discharge, catchment area, carbonate and silicate outcrops proportions, and**
379 **calculated weathering rates of carbonate and silicate of 15 subcatchments in the Beijiang River**

ID	Annual discharge (10 ⁸ m ³ /a)	Catchment area (km ²)	Percentages of carbonate (%)	Percentages of silicate (%)	Carbonate weathering rate -CWR (t km ⁻² year ⁻¹)	Silicate weathering rate -SWR (t km ⁻² year ⁻¹)	Total weathering rate -TWR (t km ⁻² year ⁻¹)
JLWs	2.23	281.13	2.95	97.05	18.63	14.94	33.56
CXs	4.06	392.35	57.44	42.56	74.21	11.42	85.64
HJTs	11.54	503.02	41.99	55.83	169.12	29.73	198.85
ZKs	16.38	1655.22	34.60	61.81	35.03	24.14	59.17
XGLs	13.56	1863.02	0.38	93.07	25.75	13.96	39.72
WJs	19.11	1960.99	12.51	73.87	55.00	17.43	72.43
LXs	56.37	2458.06	34.32	64.07	178.71	29.39	208.10
LCs	58.74	5278.14	49.67	50.21	79.70	20.59	100.29
LSs	74.83	6994.69	44.59	52.44	69.28	14.94	84.22
XSs	62.11	7497.01	7.09	87.81	18.85	20.35	39.20
GDs	137.81	9028.38	49.93	44.93	111.73	19.19	130.92
SKs	49.51	17417.24	25.43	69.35	12.71	6.11	18.82
YDs	191.07	18234.64	25.63	68.05	52.37	19.59	71.95
FLXs	396.25	34232.34	29.68	63.49	68.38	17.53	85.91
SJs(Average)	450.90	38538.06	28.12	64.65	61.15	25.31	86.46

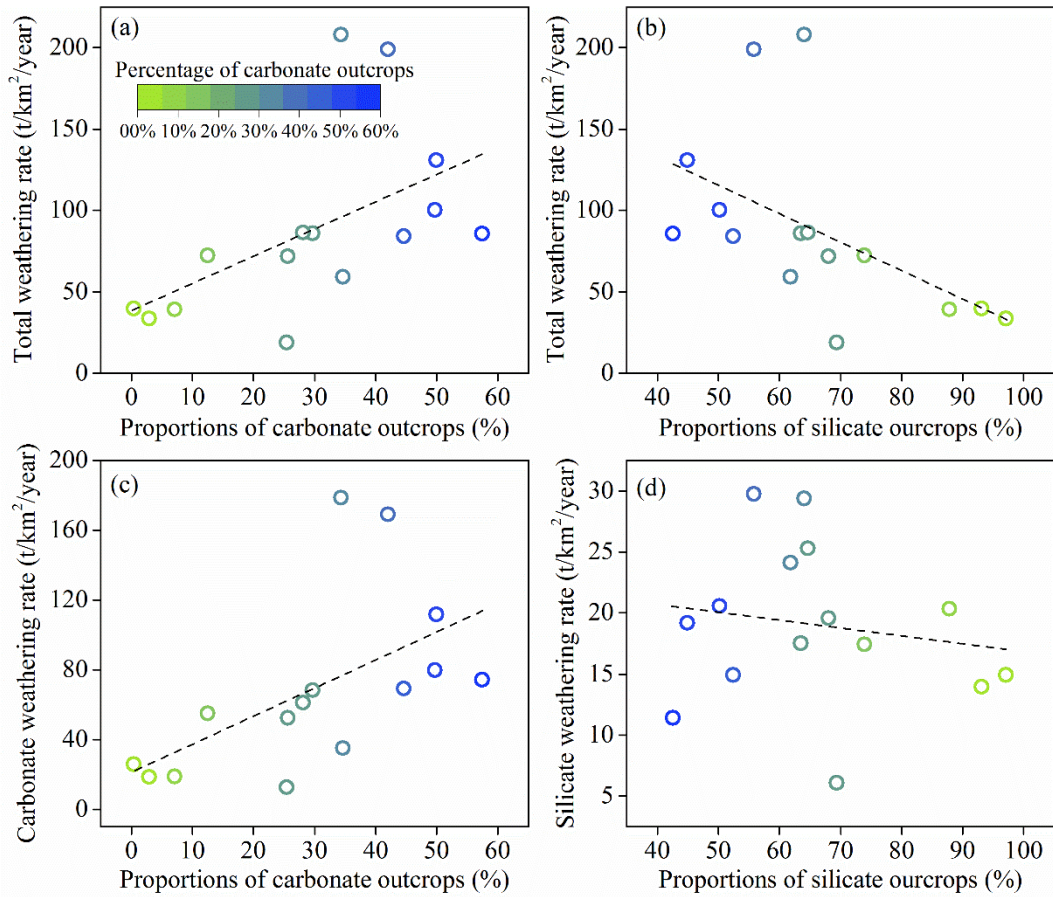
380 **5.1.2 Factors affecting chemical weathering**

