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Geochemistry of the dissolved loads of rivers in Southeast Coastal Region, China: Anthropogenic impact on chemical weathering and carbon sequestration

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Abstract:

Southeast coastal region is the most developed and populated area in China. Meanwhile, it has been the most severe acid rain impacted region for many years. The chemical compositions and carbon isotope ratio of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) of rivers were investigated to evaluate the chemical weathering and associated atmospheric CO_2 consumption rates. Mass balance calculation indicated that the dissolved loads of major rivers in the Southeast Coastal Rivers Basin (SECRB) were contributed by atmospheric (14.4%, 6.6-23.4%), anthropogenic (17.8%, 0-55.2%), silicate weathering (38.3%, 10.7-74.0%) and carbonate weathering inputs (29.4%, 3.9-62.0%). The silicate and carbonate chemical weathering rates for these river watersheds were 10.0-29.6 t km^{-2} a^{-1} and 1.0-54.1 t km^{-2} a^{-1}, respectively. The associated mean CO_2 consumption rate by silicate weathering for the whole SECRB were 167×10^3 mol km^{-2} a^{-1}. The chemical and $\delta^{13}C_{DIC}$ evidences indicated that sulfuric acid (mainly from acid deposition) was significantly involved in chemical weathering of rocks. The calculation showed an overestimation of CO_2 consumption at 0.19×10^{12} g C a^{-1} if sulfuric acid was ignored, which accounted for about 25% of the total CO_2 consumption by silicate weathering in the SECRB. This study quantitatively highlights that the role of sulfuric acid in chemical weathering, suggesting that acid deposition should be considered in studies of chemical weathering and associated CO_2 consumption.

Keywords: Southeast Coastal Rivers Basin; Chemical weathering; CO_2 consumption; acid deposition;

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1. Introduction

Chemical weathering of rocks is a key process that links geochemical cycling of solid earth to the atmosphere and ocean. It provides nutrients to terrestrial and marine ecosystems and regulates the level of atmospheric CO_2. As a net sink of atmospheric CO_2 on geologic timescales, estimation of silicate chemical weathering rates and the controlling factors are important issues related to long-term global climate change (e.g. Raymo and Ruddiman, 1992; Négrel et al. 1993; Berner and Caldeira, 1997; Gaillardet et al., 1999; Kump et al., 2000; Amiotte-Suchet et al., 2003; Oliva et al., 2003; Hartmann et al., 2009; Moon et al., 2014). As an important component in the Earth's Critical Zone (U.S. Nat. Res. Council Comm., 2001), river serves as an integrator of various natural and anthropogenic processes and products in a basin, and a carrier transporting the weathering products from continent to ocean. Therefore, the chemical compositions of river are widely used to evaluate chemical weathering and associated CO_2 consumption rates at catchment and/or continental scale, and examine their controlling factors (e.g., Edmond et al., 1995; Gislason et al., 1996; Galy and France-Lanord, 1999; Huh, 2003; Millot et al., 2002, 2003; Oliva et al., 2003; West et al., 2005; Moon et al., 2007; Noh et al., 2009; Shin et al., 2011; Calmels et al., 2011).

With the intensification of human activities, human perturbations to river basins have increased in frequency and magnitude. It is important to understand how such perturbations function on the current weathering systems and to predict how they will affect the Critical Zone of the future (Brantley and Lebedeva, 2011). In addition to CO_2, other sources of acidity (such as sulfuric, nitric and organic acids) can also produce protons. These protons react with carbonate and silicate minerals, thus enhance rock chemical weathering rate and flux compared with only considering protons deriving from CO_2 dissolution (Calmels et al., 2007; Xu and Liu, 2010). The effect of other sourced proton (especially H^+ induced by SO_2 and NO_X coming from anthropogenic activities) on chemical weathering is documented to be an important mechanism modifying atmospheric CO_2 consumption by rock weathering (Galy and France-Lanord, 1999; Semhi, et al., 2000; Spence and Telmer, 2005; Xu and Liu, 2007; Perrin et al., 2008; Gandois et al., 2011). Anthropogenic emissions of SO_2 was projected to provide 3 to 5 times greater H_2SO_4 to the continental surface than the pyrite oxidation originated H_2SO_4 (Lerman et al., 2007). Therefore, increasing acid precipitation due to stronger human activities nowadays could make this mechanism more prominently.

The role of acid precipitation on the chemical weathering and CO_2 consumption has been investigated in some river catchments (Amiotte-Suchet et al., 1995; Probst et al., 2000; Vries et al., 2003; Lerman et al., 2007; Xu and Liu, 2010). It has been documented that silicate rocks were more easily disturbed by acid precipitation during their weathering and soil leaching processes, because of their low buffeting capacity (Reuss et al., 1987; Amiotte-Suchet et al., 1995). According to Amiotte-Suchet et al. (1995), especially where crystalline rocks outcrop, the disturbance can be very high and can induce a decrease of CO_2 consumption by weathering at least 73% in the Strengbach catchment (Vosges Mountains, France). This highlights the importance of exploring anthropogenic impact on chemical weathering and CO_2 consumption under different background (e.g. lithology, climate, human activity intensity, and basin scale) for better constraining and estimation of acid precipitation effect on rock weathering. Asia, especially East Asia, is one of the world's major sulfur emissions areas. However, the effect of acid precipitation on silicate weathering and associated CO_2 consumption was not well evaluated in this area, especially lack of quantitative studies.

Southeast coastal region of China is the most highly developed and populated area in China, dominated by Mesozoic magmatic rocks (mainly granite and volcanic rocks) in lithology. Meanwhile, it is also seriously impacted by acid rain, with a volume-weighted mean value of pH lower than 4.5 for many years (Wang et al., 2000; Larssen and Carmichael, 2000; Zhao, 2004; Han et al., 2006; Larssen et al., 2006; Zhang et al., 2007a; Huang et al., 2008; Xu et al., 2011). Therefore, it is an ideal area for evaluating silicate weathering and the effect of acid rain. In this study, the chemical and carbon isotope composition of rivers in this area were first systematically investigated, in order to: (i) decipher the different sources of solutes and to quantify their contributions to the dissolved loads; (ii) calculate silicate weathering and associated CO_2 consumption rates; (iii) evaluate the effects of acid deposition on rock weathering and CO_2 consumption flux.

2. Natural setting of study area

Southeast coastal region of China, where the landscape is dominated by mountainous and hilly terrain, has rugged coastlines and develop numerous small and medium river system. Rivers in this region flow eastward or southward and finally

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inject into the East China Sea or the South China Sea (Fig. 1), and they are collectively named as 'Southeast Coastal Rivers' (SECRs). Large rivers are listed here from north to south, they are: Qiantang, Cao'e, Ling, and Ou in Zhejiang province; Jiaoxi, Huotong, Ao, Min, Jin, and Jiulong in Fujian province; Han and Rong in Guangdong province.

The Southeast Coastal Rivers Basin (SECRB) belongs to the warm and humid subtropical oceanic monsoon climate. The average annual temperature and precipitation are 17-21℃ and 1400-2000 mm, respectively. The precipitation mainly happens during May to September, and the minimum and maximum temperature often occurs in January and July. This area is one of the most developed areas in China, with a population more than 190 million (mean density of ~470 individuals/km^2), but the population mainly concentrated in the coastal urban areas. The vegetation coverage of these river basins is more than 60%, mainly subtropical evergreen-deciduous broadleaf forest and mostly distributing in mountains area. Cultivated land, and industries and cities are mainly located in the plain areas and lower reach of these rivers.

Geologically, three regional-scale fault zones are distributed across the SECRB region (Fig. 1). They are the sub-EW-trending Shaoxing-Jiangshan fault zone, the NE-trending Zhenghe-Dapu fault zone, and the NE-trending Changle-Nanao fault zone (Shu et al., 2009). These fault zones dominate the direction of the mountains ridgelines and drainages, as well as the formation of the basins and bay. The Zhenghe-Dapu fault zone is a boundary line of Caledonian uplift belt and Hercynian-Indosinian depression zone. Mesozoic magmatic rocks are widespread in the southeast coastal region with a total outcrop area at about 240,000 km^2. Over 90% of the Mesozoic magmatic rocks are granitoids (granites and rhyolites) and their volcanic counterpart with minor existence of basalts (Zhou et al., 2000, 2006; Bai et al., 2014). These crust-derived granitic rocks are mainly formed in the Yanshanian stage, and may have been related to multiple collision events between Cathaysia and Yangtze blocks. Among the major river basins, the proportions of magmatic rocks outcrop are about 36% in Qiantang river basin, above 80% in Ou, Jiaoxi and Jin river basins, and around 60% in Min, Jiulong, Han and Rong river basins (Shi, 2014). The overlying Quaternary sediment in this area is composed of brown-yellow siltstones but is rarely developed. The oldest basement complex is composed of metamorphic rocks of greenschist and amphibolite facies. Sedimentary rocks categories into two types, one is mainly composed by red clastic rocks which cover more than 40,000 km^2 in the study area; the other occurs as interlayers within volcanic formations, including varicolored mudstones and sandstones. They are mainly distributed on the west of Zhenghe-Dapu fault zone (FJBGRM, 1985; ZJBGMR, 1989; Shu et al., 2009).