381 Many factors control the chemical weathering rates, including terrain, geotectonic properties,

382 lithology, land cover, climatic conditions (temperature, precipitation, etc.), and hydrological
383 characteristics (Ding et al., 2017; Gislason et al., 2009; Hagedorn and Cartwright, 2009). For this
384 study, the lithology, hydrological characteristics and geomorphology was selected as the major
385 factors to be discussed.

386 **5.1.2.1 Lithology**

387 Among all the factors controlling the chemical weathering rates, lithology is one of the most
388 important factors because different type of rocks has different weathering abilities (Viers et al.,
389 2014). The TWR had a significant positive correlation ($p<0.01$) with the ratios of the proportion of
390 carbonate and a non-significant positive correlation with that of silicate outcrops (Fig. 9a, b).
391 Furthermore, a significant correlation ($p<0.01$) was found between the CWR and proportion of
392 carbonate outcrops (Fig. 9c), but the correlation between the SWR and the proportion of silicate
393 outcrops was low and not statistically significant ($p>0.05$, Fig. 9d). The correlation analysis
394 confirmed that carbonate outcrops ratios was the sensitive factor controlling the chemical
395 weathering rates and the rapid kinetics of carbonate dissolution played an important role in
396 weathering rates in the Beijiang River Basin.



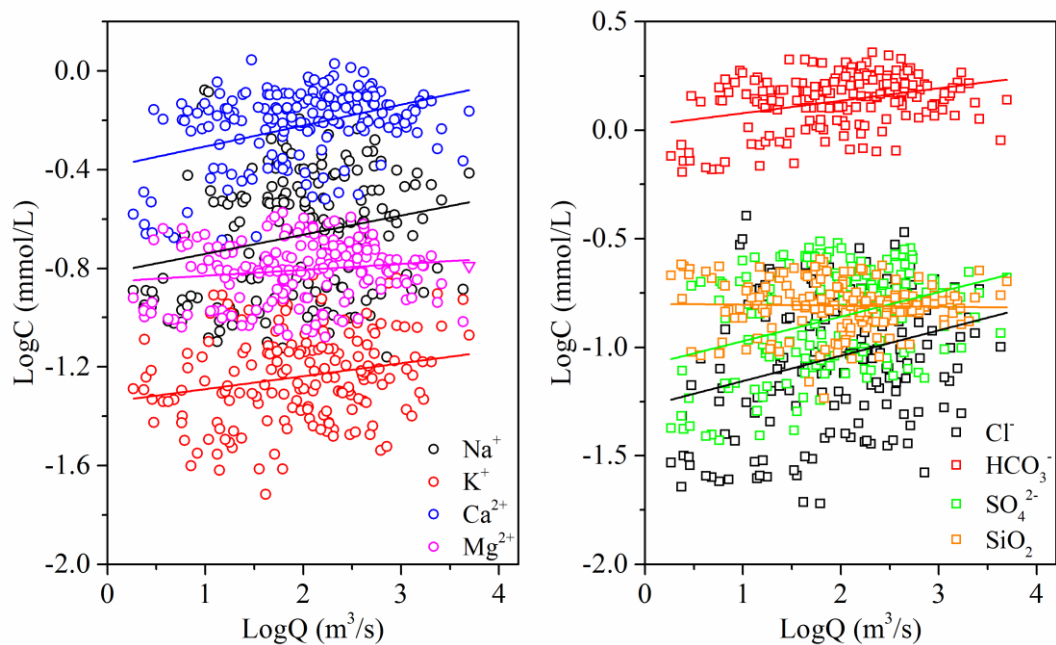
397
 398 **Fig. 9 The relationships between weathering rates and the proportions of carbonate or silicate**
 399 **outcrops**

400 **5.1.2.2 Runoff**

401 Chemical weathering is a combination of two processes, including dissolution of primary
 402 minerals and precipitation of secondary minerals growth (Eiriksdottir et al., 2011; Hartmann et al.,
 403 2014a; Liu et al., 2013). The dissolution process is quite related to the precipitation and runoff. In
 404 general, river water chemistry is usually diluted by river runoff (Q), and this dilution effect is
 405 variable in different basins (Rao et al., 2019). The dilution effects of major element caused by
 406 increasing water flow can be expressed by log linear equation, the standard rating relationship (Li
 407 et al., 2014; Walling, 1986; Zhang et al., 2007):

408
$$C_i = aQ^b \quad (34)$$

409 where C_i is the concentration of element i (mmol/L), Q is the water discharge (m^3/s), a is the
 410 regression constant and b is the regression exponent. The linear fitting result was showed by Fig. 10
 411 and the parameters b for major elements obtained from the dataset were 0.08 (Na^+), 0.05 (K^+), 0.08
 412 (Ca^{2+}), 0.02 (Mg^{2+}), 0.06 (HCO_3^-), 0.12 (Cl^-), 0.11 (SO_4^{2-}) and -0.005 (SiO_2), respectively. In many
 413 cases, b ranges from -1 to 0 due to the chemical variables that are influenced in various ways and
 414 various extents. However, in our study area, the values of b were positive and not comparable to the
 415 observations in the major Asian River such as the Yangtze (Chen et al., 2002), the Yellow (Chen et
 416 al., 2005), the Pearl Rivers (Zhang et al., 2007) and the Mekong River (Li et al., 2014). This
 417 suggested additional and significant solute sources in the river basin that might contribute and
 418 compensate considerably the effect of dilution by precipitation. The difference of slope for
 419 individual dissolved components at different stations reflected the different sources and the
 420 solubility of source materials.



421
 422 **Fig. 10 The relationship between major ion concentrations and runoff (Q) in logarithmic scales**

423 Due to the compensation effect of chemical weathering, significant positive linear relationship

424 was detected between Q and TWR, CWR and SWR. So that, the linear regression analysis between
 425 Q and TWR, CWR and SWR were conducted to further reveal the effect of runoff on chemical
 426 weathering rate. The slope of the liner regression equations for all 15 hydrological station
 427 watersheds in the Beijiing River Basin were summarized in Table 3. The linear relations indicated
 428 that the increase of runoff could accelerate the chemical weathering rates, but the variations of K
 429 values revealed that the degrees of influences were different due to multiple factor influence, such
 430 as the influence of geomorphology.

431 **Table 3 The slope of the liner regression equation between runoff (Q) and total weathering rate**
 432 **(TWR), carbonate weathering rate (CWR) and silicate weathering rate (SWR)**