3. Sampling and analytical method

Water samples were collected during the high-flow season of 2010 (sample number and locations are shown in Fig. 1). 2-L water samples were collected in the middle channel of the river from bridges or ferries, or directly from the center of some shallow streams in the source area. The lower reaches sampling sites were selected distant away from the estuary to avoid the influence of seawater. Temperature (T), pH

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and electrical conductivity (EC) were measured in the field with a portable EC/pH meter (YSI-6920, USA). All of the water samples for chemical analysis were filtered in field through 0.22 μm Millipore membrane filter, and the first portion of the filtration was discarded to wash the membrane and filter. One portion filtrate were stored directly in HDPE bottles for anion analysis and another were acidified to pH <2 with 6M double sub-boiling distilled HNO_3 for cation analysis. All containers were previously washed with high-purity HCl and rinsed with Milli-Q 18.2 MΩ water.

Alkalinity was titrated with 0.005M HCl within 12 h after sampling. Cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were determined using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP, USA). Anions (Cl^-, F^-, NO_3^- and SO_4^{2-}) were analyzed by ionic chromatography (IC) (Dionex Corporation, USA). Dissolved silica was determined by spectrophotometry using the molybdate blue method. Reagent and procedural blanks were measured in parallel to the sample treatment, and calibration curve was evaluated by quality control standards before, during and after the analyses of each batch of samples. Measurement reproducibility was determined by duplicated sample and standards, which showed ±3% precision for the cations and ±5% for the anions.

River water samples for carbon isotopic ratio ($\delta^{13}C$) of dissolved inorganic carbon (DIC) measurements were collected in 150 ml glass bottles with air-tight caps and preserved with $HgCl_2$ to prevent biological activity. The samples were kept refrigerated until analysis. For the $\delta^{13}C$ measurements, the filtered samples were injected into glass bottles with phosphoric acid. The CO_2 was then extracted and cryogenically purified using a high vacuum line. $\delta^{13}C$ isotopic ratios were analyzed on Finnigen MAT-252 stable isotope mass spectrometer at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences. The results are expressed with reference to VPDB, as follows:

$$\delta^{13}C = [((^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{standard}) - 1] \times 1000 \quad (1)$$

The $\delta^{13}C$ measurement has an overall precision of 0.1‰. A number of duplicate samples were measured and the results show that the differences were less than the range of measurement accuracy.

4. Results

The major parameter and ion concentrations of samples are given in Table 1. The pH values of water samples ranged from 6.50 to 8.24, with an average of 7.23. Total dissolved solids (TDS) of water samples varied from 35.3 to 205 mg l^{-1}, with an average of 75.2 mg l^{-1}. Comparing with the major rivers in China, the average TDS was significantly lower than Changjiang (224 mg l^{-1}, Chetelat et al., 2008) , Huanghe (557 mg l^{-1}, Fan et al., 2014) and Zhujiang (190 mg l^{-1}, Zhang et al., 2007b). However, the average TDS was comparable to the rivers draining silicate rock dominated areas, e.g. the upper Ganjiang (63 mg l^{-1}, Ji and Jiang, 2012), the Amur (70 mg l^{-1}, Moon et al., 2009), Xishui (101 mg l^{-1}, Wu et al., 2013), and north Han river in South Korea (75.5 mg l^{-1}, Ryu et al., 2008). Among the major rivers in the SECRB, the Qiantang river had the highest TDS value (averaging at 121 mg l^{-1}), and the Ou river had the lowest TDS value (averaging at 48.8 mg l^{-1}).

Major ion compositions are shown in the cation and anion ternary diagrams (Fig.

2a and b). In comparison with rivers (e.g. the Wujiang and Xijiang) draining carbonate rocks dominated area (Han and Liu, 2004; Xu and Liu, 2010), these rivers in the SECRB have distinctly higher proportions of Na^+, K^+, and dissolved SiO_2. As shown in the Fig. 2, most samples have high Na^+ and K^+ proportions, with an average higher than 50% (in μmol l^{-1}) of the total cations, except for samples from the Qiantang river. The concentrations of Na^+ and K^+ range from 43.5 to 555 μmol l^{-1} and 42.9 to 233 μmol l^{-1}, with average values of 152 and 98 μmol l^{-1}, respectively. The concentrations of dissolved SiO_2 range from 98.5 to 370 μmol l^{-1}, with an average of 212 μmol l^{-1}. Ca^{2+} and Mg^{2+} account for about 38% and 11.6%of the total cation concentrations. HCO_3^- is the dominant anion with concentrations ranging from 139 to 1822 μmol l^{-1}. On average, it comprises 60.6% (36-84.6%) of total anions on a molar basis, followed by SO_4^{2-} (14.6%), Cl^- (13.1%) and NO_3^- (11.8%). The major ionic compositions indicate that water chemistry of these rivers in the SECRB is controlled by silicate weathering. Meanwhile, it is also influenced by carbonate weathering, especially in the Qiantang river system.

The $\delta^{13}C$ of dissolved inorganic carbon in the rivers of the SECRB are given in Table 1. The $\delta^{13}C$ of the water samples show a wide range, from -11.0‰ to -24.3‰ (average -19.4‰), and with majority falling between -15 of -23‰. The values are similar to most rivers draining Deccan Traps (Das et al., 2005).

5. Discussion

The dissolved solids in river water are commonly from atmospheric and anthropogenic inputs and weathering of rocks within the drainage basin. It is necessary to quantify the contribution of different sources to the dissolved loads before deriving chemical weathering rates and associated CO_2 consumption.

5.1 Atmospheric and anthropogenic inputs

To evaluate atmospheric inputs to river waters, chloride is the most common used reference. Generally, water samples that have the lowest Cl^- concentrations are employed to correct the proportion of atmospheric inputs in a river system (Négrel et al., 1993; Gaillardet et al., 1997; Viers et al., 2001; Xu and Liu, 2007). In pristine areas, the concentration of Cl^- in river water is assumed to be entirely derived from the atmosphere, provided that the contribution of evaporites is negligible. In the SECRB, the lowest Cl^- concentration was mainly found in the headwater of each river. According to the geologic setting, no salt-bearing rocks was found in these headwater area (FJBGRM, 1985; ZJBGMR, 1989). In addition, these areas are mainly mountainous and sparsely populated. Therefore, we assumed that the lowest Cl^- concentration of samples from the headwater of each major river came entirely from atmosphere.

The proportion of atmosphere-derived ions in the river waters can then be calculated by using the element/Cl ratios of the rain. Chemical compositions of rain in the studied area have been reported at different sites, including Hangzhou, Jinhua, Nanping, Fuzhou and Xiamen (Zhao, 2004; Zhang et al., 2007a; Huang et al., 2008; Cheng et al., 2011; Xu et al., 2011) (Fig. 1). The volume-weighted mean concentration of ions and Cl-normalized molar ratios are compiled in Table 2. According to this procedure, 6.6-23.4% (averaging 14.4%) of total dissolved cations

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in the major rivers of the SECRB originated from rain. Among the anions, SO_4^{2-} and NO_3^- in the rivers are mainly from the atmospheric input, averaging at 74.7% for SO_4^{2-} and 68.6% for NO_3^-, respectively.

As the most developed and populated areas in China, the chemistry of rivers in the SECRB could be significantly impacted by anthropogenic inputs. Cl^-, NO_3^- and SO_4^{2-} are commonly associated with anthropogenic sources and have been used as tracers of anthropogenic inputs in watershed. High concentrations of Cl^-, NO_3^- and SO_4^{2-} can be found at the lower reaches of rivers in the SECRB, and an obvious increase after flowing through plain areas and city. This tendency indicates that river water chemistry is affected by anthropogenic inputs while passing through the catchments. After correcting for the atmospheric contribution to river waters, the following assumption is needed to quantitatively estimate the contributions of anthropogenic inputs. That is, Cl^- originates from only atmospheric and anthropogenic inputs, the excess of atmospheric Cl^- is regarded to present anthropogenic inputs and balanced by Na.

5.2 Chemical weathering inputs

Water samples were displayed on a plot of Na-normalized molar ratios (Fig. 3). The values of the world's large rivers (Gaillardet et al. 1999) are also shown for comparison in the figure. A best correlations between elemental ratios were observed for Ca^{2+}/Na^+ vs. Mg^{2+}/Na^+ (R^2 = 0.95, n = 120) and Ca^{2+}/Na^+ vs. HCO_3^-/Na^+ (R^2 = 0.98, n = 120). The samples cluster on a mixing line mainly between silicate and carbonate end members, closer to the silicate end-member, and with little evaporite contribution. This corresponds with the distribution of rock types in the SECRB. In addition, all water samples have equivalent ratios of $(Na^{+}+K^{+})/Cl^{-}$ larger than one, indicating silicate weathering as the source of Na^{+} and K^{+} rather than chloride evaporites dissolution.