Hydrological stations	Total weathering rate =K ₁ Q		Carbonate weathering rate =K ₂ Q		Silicate weathering rate =K ₃ Q	
	K ₁	R ²	K ₂	R ²	K ₃	R ²
JLWs	0.3912	0.99	0.2091	0.99	0.1821	0.99
CXs	0.6492	0.93	0.5631	0.93	0.0860	0.94
HJTs	0.5117	0.97	0.4421	0.96	0.0695	0.99
ZKs	0.0953	0.97	0.0525	0.76	0.0429	0.80
XGLs	0.0835	0.98	0.0558	0.97	0.0278	0.98
WJs	0.1017	0.99	0.0842	0.99	0.0175	0.88
LXs	0.0968	0.98	0.0843	0.98	0.0125	0.99
LCs	0.0486	0.90	0.0401	0.87	0.0085	0.97
LSs	0.0359	0.97	0.0286	0.96	0.0073	0.94
XSs	0.0180	0.98	0.0080	0.97	0.0100	0.96
GDs	0.0252	0.99	0.0216	0.99	0.0036	0.99
SKs	0.0116	0.98	0.0083	0.98	0.0033	0.95
Yds	0.0106	0.99	0.0081	0.99	0.0026	0.92
FLXs	0.0050	0.97	0.0039	0.95	0.0010	0.99
SJs	0.0053	0.99	0.0037	0.97	0.0016	0.98

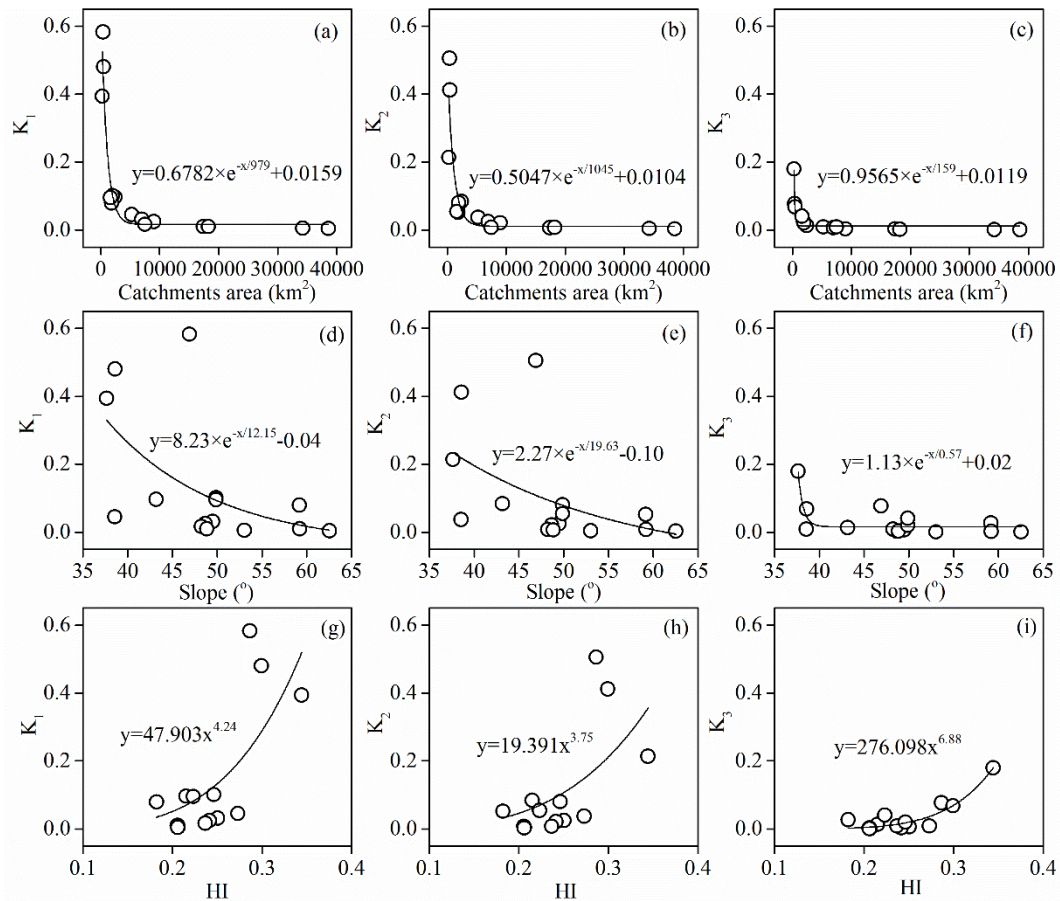
433 5.1.2.3 Geomorphology

434 The geomorphology factors including catchment area, average slope and HI, which could quite

435 influence the runoff generation process and physical and chemical weathering, were selected to give
436 a further explanation of the variation of K values. As showed in Fig. 11a, the K values were found
437 a non-linear relationship with the areas of subcatchment and could be fitted by exponential decay
438 model, which showed that the K values decreased dramatically with the initial increasing of area
439 and quickly become stable after reaching the threshold. The threshold value for K_1 , K_2 and K_3 was
440 about 5000 km². It indicated that the compensation effect was more significant in small catchment.