The geochemical characteristics of the silicate and carbonate end-members can be deduced from the correlations between elemental ratios and referred to literature data for catchments with well-constrained lithology. After correction for atmospheric inputs, the Ca^{2+}/Na^{+}, Mg^{2+}/Na^{+} and HCO_3^{-}/Na^{+} of the river samples ranged from 0.31 to 30, 0.16 to 6.7, and 1.1 to 64.2, respectively. According to the geological setting (Fig. 1), there are some small rivers draining purely silicate areas in the SECRs drainage basins. Based on the elemental ratios of these rivers, we assigned the silicate end-member for this study as Ca^{2+}/Na^{+}=0.41±0.10, Mg^{2+}/Na^{+}=0.20±0.03 and HCO_3^{-}/Na^{+}=1.7±0.6. The ratio of $(Ca^{2+}+Mg^{2+})/Na^{+}$ for silicate end-member was 0.61, which is close to the silicate end-member of world rivers ($(Ca^{2+}+Mg^{2+})/Na^{+}$=0.59±0.17, Gaillardet et al., 1999). Moreover, several previous researches have documented the chemical composition of rivers, such as the Amur and the Songhuajiang in North China, the Xishui in the lower reaches of the Changjiang, and major rivers in South Korea (Moon et al., 2009; Liu et al., 2013; Wu et al., 2013; Ryu et al., 2008; Shin et al., 2011). These river basins has similar geological setting with the study area, we could further validate the composition of silicate end-member with their results. Ca^{2+}/Na^{+} and Mg^{2+}/Na^{+} ratios of silicate end-member were reported for the Amur (0.36 and 0.22), the Songhuajiang (0.44±0.23 and 0.16), the Xishui (0.6±0.4 and

0.32±0.18), the Han (0.55 and 0.21) and six major rivers in South Korea (0.48 and 0.20) in the studies above, well bracketing our estimation for silicate end-member.

Whereas, some samples show high concentrations of Ca^{2+}, Mg^{2+} and HCO_3^-, indicating the contribution of carbonate weathering. The samples collected in the upper reaches (Sample 12 and 13) in the Qiantang river fall close to the carbonate end-member documented for world large rivers (Gaillardet et al., 1999). In the present study, Ca^{2+}/Na^+ ratio of 0.41±0.10 and Mg^{2+}/Na^+ ratio of 0.20±0.03 for silicate end-member are used to calculate the contribution of Ca^{2+} and Mg^{2+} from silicate weathering. Finally, residual Ca^{2+} and Mg^{2+} are apportioned to carbonate weathering.

5.3 Chemical weathering rate in the SECRBs

Based on the above assumption, a forward model is employed to quantify the relative contribution of the different sources to the rivers of the SECRB in this study. (e.g. Galy and France-Lanord, 1999; Moon et al., 2007; Xu and Liu, 2007; 2010; Liu et al., 2013). The calculated contributions of different reservoir to the total cationic loads for large rivers and their major tributaries in the SECRB are presented in Fig. 4. On average, the dissolved cationic loads of the rivers in the study area originate dominantly from silicate weathering, which accounts for 38.3% (10.7-74.0%) of the total cationic loads in molar unit. Carbonate weathering and anthropogenic inputs account for 29.4% (3.9-62.0%) and 17.8% (0-55.2%), respectively. Contributions from silicate weathering are high in the Ou (55.7%), Huotong (55%), Ao (48%) and Min (48.4%) river catchments, which dominated by granitic and volcanic bedrocks. In contrast, high contribution from carbonate weathering is observed in the Qiantang

(56.6%) and Jiulong (38.5%) river catchments. The results manifest the lithology control on river solutes of drainage basin.

The chemical weathering rate of rocks is estimated by the mass budget, basin area and annual discharge, expressed in ton km^{-2} a^{-1}. The silicate weathering rate (SWR) is calculated using major cationic concentrations from silicate weathering and assuming that all dissolved SiO_2 is derived from silicate weathering (Xu and Liu, 2010), as the equation below:

$$SWR = ([Na]_{sil} + [K]_{sil} + [Ca]_{sil} + [Mg]_{sil} + [SiO_2]_{riv}) \times discharge/area \quad (2)$$

The assumption about Si could lead to overestimation of the silicate weathering rate, as part of silica may come from dissolution of biogenic sources rather than the weathering of silicate minerals (Millot et al., 2003; Shin et al., 2011). Thus, the cationic silicate weathering rates (Cat_{sil}) were also calculated.

The carbonate weathering rate (CWR) is calculated based on the sum of Ca^{2+}, Mg^{2+} and HCO_3^- from carbonate weathering, with half of the HCO_3^- coming from carbonate weathering being derived from the atmosphere CO_2, as the equation below:

$$CWR = ([Ca]_{carb} + [Mg]_{carb} + 1/2[HCO_3]_{carb}) \times discharge/area \quad (3)$$

The chemical weathering rates and fluxes are calculated for major rivers and their main tributaries in the SECRB, and the results are shown in Table 3. Silicate and carbonate weathering fluxes of these rivers (SWF and CWF) range from 0.02×10^6 t a^{-1} to 1.29×10^6 t a^{-1}, and from 0.002×10^6 t a^{-1} to 1.33×10^6 t a^{-1}, respectively. Among the rivers, Min river has the highest silicate weathering flux, and Qiantang river has the highest carbonate weathering flux. On the whole SECRB scale, 5.23×10^6 t a^{-1} and

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4.90×10^6 t a^{-1} of dissolved solids originating from silicate and carbonate weathering, respectively, are transported into the East and South China Sea by rivers in this region. Comparing with three largest three river basins (Changjiang, Huanghe and Xijiang) in China, the flux of silicate weathering calculated for the SECRB is lower than Changjiang (9.5×10^6 t a^{-1}, Gaillardet et al. 1999), but higher than Huanghe (1.52×10^6 t a^{-1}, Fan et al., 2014) and Xijiang (2.62×10^6 t a^{-1} , Xu and Liu, 2010).

The silicate and carbonate chemical weathering rates for these river watersheds were 10.0-29.6 t km^{-2} a^{-1} and 1.0-54.1 t km^{-2} a^{-1}, respectively. The total rock weathering rate (TWR) for the whole SECRB is 35.3 ton km^{-2} a^{-1}, higher than the world average (24 ton km^{-2} a^{-1}, Gaillardet et al., 1999). The cationic silicate weathering rates (Cat_{sil}) ranges from 2.4 to 10.8 ton km^{-2} a^{-1} for the river watersheds in the SECRB, averaging at 6.0 ton km^{-2} a^{-1}. Furthermore, a good linear correlation (R^2 = 0.85, n = 28) is observed between the Cat_{sil} and runoff (Fig. 5), indicating silicate weathering rates is controlled by the runoff as documented in previous researches (e.g., Bluth and Kump, 1994; Gaillardet et al., 1999; Millot et al., 2002; Oliva et al., 2003; Wu et al., 2013; Pepin et al., 2013).

5.4 CO_2 consumption and the role of sulfuric acid

To calculate atmospheric CO_2 consumption by silicate weathering (CSW) and by carbonate weathering (CCW), a charge-balanced state between rock chemical weathering-derived alkalinity and cations was assumed (Roy et al., 1999).

$$[CO_2]_{CSW} = [HCO_3]_{CSW} = [Na]_{sil} + [K]_{sil} + 2[Ca]_{sil} + 2[Mg]_{sil} \quad (4)$$

$$[CO_2]_{CCW} = [HCO_3]_{CCW} = [Ca]_{carb} + [Mg]_{carb} \quad (5)$$

The calculated CO_2 consumption rates by chemical weathering for each river in SECRB are shown in Table 3. CO_2 consumption rates by carbonate and silicate weathering are from 11.6 to 550×10^3 mol km^{-2} a^{-1} (averaging at 166×10^3 mol km^{-2} a^{-1}) and from 67.1 to 417×10^3 mol km^{-2} a^{-1} (averaging at 214×10^3 mol km^{-2} a^{-1}) for major river catchments in the SECRB. The regional fluxes of CO_2 consumption by silicate and carbonate weathering is about 63.6×10^9 mol a^{-1} (0.76×10^{12} g C a^{-1}) and 50.4×10^9 mol a^{-1} (0.0.60×10^{12} g C a^{-1}) in the SECRB.

However, in addition to CO_2, H_2SO_4 is well documented as a significant proton provider in rock weathering process (Galy and France-Lanord, 1999; Karim and Veizer, 2000; Yoshimura et al., 2001; Han and Liu, 2004; Spence and Telmer, 2005; Lerman and Wu, 2006; Xu and Liu 2007; 2010). Sulfuric acid can be generated by natural oxidation of pyrite and anthropogenic emissions of SO_2 from coal combustion and subsequently dissolve carbonate and silicate minerals. The consumption of CO_2 by rock weathering would be overestimated if H_2SO_4 induced rock weathering is ignored (Spence and Telmer, 2005; Xu and Liu, 2010; Shin et al., 2011). Thus, the role of sulfuric acid on the chemical weathering is crucial for an accurate estimation of CO_2 consumption by rock weathering.