441 The average topographic slope of each subcatchment ranged from 37° to 63°. With the
442 increasing of average slope, the residence time of both surface water and groundwater decrease.
443 Kinetics of carbonate and silicate reactions was determined by the reaction time which could be
444 related by the residence time of water. In our study area, the K values showed non-linear negative
445 correlation with average slope (Fig. 11e, f, g). When the average slope increase, the resulted small
446 residence time (time of water-rock reactions) make the compensation effect also weak in the study
447 area.

448 Hypsometric analysis showed that the HI ranged from 0.18 to 0.34. According to the empirical
449 classification by HI ($HI > 0.6$, inequilibrium or young stage, $0.35 < HI \leq 0.6$, equilibrium or mature
450 stage, $HI \leq 0.35$, monadnock or old age), the geomorphological development in the Beijiang River
451 was recognized as the old age, which reflect the erodible degree and erosion trend of the
452 geomorphology was high. Furthermore, the non-linear positive correlations between HI and K
453 values (Fig. 11g, h, i) also addressed that geomorphology development have significant influence
454 on chemical weathering and relating CO₂ consumption processes.



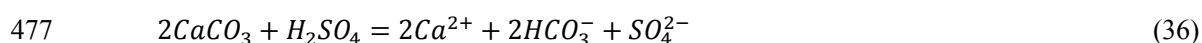
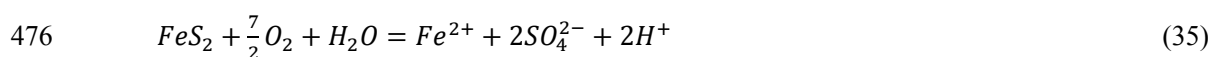
455
 456 **Fig. 11 The relationships between K values and catchments area (a, b, c), average slope (d, e, f)**
 457 **and HI (g, h, i) for the Beijiang River.**

458 **5.2 Temporary and net sink of atmospheric CO₂**

459 **5.2.1 Sulfate origin and DIC apportionment**

460 The successful application of DIC apportionment calculation mentioned in section 3.2.2 is
 461 depended on the origins of sulfate (SO₄²⁻). Three origins of SO₄²⁻ should be discriminated
 462 including atmospheric acid deposition (Larssen and Carmichael, 2000), acid mining discharge
 463 (AMD) (Li et al., 2018; Li et al., 2019) and chemical weathering of evaporite such as the dissolution
 464 of gypsum (Appelo and Postma, 2005). Acid rain events occurred frequently in South and East
 465 China after 1980 (Larssen et al., 2006). The pH isolines based on data from 86 monitoring stations
 466 (Larssen et al., 2006) showed that in the Beijiang River the rain pH was lower than 4.5 and our
 467 monitoring dataset also proved this result. Sulfur wet deposition estimated based on the observed

468 bulk wet sulfur deposition data and the RAINS-Asia model (Larssen and Carmichael, 2000) ranged
469 from 2000-5000 eq ha⁻¹ a⁻¹, which showed that the acid sulfur deposition was one of the most
470 important sources of river sulfate. In addition, considering the abundant ore resources in the Beijiang
471 River, the second possible source of SO₄²⁻ is sulfide oxidation due to mining. In our previous study,
472 the SO₄²⁻ with AMD origin mainly came from the tributary Wenjiang River (Wen et al., 2018). These
473 two sources could offer sufficient chemical weathering agent H₂SO₄ and actively involved in the
474 chemical weathering due to the following reaction mechanism (take carbonate for example) (Taylor
475 et al., 1984; van Everdingen and Krouse, 1985).