Rapid economic growth and increased energy command have result in severe air pollution problems in China, indicated by the high levels of mineral acids (predominately sulfuric) observed in precipitation (Lassen and Carmichael, 2000; Pan et al., 2013; Liu et al., 2016). The national SO_2 emissions in 2010 reached to 30.8 Tg/year (Lu et al., 2011). Previous study documented that fossil fuel combustion

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accounts for the dominant sulfur deposition (~77%) in China (Liu et al., 2016). Southeast coastal region is the most severe acid rain polluted region in China, with a volume-weighted mean value of pH lower than 4.5 for many years (Wang et al., 2000; Larssen and Carmichael, 2000; Zhao, 2004; Larssen et al., 2006). Current sulfur and nitrogen depositions in the Southeast coastal region are still among the highest in China (Fang et al., 2013; Cui et al., 2014; Liu et al., 2016).

The involvement of protons originating from H_2SO_4 in the river waters can be verified by the stoichiometry between cations and anions, shown in Fig. 6. In the rivers of the SECRB, the sum cations released by silicate and carbonate weathering were not balanced by either HCO_3^- or SO_4^{2-} (Fig. 6a), but were almost balanced by the sum of HCO_3^- and SO_4^{2-} (Fig. 6b). This implies that both H_2CO_3 and H_2SO_4 are the potential erosion agents in chemical weathering in the SECRB. The $\delta^{13}C$ values of the water samples show a wide range, from -11.0‰ to -24.3‰, with an average of -19.4‰. The $\delta^{13}C$ from soil is governed by the relative contribution from C_3 and C_4 plant (Das et al., 2005). The studied areas have subtropical temperatures and humidity, and thus C_3 processes are dominant. The $\delta^{13}C$ of soil CO_2 is derived primarily from $\delta^{13}C$ of organic material which typically has a value of -24 to -34‰, with an average of -28‰ (Faure, 1986). According to previous studies, the average value for C_3 trees and shrubs are from -24.4 to -30.5‰, and most of them are lower than -28‰ in south China (Chen et al., 2005; Xiang, 2006; Dou et al., 2013). After accounting for the isotopic effect from diffusion of CO_2 from soil, the resulting $\delta^{13}C$ (from the terrestrial C_3 plant process) should be ~ -25‰ (Cerling et al., 1991). This mean DIC derived from silicate weathering by carbonic acid (100% from soil CO_2) would yield a $\delta^{13}C$ value of -25‰. Carbonate rocks are generally derived from marine system and, typically, have $\delta^{13}C$ value close to zero. Thus, the theoretical $\delta^{13}C$ value of DIC derived from carbonate weathering by carbonic acid (50% from soil CO_2 and 50% from carbonate rocks) is -12.5‰. DIC derived from carbonate weathering by sulfuric acid are all from carbonate rocks, thus the $\delta^{13}C$ of the DIC would be 0‰. Based on these conclusions, sources of riverine DIC from different end-members in the SECRB were plotted in Fig. 7. Most water samples drift away from the three endmember mixing area (carbonate and silicate weathering by carbonic acid and carbonate weathering by sulfuric acid) and towards the silicate weathering by H_2SO_4 area, clearly illustrating the effect of sulfuric acid on silicate weathering.

Considering the H_2SO_4 effect on chemical weathering, CO_2 consumption by silicate weathering can be determined from the equation below (Moon et al., 2007; Ryu et al., 2008; Shin et al., 2011):

$$[CO_2]_{SSW} = [Na]_{sil} + [K]_{sil} + 2[Ca]_{sil} + 2[Mg]_{sil} - \gamma \times 2[SO_4]_{atmos} \quad (6)$$

Where γ is calculated by $cation_{sil}/(cation_{sil} + cation_{carb})$.

Based on the calculation in section 5.1, SO_4^{2-} in river waters were mainly derived from atmospheric input. Assuming sulfate in rivers derived from atmospheric input (after correction for sea-salt contribution) are all from acid precipitation, CO_2 consumption rates by silicate weathering (SSW) are estimated between 31.8×10^3 mol km^{-2} a^{-1} and 363×10^3 mol km^{-2} a^{-1} for major river watersheds in the SECRB. For the whole SECRB, the actual CO_2 consumption rates by silicate is 167×10^3 mol km^{-2} a^{-1}

when the effect of H_2SO_4 is considered. The flux of CO_2 consumption is overestimated by 15.8×10^9 mol a^{-1} (0.19×10^{12} g C a^{-1}) due to the involvement of sulfuric acid from acid precipitation, accounting for approximately 24.9% of total CO_2 consumption flux by silicate weathering in the SECRB. It highlights the fact that the drawdown of atmospheric CO_2 by silicate weathering can be significantly overestimated if acid deposition is ignored in short- and long-term perspectives. The result is important as it quantitatively shows that anthropogenic activities can significantly affect rock weathering and associated atmospheric CO_2 consumption. The quantification of this effect needs to be well evaluated in Asian and global scale within the current and future human activity background.

6. Conclusions

River waters in the Southeast coastal region of China are characterized by high proportions of Na^+, K^+ and dissolved SiO_2, indicating water chemistry of the rivers in the SECRB is mainly controlled by silicate weathering. The dissolved cationic loads of the rivers in the study area originate dominantly from silicate weathering, which accounts for 38.3% (10.7-74.0%) of the total cationic loads. Carbonate weathering, atmospheric and anthropogenic inputs account for 29.4% (3.9-62.0%), 14.4% (6.6-23.4%) and 17.8% (0-55.2%), respectively. Meanwhile, more than 70% of SO_4^{2-} in the rivers derived from atmospheric input. The chemical weathering rate of silicates and carbonates for the whole SECRB are estimated to be approximately 18.2 and 17.1 ton km^{-2} a^{-1}. About 10.1×10^6 t a^{-1} of dissolved solids originating from rock weathering are transported into the East and South China Sea by these rivers. With the

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assumption that all the protons involved in the weathering reaction are provided by carbonic acid, the CO_2 consumption rates by silicate and carbonate weathering are 222 and 176×10^3 mol km^{-2} a^{-1}, respectively. However, both water chemistry and carbon isotope data provide evidence that sulfuric acid from precipitation serves as a significant agent during chemical weathering. Considering the effect of sulfuric acid, the CO_2 consumption rate by silicate weathering for the SECRB are 167×10^3 mol km^{-2} a^{-1}. Therefore, the CO_2 consumption flux would be overestimated by 15.8×10^9 mol a^{-1} (0.19×10^{12} g C a^{-1}) in the SECRB if the effect of sulfuric acid is ignored. This work illustrates that anthropogenic disturbance by acid precipitation has profound impact on CO_2 sequestration by rock weathering.

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Table 1 Chemical and carbon isotopic compositions of river waters in the Southeast Coastal Rivers Basin (SECRB) of China.