478 The third source came from dissolution of gypsum could not offer active H₂SO₄ to induce
479 carbonate and silicate dissolution. Two evidences were summarized to indicate the absence of
480 gypsum in the study area, (1) Lithology in the river basin is composed of limestone, sandstone,
481 gneiss and glutenite. HI showed that geomorphology development has entered into the “old” age,
482 the evaporite such as halite and gypsum has been consumed by the dissolution. (2) The
483 stoichiometric relationship between Ca²⁺ and SO₄²⁻ (Fig. 2) showed that all of the samples in the
484 study area located below the 1:1 gypsum dissolution line, and they also below the 1:2 carbonate
485 weathering induced by sulfuric acid (SCW) line. These two points combined gave the evidence to
486 prove the absence of contribution of gypsum dissolution to river SO₄²⁻. So that, the DIC
487 apportionment could be calculated according to equation (18) to (21) and the result of three main
488 processes (CCW, CSW and SCW) contributing to the DIC origin in the Beijiang River water are
489 showed in Table 4. It was found that CCW was the dominant origin of DIC (35%~87%) and that

490 SCW (3%~15%) and CSW (7%~59%) were non-negligible weathering processes.

491 **5.2.2 Temporary and net CO₂ sink**

492 According to the classical view of the global carbon cycling (Berner and Kothavala, 2001),
493 the CO₂ sink induced by chemical weathering varies for different time scales. At short-term
494 timescale, carbonic acid based carbonate and silicate weathering (CCW and CSW) and transport of
495 the HCO₃⁻ to oceans through rivers is an important “temporary” carbon sink (Khadka et al., 2014)
496 and can be calculated by the sum of CCR_{CCW} and CCR_{CSW}. Thus, it was significant to estimate the
497 CCR of CCW and CSW (Liu and Dreybrodt, 2015; Liu et al., 2011). However, at the geological
498 timescale (>10⁶ years), when over the timescale typical of residence time of HCO₃⁻ in the ocean
499 (10⁵ years), the CCW is not a mechanism that can participate in the net sink of CO₂ in the atmosphere
500 because all of the atmospheric CO₂ fixed through CCW is returned to the atmosphere during
501 carbonate precipitation in the ocean. Meanwhile, in case of CSW, followed by carbonate deposition,
502 one of the two moles of CO₂ involved is transferred from the atmosphere to the lithosphere in the
503 form of carbonate rocks, while the other one returns to the atmosphere. The CSW is recognized as
504 the net sink of atmosphere CO₂. In addition, when sulfuric acid is involved as a proton donor in
505 carbonate weathering, half of the carbon dissolved to the atmospheric during carbonate precipitation.
506 Thus, SCW leads to a net release of CO₂ in ocean-atmosphere system. So that the net CO₂ sink
507 (expressed by CCR_{Net} in this study) is controlled by the DIC apportionment according to equation
508 (31).

509 The results of CCR_{Total}, CCR_{CCW}, CCR_{CSW} and CCR_{Net} were summarized in Table 4. The
510 CCR_{Total} was 823.41 10³ mol km⁻² a⁻¹. Comparing with other Chinese rivers, such as the Songhua
511 River (189×10³ mol km⁻² a⁻¹) (Cao et al., 2015) and other rivers calculated by (Gaillardet et al.,

1999) including the Heilong River ($53 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Changjiang River ($609 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Huanghe River ($360 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Xijiang River ($960 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Jinshajiang River ($420 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Lancangjiang River ($980 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Nujiang River ($1240 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Yalongjiang River ($870 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), the Daduhe River ($1280 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$) and Minjiang River ($660 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$), our study area showed relative high CCR due to high chemical weathering rate. In addition, the CCR_{CCW} and CCR_{CSW} were 536.59×10^3 (65%) and 286.82×10^3 (35%) $\text{mol km}^{-2} \text{ a}^{-1}$, respectively. Compared with the “temporary” sink, the net sink of CO_2 for the Beijiang River was approximately $23.18 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ of CO_2 sinking in the perspective of global carbon cycling. It was about 3% of the “temporary” CO_2 sink. In addition, the CO_2 net sink of each sub basin were also different and show large spatial variations due to heterogeneity of geology and human activities. The geology showed weak correlation with the CO_2 net sink (Fig. 12a), while the $[\text{SO}_4^{2-}]_{SCW}$ and $[\text{SO}_4^{2-}]_{SSW}$ have weak negative correlation with the CO_2 net sink (Fig. 12b). It proved that human activities (sulfur acid deposition and AMD) decreased the CO_2 net sink and even make chemical weathering a CO_2 source to the atmosphere.

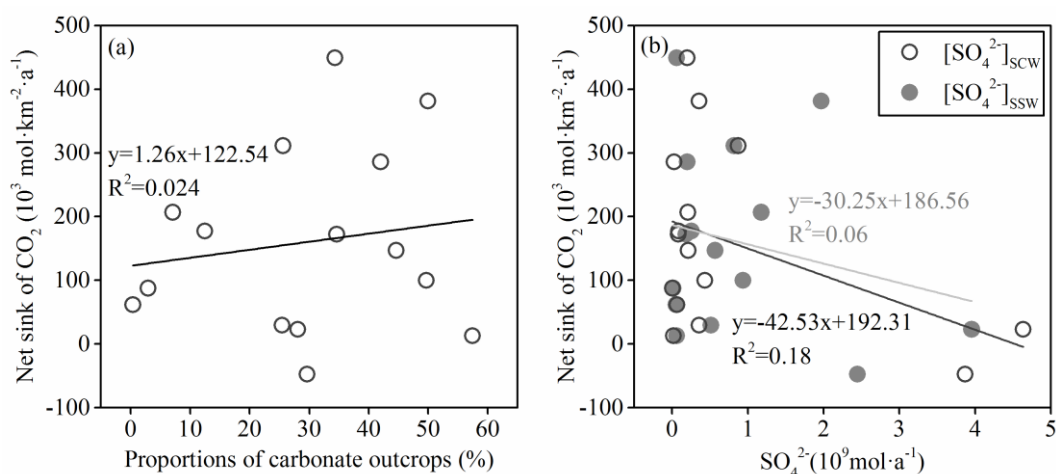
Table 4 Calculated CO_2 consumption rate and net sink of 15 nested subcatchments in the

Beijiang River Basin

Hydrological stations	DIC apportionment (10^9 mol a^{-1})			“Temporary” Sink (CO_2 consumption rate) ($10^3 \text{ mol km}^{-2} \text{ a}^{-1}$)			Net Sink ($10^3 \text{ mol km}^{-2} \text{ a}^{-1}$)
	CCW	SCW	CSW	CCR_{CCW}	CCR_{CSW}	CCR_{Total}	CCR_{Net}
JLWs	0.10	0.00	0.05	175.23	191.14	366.36	87.73
CXs	0.57	0.04	0.05	732.05	118.18	850.23	13.18
HJTs	1.57	0.06	0.34	1563.64	683.41	2247.05	286.14
ZKs	1.24	0.16	0.73	375.23	439.77	815.00	172.27
XGLs	0.85	0.14	0.37	227.05	195.91	422.95	61.59

WJs	1.76	0.17	0.87	449.32	443.18	892.50	177.50
LXs	7.30	0.40	2.61	1485.45	1060.45	2545.91	449.09
LCs	8.07	0.86	1.92	764.32	363.41	1127.95	99.77
LSs	10.13	0.42	2.48	724.55	354.32	1078.64	147.05
XSs	2.08	0.41	3.52	138.64	469.09	607.73	207.05
GDs	16.48	0.71	7.60	912.73	841.82	1754.55	381.36
SKs	4.00	0.72	1.74	114.77	100.23	215.00	29.55
YDs	14.11	1.75	13.10	386.82	718.64	1105.45	311.14
FLXs	40.38	7.74	4.46	589.77	130.45	720.23	-47.73
SJs	41.36	9.27	11.05	536.59	286.82	823.41	23.18