Rivers	Sample number	Date (M/D/Y)	pH	T	EC	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	SiO_2	TZ+	TZ-	NICB	$\delta^{13}C$	TDS
				℃	μs cm^{-1}	μM	μM	μM	μM	μM	μM	μM	μM	μM	μM	μEq	μEq	%	‰	mg l^{-1}
Qiantang R.	1	07-8-10	7.42	28.78	190	347	197	106	473	12.0	303	62.6	147	1130	148	1703	1789	-5.0	-19.0	144
	2	07-9-10	7.60	23.84	146	87.5	204	80.9	496	11.7	75.2	124	121	907	156	1446	1348	6.7	-19.8	119
	3	07-9-10	7.37	27.83	308	555	233	208	698	41.8	312	223	437	1170	170	2601	2579	0.9	-17.8	204
	4	07-10-10	7.27	26.28	177	176	135	116	544	15.7	151	142	170	985	175	1632	1618	0.8	-19.3	135
	5	07-10-10	7.05	24.15	123	130	101	66.2	349	17.7	94.3	124	157	529	169	1061	1061	0.0	-18.7	91.2
	6	07-10-10	7.24	23.75	140	97.6	69.7	81.0	451	20.0	62.1	109	204	703	164	1231	1282	-4.2	-21.3	106.6
	7	07-11-10	7.40	23.23	107	92.5	70.5	68.3	327	14.9	74.9	104	147	486	156	954	960	-0.6	-21.0	82.2
	8	07-11-10	7.16	27.61	281	361	87.5	128	469	26.8	245	191	239	810	179	1642	1724	-5.0	-12.9	137.5
	9	07-11-10	7.02	26.48	140	275	120	60.7	319	36.2	199	150	180	437	236	1155	1146	0.8	-13.9	100.2
	10	07-12-10	7.05	24.24	99	205	114	58.3	285	14.6	191	114	132	305	278	1005	874	13.1	-20.9	85.4
	11	07-12-10	7.05	27.01	102	123	133	49.8	284	18.6	86.5	123	144	377	183	924	874	5.4	-19.2	79.4
	12	07-12-10	7.99	24.18	260	50.0	85.4	212	993	-	66.8	153	235	1822	172	2546	2512	1.4	-17.6	205.2
	13	07-12-10	7.86	24.59	231	43.5	88.4	189	859	-	55.1	97.6	169	1763	170	2228	2253	-1.1	-18.7	185.4
	14	07-12-10	7.69	22.66	131	44.1	81.0	113	458	-	19.1	95.2	107	920	143	1266	1248	1.4	-18.1	106.8
	15	07-12-10	7.65	24.48	106	61.1	98.3	87.9	335	-	37.2	68.3	112	663	164	1005	992	1.4	-18.6	87.3
	16	07-12-10	7.46	23.68	125	64.3	108	117	406	-	25.9	75.0	174	687	164	1218	1136	6.7	-20.0	98.8
	17	07-13-10	7.33	24.08	139	59.8	116	136	429	-	29.6	80.4	209	752	162	1305	1281	1.9	-20.8	108.1
	18	07-10-10	7.27	25.74	141	163	114	69.6	396	27.3	126	148	161	597	153	1209	1195	1.1	-21.0	101.0
Cao'e R.	19	07-16-10	7.17	22.27	108	212	86.3	69.4	183	5.1	151	148	114	384	216	803	912	-13.5	-21.2	79.1
	20	07-16-10	7.06	26.57	182	401	77.6	145	275	18.3	269	185	245	534	215	1318	1478	-12.2	-20.5	116.9
	21	07-16-10	7.14	27.26	171	333	91.3	164	362	18.1	224	194	207	658	225	1475	1490	-1.0	-20.9	123.3
	22	07-16-10	7.08	27.17	173	346	94.4	168	364	18.8	247	200	211	656	222	1506	1526	-1.3	-13.0	125.2
Ling R.	23	07-15-10	7.07	24.14	52	164	42.9	34.9	140	4.9	40.7	61.5	68.3	277	190	558	516	7.6	-12.8	52.1
	24	07-15-10	7.02	26.04	74	169	92.0	34.2	150	6.4	87.0	77.3	92.8	272	196	629	622	1.1	-20.8	59.5
	25	07-16-10	7.34	25.03	92	159	80.1	47.3	235	19.3	78.0	71.4	105	455	187	804	815	-1.4	-22.5	73.9
	26	07-16-10	7.40	26.75	113	216	77.8	57.1	249	20.2	133	90.0	115	494	196	905	946	-4.5	-12.7	82.8
	27	07-16-10	7.39	26	89	174	86.4	56.4	209	9.0	99.3	78.4	99.9	420	199	792	798	-0.8	-14.0	72.7
	28	07-15-10	6.79	22.33	75	159	82.7	44.1	143	-	107	61.8	83.4	306	144	616	641	-4.1	-21.1	56.5
	29	07-15-10	8.24	27.15	129	228	92.1	83.1	317	17.2	177	90.5	120	641	194	1120	1148	-2.5	-19.2	97.8
Ou R.	30	07-13-10	8.08	28.45	48	95.2	107	38.4	92.1	15.2	31.8	43.3	47.4	291	221	463	461	0.4	-21.7	50.6
	31	07-13-10	6.71	22.97	32	60.7	106	12.6	65.0	10.8	28.9	45.0	48.9	158	169	322	329	-2.2	-23.8	36.9
	32	07-13-10	7.18	27.59	73	107	127	36.2	175	4.3	57.1	111	92.0	283	210	655	634	3.2	-23.4	62.9
	33	07-13-10	6.94	24.2	44	76.9	112	20.0	99.1	10.9	27.9	63.1	58.6	249	184	427	457	-7.0	-22.5	47.5
	34	07-14-10	7.16	27.45	90	187	127	41.2	199.5	17.0	85.6	102	116	367	251	796	787	1.1	-22.4	76.5
	35	07-14-10	6.97	24.56	54	105	50.9	29.2	122	12.2	46.1	67.8	73.1	218	193	460	478	-4.1	-22.5	47.9
	36	07-14-10	6.82	21.12	31	76.4	133	12.7	74.5	7.7	20.7	36.8	49.1	192	162	383	348	9.3	-	39.5
	37	07-14-10	6.82	23.69	45	89.5	105	19.0	97.8	10.6	39.6	52.8	59.1	231	185	428	441	-3.0	-22.9	46.2
	38	07-15-10	6.92	24.69	37	100	89.3	21.1	49.7	1.7	36.9	45.5	52.7	153	202	331	341	-2.9	-	38.9
	39	07-15-10	6.90	23.86	35	92.2	92.0	19.8	61.4	1.9	43.9	47.9	55.5	139	193	347	342	1.4	-22.3	38.5
	40	07-15-10	7.09	25.56	47	117	112	25.7	83.4	8.0	52.4	63.1	57.4	232	193	447	462	-3.3	-22.5	48.1
	41	07-14-10	6.97	24.25	53	102	107	27.6	119	13.4	43.5	59.4	73.2	277	183	502	526	-4.9	-13.7	52.3

Feiyun R.	42	07-17-10	7.28	25.19	38	94.0	81.7	24.0	75.6	11.4	59.9	45.7	51.9	149	151	375	358	4.5	-	37.2
	43	07-17-10	7.08	25.61	46	101	79.9	33.9	93.4	4.6	66.2	55.1	52.8	223	151	435	450	-3.3	-23.7	43.5
Jiaoxi R.	44	07-17-10	7.52	26.92	47	116	81.5	25.2	92.0	4.1	73.3	80.3	25.0	226	151	432	430	0.5	-23.4	43.0
	45	07-17-10	7.45	27.46	61	152	90.2	34.2	119	-	136	59.8	53.5	238	184	548	542	1.2	-23.1	51.8
	46	07-18-10	6.90	27.66	53	127	88.1	33.4	94.4	7.0	123	93.1	30.4	209	177	471	486	-3.3	-14.4	47.4
Huotong R.	47	07-18-10	7.34	24	43	116	78.8	26.1	58.4	5.4	68.7	49.7	20.1	197	190	364	355	2.3	-22.8	39.6
Ao R.	48	07-19-10	7.24	31.44	124	294	121	102	209	24.3	204	73.6	52.0	717	370	1036	1100	-6.1	-19.4	105.4
	49	07-19-10	7.13	27.82	46	109	96.3	30.0	73.8	-	72.0	51.3	22.5	234	236	413	402	2.6	-	46.2
	50	07-18-10	6.98	28.65	53	140	88.4	40.8	100	3.0	82.9	58.6	20.9	294	233	511	477	6.6	-22.3	52.2
Min R.	51	07-27-10	7.11	28.4	42	116	92.0	40.5	119	18.0	43.9	35.5	26.0	382	182	526	513	2.4	-19.4	52.7
	52	07-27-10	7.17	30	51	102	97.9	41.7	107	4.6	29.4	45.3	35.0	350	221	496	495	0.2	-	53.3
	53	07-27-10	7.08	29.4	99	214	92.7	46.4	126	18.4	50.1	39.8	118	327	154	651	654	-0.4	-20.8	74.0
	54	07-27-10	7.06	29.1	44	107	99.6	28.1	114	16.4	18.7	36.4	44.3	305	265	491	449	8.5	-17.6	53.6
	55	07-27-10	7.42	29.4	57	139	93.7	49.8	113	3.1	67.1	56.3	26.6	384	236	558	561	-0.5	-16.4	58.6
	56	07-27-10	7.12	27.8	51	103	91.0	50.8	106	4.7	82.8	35.1	63.5	249	225	507	494	2.5	-	51.3
	57	07-27-10	7.08	27.5	40	125	45.0	36.8	107	12.1	43.6	44.5	29.3	288	211	457	435	5.0	-21.1	47.4
	58	07-27-10	6.99	27.2	52	121	98.0	42.4	115	16.7	87.1	36.6	70.9	277	228	535	542	-1.4	-11.4	55.3
	59	07-27-10	6.87	29	59	154	91.4	59.4	124	16.5	77.8	36.7	88.3	272	222	612	563	8.0	-20.3	57.2
	60	07-27-10	7.31	27.1	78	109	92.1	59.1	181	21.2	123	37.5	78.4	355	202	682	672	1.4	-18.7	63.1
	61	07-27-10	7.22	27.8	37	122	83.3	52.8	142	17.4	111	37.3	80.4	288	221	596	597	-0.2	-22.3	58.1
	62	07-27-10	7.16	28.1	58	104	83.3	59.3	163	24.0	34.6	34.5	118	294	214	632	599	5.2	-13.4	59.5
	63	07-27-10	7.26	28.3	87	139	86.1	60.9	191	14.8	48.0	93.0	109	347	226	729	707	3.0	-21.4	68.6
	64	07-27-10	7.00	28.8	87	127	93.1	58.7	195	6.6	59.8	81.1	60.9	480	232	729	743	-2.0	-11.0	74.0
	65	07-28-10	6.97	27.9	37	163	82.1	52.2	140	20.2	53.1	60.0	106	306	221	630	632	-0.2	-	61.9
	66	07-13-10	7.07	27.96	59	91.9	110	40.0	127	24.8	62.0	79.3	62.3	249	228	535	515	3.8	-	54.8
	67	07-28-10	7.12	29.7	38	108	93.4	45.9	133	12.4	48.3	34.0	56.6	368	220	560	564	-0.7	-	57.7
	68	07-27-10	7.03	29.9	62	128	96.7	57.6	148	23.3	81.6	36.8	74.1	374	203	635	641	-0.9	-12.4	61.7
	69	07-27-10	7.01	28.8	60	102	89.1	73.6	138	9.6	50.6	74.1	32.7	417	233	615	607	1.3	-21.0	62.3
	70	07-27-10	7.06	26.5	37	93.5	93.1	34.7	87.3	-	26.6	34.8	37.1	312	222	431	448	-3.9	-13.1	49.1
	71	07-27-10	7.09	26.5	25	62.6	92.7	27.0	61.5	4.7	21.5	18.6	43.4	191	154	332	318	4.2	-16.0	35.3
	72	07-28-10	7.07	30.1	39	76.3	87.9	35.1	87.6	7.4	43.1	36.6	35.5	266	175	409	416	-1.7	-19.4	43.5
	73	07-27-10	7.01	28.7	47	84.9	95.4	56.7	106	12.7	51.8	49.2	57.2	315	211	506	531	-4.8	-	53.8
	74	07-27-10	6.85	28.7	50	93.6	85.9	52.4	107	14.1	62.8	57.5	57.0	252	217	498	487	2.2	-19.9	50.9
	75	07-27-10	7.11	29.7	69	117	85.2	73.4	159	7.6	63.7	75.2	47.4	418	230	666	652	2.2	-22.2	65.0
	76	07-28-10	6.93	28.9	59	112	88.0	61.8	122	6.0	57.4	89.3	42.0	349	224	568	580	-2.2	-22.0	58.8
	77	07-21-10	7.76	32.4	51.2	163	85.5	52.8	151	20.2	55.3	70.3	78.6	372	175	656	655	0.3	-12.5	61.8
	78	07-28-10	7.29	26.8	106	129	75.3	84.0	321	24.0	56.2	41.0	166	599	202	1013	1028	-1.4	-16.3	90.3
	79	07-21-10	7.09	26.96	56	112	87.6	37.1	129	4.5	51.5	44.9	61.9	327	276	531	547	-2.9	-22.2	59.1
	80	07-21-10	7.64	33.37	83	114	96.2	60.6	151	16.7	53.0	40.6	102	371	242	633	670	-5.8	-12.8	66.2
	81	07-21-10	7.83	31.27	65	131	102	52.7	141	16.1	45.3	49.7	91.8	324	239	620	603	2.8	-13.4	61.8
	82	07-21-10	6.84	28.35	66	132	101	52.5	141	5.8	63.8	54.1	91.6	304	243	621	606	2.5	-22.7	61.5
	83	07-21-10	7.42	30.7	98	217	113	59.2	210	18.4	98.7	63.5	84.7	496	320	868	827	4.6	-18.9	84.5
	84	07-27-10	7.26	26.3	46	104	102	29.7	121	3.6	55.2	51.9	55.5	294	193	507	512	-0.9	-21.6	51.9
	85	07-27-10	7.07	25.4	30	73.3	99.2	19.6	78.8	-	22.9	40.0	49.2	203	170	369	365	1.3	-21.1	39.8
	86	07-27-10	7.50	27.3	45	102	102	26.5	114	2.4	35.1	39.7	57.2	260	217	484	449	7.3	-15.7	49.6
	87	07-27-10	7.47	26.9	51	141	100	43.6	109	7.9	79.7	42.4	57.7	311	217	547	548	-0.3	-20.1	55.6

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	88	07-19-10	7.99	31.74	63	167	96.5	33.5	115	8.0	105	35.5	38.1	331	218	561	548	2.3	-13.5	55.9
	89	07-21-10	6.77	28.19	65	132	93.6	56.0	145	15.6	60.6	78.8	75.4	333	243	627	624	0.5	-22.6	63.3
Jin R.	90	07-27-10	7.36	25.8	128	126	94.8	88.9	406	22.9	51.4	39.4	229	595	208	1211	1143	5.6	-20.7	100
	91	07-27-10	7.40	26.9	123	143	103	82.7	347	21.0	83.5	203	182	463	226	1105	1115	-0.9	-21.3	98.4
	92	07-27-10	7.00	27.4	88	170	98.8	56.8	205	7.2	137	117	106	327	205	793	792	0.1	-22.5	71.8
	93	07-27-10	7.32	28.7	73	201	116	87.1	318	20.0	93.5	41.5	189	508	267	1128	1020	9.6	-21.7	95.3
Jiulong R.	94	07-30-10	6.50	23.47	29	72.3	92.4	22.8	59.8	12.4	25.1	27.0	50.0	189	213	330	341	-3.4	-18.1	40.1
	95	07-30-10	7.06	29.35	120	136	96.9	106	339	5.1	67.7	66.3	249	469	202	1124	1100	2.1	-20.8	94.2
	96	07-30-10	7.45	27.6	104	79.5	97.5	106	363	14.4	70.7	50.0	99.9	729	184	1116	1049	6.0	-18.9	93.7
	97	07-31-10	7.36	26.59	139	140	100	142	432	15.5	79.6	78.3	274	573	196	1388	1278	8.0	-19.7	108.8
	98	07-31-10	7.72	26.18	88	77.6	96.2	69.0	313	19.9	39.7	34.6	63.8	731	251	938	933	0.5	-18.4	89.4
	99	07-30-10	7.43	26.96	119	200	93.8	100.2	298	19.9	122	80.5	225	387	202	1091	1040	4.7	-20.5	89.5
	100	07-28-10	7.41	26.66	112	173	97.9	94.4	286	46.1	118	152	201	364	207	1033	1036	-0.3	-20.9	92.2
	101	07-29-10	7.16	29.35	82	151	110	55.4	178	4.9	71.2	170	53.2	385	305	727	732	-0.7	-21.2	76.1
	102	07-29-10	7.10	28.9	100	222	98.3	49.4	249	3.6	126	157	52.7	532	303	917	920	-0.3	-21.7	90.0
	103	07-28-10	7.20	31.15	138	339	111	81.2	277	9.2	280	285	88.6	515	317	1165	1256	-7.8	-19.0	112
	104	07-28-10	7.16	27.09	101	261	95.8	81.7	235	40.3	173	80.1	174	291	136	990	892	9.9	-24.3	75.4
Zhang R.	105	07-28-10	8.08	30.6	93	195	96.1	61.1	167	16.8	157	193	55.2	281	288	748	741	0.9	-21.5	73.8
Dongxi R.	106	07-28-10	7.20	30.9	78	263	99.0	41.5	115	14.5	238	65.3	30.0	283	309	675	646	4.4	-20.8	66.7
Huangang R.	107	07-28-10	7.40	30.5	99	253	85.6	53.0	154	7.7	190	63.5	56.4	460	278	754	827	-9.6	-20.0	77.4
Han R.	108	07-31-10	7.31	27.1	68	136	61.5	45.2	195	16.1	37.7	45.3	93.7	345	218	678	615	9.2	-21.9	62.0
	109	07-30-10	7.38	26.94	88	116	103	63.6	265	6.4	53.4	72.2	84.9	584	244	876	879	-0.4	-20.4	83.7
	110	07-30-10	6.66	25.55	71	114	96.2	47.6	168	8.0	56.9	54.6	143	230	203	642	628	2.2	-17.9	59.7
	111	07-30-10	6.66	27.76	83	135	104	63.8	203	8.6	54.5	74.9	173	302	336	774	777	-0.4	-20.6	78.7
	112	07-30-10	7.31	30.81	56	168	74.0	39.1	118	13.5	62.9	44.4	81.4	237	245	556	507	8.8	-21.4	54.6
	113	07-31-10	7.28	28.73	98	137	99.3	85.6	270	9.2	88.8	59.1	118	565	233	948	949	-0.1	-19.7	86.6
	114	07-31-10	7.27	31.42	123	193	105	98.2	319	20.7	120	102	157	570	229	1132	1107	2.2	-19.7	98.2
	115	07-30-10	7.43	29.89	85	115	97.5	65.5	244	6.5	46.5	58.6	103	511	251	832	822	1.1	-20.8	79.3
	116	07-31-10	7.61	30.98	99	123	104	85.9	264	5.6	58.8	90.9	108	588	98	926	952	-2.9	-20.0	79.4
	117	07-31-10	7.31	29.96	93	151	103	78.1	250	15.4	68.0	99.1	173	379	233	909	891	1.9	-21.9	81.8
	118	07-31-10	7.35	28.4	2	233	84.2	101	323	12.8	84.0	101	203	460	229	1165	1051	9.8	-21.1	94.7
	119	07-31-10	7.67	30.38	93	136	87.8	73.6	231	16.4	64.6	94.4	184	382	226	834	909	-9.1	-20.8	80.5
Rong R.	120	07-30-10	7.57	31.83	68	193	79.1	50.3	146	16.4	192	84.0	31.5	344	309	664	683	-2.8	-20.3	65.8
	121	07-30-10	6.96	30.62	94	509	103	56.1	213	15.9	511	78.5	82.3	379	222	1150	1133	1.5	-20.0	94.4

Table 2 Chemical compositions of precipitation at different sites located within the studied area (in µmol/l and molar ratio).