529



530

531 **Fig. 12 Correlations between CO₂ net sinks and proportions of carbonate (a) and**
 532 **correlations between CO₂ net sinks and [SO₄²⁻]_{scw} or [SO₄²⁻]_{ssw} (b)**

533 6 Conclusions

534 This study revealed the temporary and net sinks of atmospheric CO₂ due to chemical
 535 weathering in a subtropical hyperactive catchment with mixing carbonate and silicate lithology
 536 under the stress of chemical weathering induced by anthropogenic sulfuric acid agent. During the
 537 sampling period, the pH values ranged from 7.5 to 8.5 and TDS varied from 73.8 to 230.2 mg·L⁻¹.
 538 Ca²⁺ and HCO₃⁻ were the dominated cation and anion. Water chemical patterns and PCA showed
 539 that carbonate and silicate weathering were the most important processes controlling the local

540 hydrochemistry. In average, carbonate and silicate weathering contributed approximately 50.06%
541 and 25.71% of the total cationic loads, respectively.

542 The average of carbonate and silicate weathering rate in the Beijiang River Basin were 61.15
543 and 25.31 $t \cdot km^{-2} \cdot a^{-1}$, respectively. The high rate was comparable to other rivers located in the
544 hyperactive zone between the latitude 0-30°. The lithology, runoff and geomorphology had
545 significant influences on the chemical weathering rate. (1) Due to the difference between kinetics
546 of carbonate and silicate dissolution processes, the proportion of carbonate outcrops had significant
547 positive correlation with the chemical weathering rate and confirmed that carbonate outcrops ratios
548 was the sensitive factor controlling the chemical weathering rates and the rapid kinetics of carbonate
549 dissolution played an important role in weathering rates. (2) Runoff mainly controlled the season
550 variations and the dilution effect was weak in the study area. Due to the compensation effect of
551 chemical weathering, significant positive linear relationship was detected between Q and TWR,
552 CWR and SWR. (3) The geomorphology factors such as slope and HI had non-linear correlation on
553 chemical weathering rate and showed significant scale effect, which revealed the complexity in
554 chemical weathering processes.

555 DIC apportionment showed that CCW was the dominant origin of DIC (35%-87%) and that
556 SCW (3%-15%) and CSW (7%-59%) were non-negligible weathering processes. The CCR_{Total} was
557 $823.41 \cdot 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$, relative high CCR due to high chemical weathering rate. In addition, the
558 CCR_{CCW} and CCR_{CSW} were 536.59×10^3 (65%) and 286.82×10^3 (35%) $\text{mol km}^{-2} \text{ a}^{-1}$, respectively.
559 Compared with the “temporary” sink, the net sink of CO_2 for the Beijiang River was approximately
560 $23.18 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ of CO_2 sinking in the perspective of global carbon cycling. It was about
561 2.82% of the “temporary” CO_2 sink. Human activities such as sulfur acid deposition and AMD have

562 significantly altered the CO₂ sinks.

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787 **Supplementary material**

788 **Table S1 The major ions concentrations of rain water samples at 5 hydrological stations in the**

789 **Beijiang River (mean±SD).**

Hydrological stations	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	Cl ⁻ (μmol/L)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)
XGLs	12.8±9.7	21.0±16.8	22.2±20.5	10.9±10.3	25.9±22.6	320.2±370.7	83.3±85.2
XSs	20.4±11.8	7.8±4.5	86.9±30.4	10.1±5.2	10.0±0.0	606.5±511.5	36.3±23.4
Yds	16.3±9.5	10.1±10.8	161.1±56.5	9.0±7.8	23.9±12.4	136.9±169.5	143.1±135.5
FLXs	18.8±12.3	3.2±2.5	31.1±17.7	4.2±2.7	23.1±16.6	45.4±27.5	77.1±70.4
SJs	12.6±9.2	12.5±16.3	22.9±13.8	15.4±18.1	25.4±16.0	79.0±79.8	156.7±206.4

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