Province	Location	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	NO_3/Cl	SO_4/Cl	K/Cl	Na/Cl	Ca/Cl	Mg/Cl	Reference
Zhejiang	Hangzhou	4.5	5.76	13.9	38.4	55	79.9	4.18	12.2	26	3.53	2.76	3.96	0.3	0.88	1.87	0.25	Xu et al., 2011
	Jinhua	4.54	9.05	8.51	31.2	47.6	81.1	4.73	6.27	24	1.73	3.67	5.59	0.56	0.74	2.81	0.2	Zhang et al., 2007
Fujian	Nanping	4.81	0.8	5.8	26.6	18.3	38	4.9	5.4	12.9	2.7	4.59	3.16	0.84	0.93	2.22	0.47	Cheng et al., 2011
	Fuzhou		5.26	21.4	24.9	48.5	78.1	4.1	2.61	32.7	1.25	1.16	2.26	0.19	0.12	1.53	0.06	Zhao, 2004
	Xiamen	4.57	15.3	23.7	22.1	31.3	37.7	3.58	36.1	21.5	4.94	0.93	1.32	0.15	1.52	0.91	0.21	Zhao, 2004
Average												2.62	3.26	0.41	0.84	1.87	0.24	

Table 3 Contribution of each reservoir, fluxes, chemical weathering and associated CO_2 consumption rates for the major rivers and their main tributaries in the SECRB.

Major river	Tributaries	Location	Discharge	Area	Runoff	Contribution (%)				Fluxes (10^6 ton a^{-1})		Weathering rate (ton $km^{-2}a^{-1}$)				CO_2 consumption rate (10^3 mol km^{-2} a^{-1})		
			10^9 m^3a^{-1}	10^3 km^2	mm a^{-1}	Rain	Anth.	Sil.	Carb.	SWF	CWF	Cat_{sil}[a]	SWR[b]	CWR[b]	TWR[b]	CSW[c]	CCW[c]	SSW[d]
Qiantang		Fuyang	33.6	38.32	877	9	14	23	54	0.51	1.33	5.2	13.3	34.8	48.0	171	352	150
	Fenshui	Tonglu	3.13	3.43	913	7	14	18	62	0.05	0.19	5.7	15.3	54.1	69.3	173	550	158
Cao'e		Shangyu	4.53	5.092	890	7	23	26	44	0.10	0.19	7.0	18.9	36.7	55.5	279	383	249
Ling		Linhai	5.4	6.613	817	9	22	24	45	0.09	0.17	4.7	14.2	26.1	40.3	167	267	143
Ou		Wenzhou	18.11	18.1	1001	20	6	56	18	0.32	0.12	6.6	17.6	6.5	24.0	235	66	148
	Songyang	Longli	2.03	1.995	1018	16	8	46	30	0.04	0.03	7.1	19.9	13.6	33.5	240	137	176
	Xiaoxi	Qingtian	3.98	3.405	1169	23	0	74	4	0.07	0.00	8.7	20.1	1.4	21.5	298	14	154
	Nanxi	Huangtian	2.85	2.49	1145	21	9	63	7	0.05	0.01	8.1	21.3	2.6	24.0	292	27	162
Jiaoxi		Saiqi	4.0	5.638	709	20	30	26	23	0.06	0.03	2.4	10.0	5.4	15.4	67	57	32
Huotong		Badu	1.804	2.244	804	22	18	54	5	0.03	0.00	4.0	13.2	1.0	14.2	147	12	62
Ao		Lianjiang	2.77	3.17	874	17	17	48	17	0.05	0.02	5.1	17.3	5.4	22.7	188	56	122
Min		Minhou	60.55	60.99	993	15	10	48	27	1.29	0.67	6.6	21.1	11.0	32.1	250	115	187
	Futun	Nanping	14.2	13.733	1034	15	14	49	22	0.29	0.13	7.0	20.8	9.4	30.2	268	100	195
	Shaxi	Qingzhou	11.16	11.793	946	13	9	42	36	0.23	0.19	6.1	19.3	15.8	35.1	230	162	182
	Jianxi	Daheng	16.4	16.396	1000	16	10	45	29	0.31	0.17	5.7	19.1	10.4	29.5	208	110	148
	Youxi	Youxikou	4.621	5.436	850	15	8	46	31	0.10	0.06	5.4	17.7	10.8	28.5	197	113	148
	Dazhangxi	Minhou	4.758	4.843	982	15	21	47	17	0.09	0.03	6.2	19.1	6.7	25.8	228	69	153
Jin		Nan'an	3.65	3.101	1177	9	10	40	41	0.09	0.11	10.8	29.6	34.4	64.0	417	351	363
	Dongxi	Honglai	1.4	1.917	730	12	22	28	38	0.02	0.03	3.8	12.7	14.3	27.0	126	146	99
Jiulong		Longhai	14.07	14.741	954	12	22	35	31	0.22	0.28	7.1	14.8	19.1	34.0	277	198	212
	Beixi	Shajian	9.28	9.64	963	13	14	28	45	0.17	0.26	5.8	17.8	27.2	45.0	211	281	168
	Xi'xi	Zhangzhou	3.657	3.74	978	10	32	25	33	0.09	0.09	6.6	25.2	25.3	50.5	236	260	186
Zhang		Yunxiao	1.01122	1.038	974	16	25	29	29	0.02	0.01	5.1	21.9	14.1	36.0	174	146	114
Dongxi		Zhao'an	0.958	1.127	850	16	41	26	17	0.02	0.01	4.0	19.8	7.0	26.8	129	74	64
Huanggang		Raoping	1.637	1.621	1010	15	30	34	21	0.04	0.02	6.0	22.8	11.1	33.9	227	115	145
Han		Chaozhou	25.4	30.112	844	16	7	38	39	0.51	0.51	5.4	16.8	16.9	33.7	206	174	155

Dingjiang	Chayang	11.5	11.802	974	17	6	46	32	0.32	0.18	7.2	26.9	15.4	42.3	275	158	201
Rong	Jieyang	3.11	4.408	706	10	55	11	24	0.05	0.07	2.6	12.0	14.8	26.8	67	152	46
Whole SECRB		270	287	939					5.23	4.90	6.0	18.2	17.1	35.3	222	176	167

[a] Cat_{sil} are calculated based on the sum of cations from silicate weathering.

[b] SWR, CWR and TWR represent silicate weathering rates (assuming all dissolved silica is derived from silicate weathering), carbonate weathering rates and total weathering rates, respectively.

[c] CO_2 consumption rate with assumption that all the protons involved in the weathering reaction are provided by carbonic acid.

[d] Estimated CO_2 consumption rate by silicate weathering when H_2SO_4 originating from acid precipitation is taken into account.

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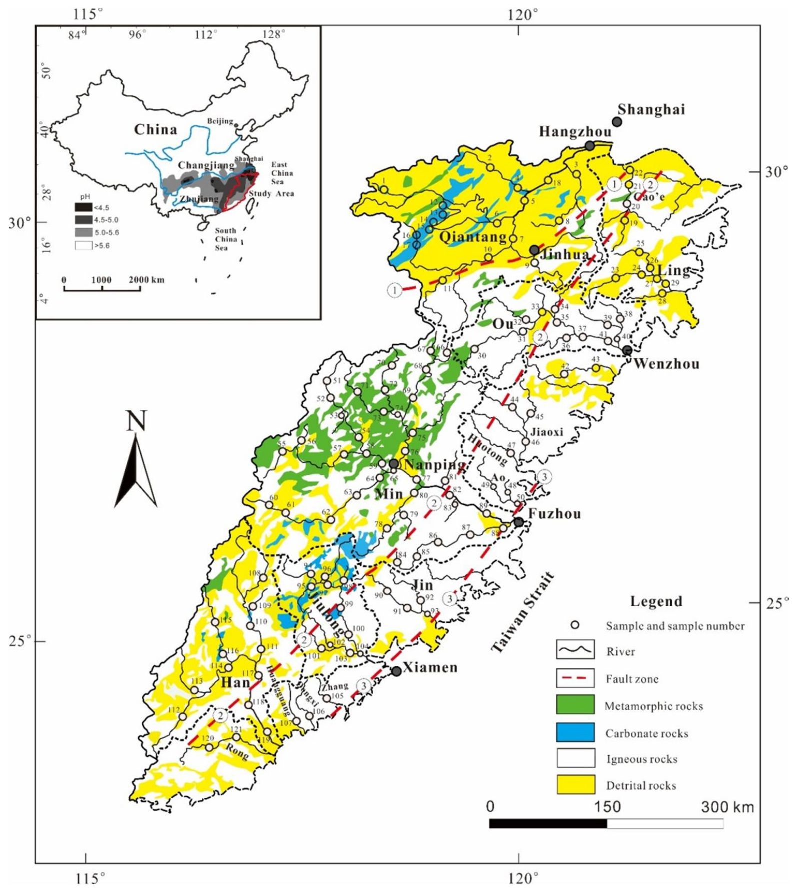

Fig. 1. Sketch map showing the lithology, sampling locations, and sample number of the SECRs drainage basin, and regional rain water pH ranges are shown in the sketch map at the upper-left. (modified from Zhou and Li, 2000; Shu et al., 2009; Xu et al., 2016, rain water acidity distribution of China mainland is from State Environmental Protection Administration of China). ①Shaoxing-Jiangshan fault zone; ②Zhenghe-Dapu fault zone; ③Changle-Nanao fault zone. The figure was created by CorelDraw software version 17.1.

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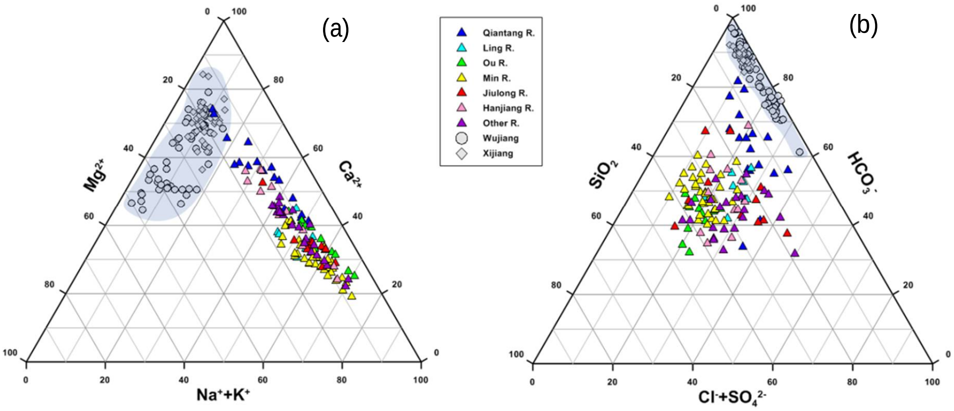

Fig. 2. Ternary diagrams showing cations (a), anions and dissolved SiO_2 (b) compositions of river waters in the SECRB. Chemical compositions from case studies of rivers draining carbonate rocks are also shown for comparison (data from Han and Liu 2004; Xu and Liu 2007, 2010)

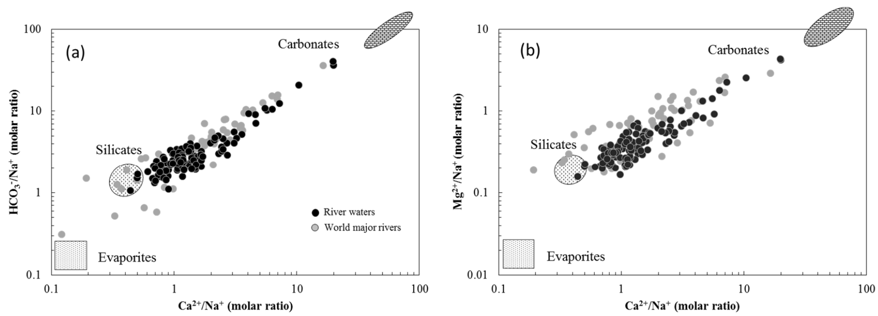

Fig. 3. Mixing diagrams using Na-normalized molar ratios: HCO_3^-/Na^+ *vs.* Ca^{2+}/Na^+ (a) and Mg^{2+}/Na^+ *vs.* Ca^{2+}/Na^+ (b) for the SECRB, showing a mixing line between silicate and carbonate end-members. Data for world major rivers are also plotted for comparison (data from Gaillardet et al. 1999).

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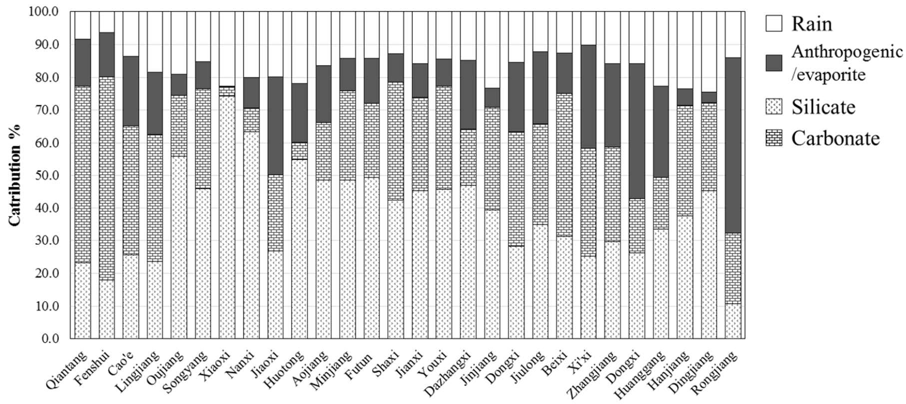

Fig. 4. Calculated contributions (in %) from the different reservoirs to the total cationic load for major rivers and their main tributaries in the SECRB. The cationic load is equal to the sum of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} from the different reservoirs.

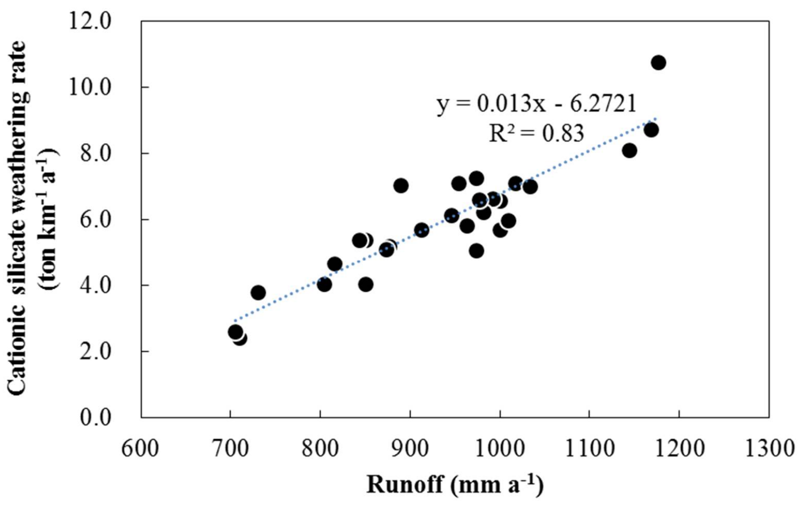

Fig. 5. Plots of the cationic-silicate weathering rate (Cat_{sil}) *vs.* runoff for the SECRB, showing that runoff has a strong control on chemical weathering rates of silicates.

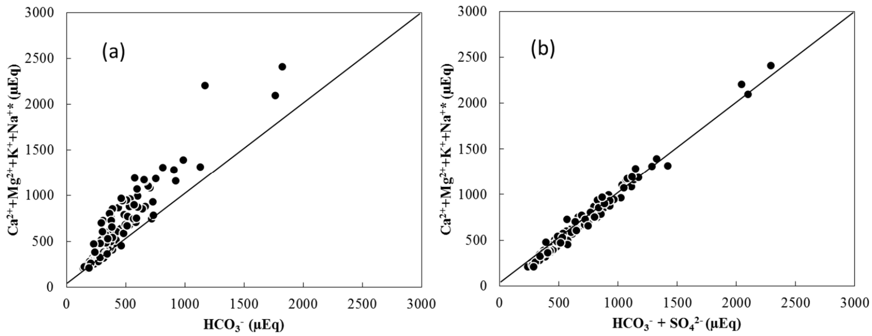

Fig. 6. Plots of total cations derived from carbonate and silicate weathering *vs.* HCO_3^- (a) and $HCO_3^-+SO_4^{2-}$ (b) for river waters in the SECRB.

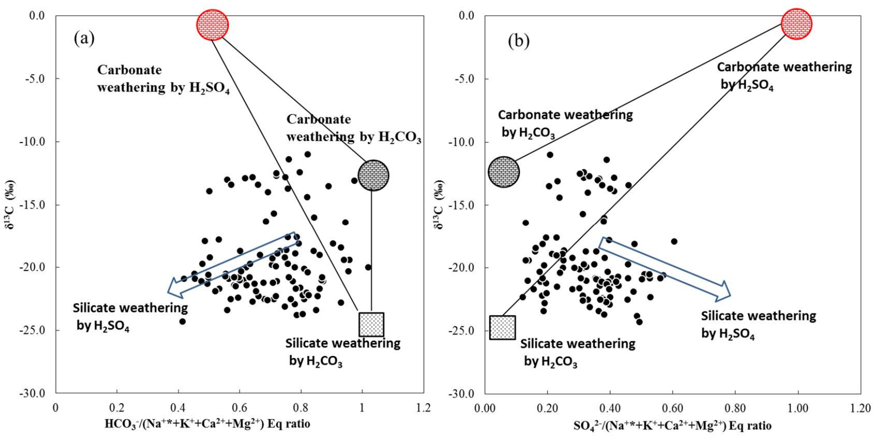

Fig. 7. $\delta^{13}C_{DIC}$ *vs.* $HCO_3/(Na^*+K+Ca+Mg)$ (a) and $SO_4/(Na^*+K+Ca+Mg)$ Eq ratio (b) in river waters draining the SECRB. The plot show that most waters deviate from the three endmember mixing area (carbonate weathering by carbonic acid and sulfuric acid and silicate weathering by carboinic acid), illustrating the effect of sulfuric acid on silicate weathering.