**Reply to interactive comments on "Temporary and net sinks of atmospheric $CO_2$ due to chemical weathering in subtropical catchment with mixing carbonate and silicate lithology" (bg-2019-310)**

**Responses to Anonymous Referee #2:**

Thank you for your time and sincere evaluation for our manuscript. Thank you very much for your constructive comments, and they are very useful for improving our manuscript. We have revised the manuscript according to the suggestions and comments, and the responses to questions one by one are as follows.

**Question 1**: I understand that the authors have collected abundant data in different sampling stations and seasons. However, I have serious concerns over the description of the data and calculation methods. For example, the mass and chemical parameters of rainwater are not provided, and I couldn't assess the results.

**Answer 1:** Thank you very much for your suggestion about data of rainwater. We attach the major ions concentrations of rainwater in Table S1 in the supplementary material in the lines 139-140 and lines 799-800. We also present the data of rainwater here.

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

**Question 2**: There are no information about analytical errors.

**Answer 2:** Thank you very much for your suggestion. Reference, blank and replicate samples were employed to check the accuracy of all the analysis and the relative standard deviations of all the analysis were within ±5%. The ionic charge balance defined by the equation of $\frac{meq(sum\ of\ cations)-meq(sum\ of\ anions)}{meq(sum\ of\ cations\ and\ anions)}$ of the water samples was less than 5%. The modified part was in the lines 125-131.

**Question 3**: The authors seem to confuse alkalinity, DIC, and [$HCO_3^-$], which have totally different definitions (although I understand that these parameters are similar at pH 8 in the river waters, $HCO_3^-$ is the main topic of this paper and the authors should calculate and explain accurately).

**Answer 3:** Thank you very much for your question. The definitions of alkalinity, DIC, and [$HCO_3^-$] are different. The alkalinity describes the acid neutralizing capacity. It is determined by titrating with acid down to a pH of about 4.5. Equal to the concentrations of [$HCO_3^-$]+2[$CO_3^{2-}$] (mmol/L) in most samples. DIC is the abbreviation of the dissolved inorganic carbon and is defined as the sum of [$CO_2$] + [$HCO_3^-$]+[$CO_3^{2-}$] in water samples. In this study the alkalinity is determined by titration in situ.

The DIC which is defined as the sum of [$CO_2$]+ [$HCO_3^-$]+[$CO_3^{2-}$] can be calculated by using the [$HCO_3^-$], water temperature (T) and pH measured in the field according to the equation as follows:

$$H_2CO_3^*\leftrightarrow H^++HCO_3^-$$

$$HCO_3^-\leftrightarrow 2H^++CO_3^{2-}$$

$$K_1=\frac{[H^+]\times[HCO_3^-]}{[H_2CO_3^*]}=10^{(-1.1\times10^{-4}\times T^2-0.012T-6.58)}$$

$$K_2=\frac{[H^+]\times[CO_3^{2-}]}{[HCO_3^-]}=10^{(-9\times10^{-5}\times T^2+0.0137T-10.62)}$$

In addition, for all the samples, the pH values ranged from 7.5 to 8.5 with an average of 8.05. Under this pH conditions, the major species of DIC is $HCO_3^-$ (Fig.C1). Based on our calculation, $H_2CO_3$* and $CO_3^{2-}$ only account for less than 5% in all sampling sites, so we use the concentrations of $HCO_3^-$ (mmol/L) to represent the DIC in this study.

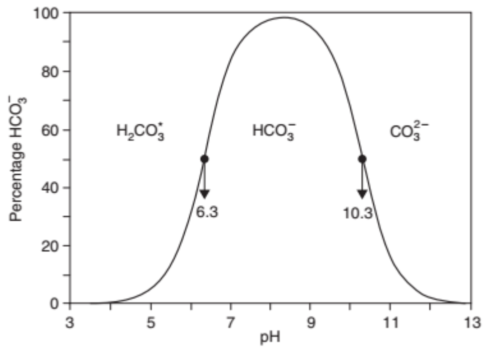


Fig.C1 Percentage of $HCO^{3-}$ of total dissolved carbonate as function of pH (Appelo and Postma, 2004)

**Question 4**: Are the chemical parameters of the river (and relevant calculation results) weighted average over 12 months?

**Answer 4:** Thank you very much for your question. In this study, the chemical parameters of river water in Table 1 in the paper were the flow-weighted average over 12 months. For every sampling station, the flow-weighted average of ion concentration can be expressed as followed equation:

$$[X]_{avarage}=\frac{\sum_{i=1}^{n=12}[X]_i\times Q_i}{\sum_{i=1}^{n=12}Q_i}$$

Where [*X*] is denotes the elements of the elements of $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ in mmol·$L^{-1}$. Q denotes average monthly discharge in $m^3\cdot s^{-1}$. The subscripts i denotes 12 moths from January to December. Also, we add this information in the lines 266-271 in the manuscript. For the relevant calculation results, we did the calculations using month data and sum the month results to obtain the year result by equation (15), (16) and (17) in the lines 181-184 in the manuscript.

**Question 5**: What kind of methods do the authors use to calculate the area of silicate/carbonate outcrops or river water discharge?

**Answer 5:** Thank you very much for your question. The area of silicate/carbonate outcrops was calculated by hydrological module of ArcGIS based on geology map from provided by China Geological Survey. The data of river water discharge was provided by the local hydrology bureau. The information has been added in the lines 255-258.

**Question 6**: The background of this study is unclear, and the authors should provide more basic information. What is "hyperactive region"?

**Answer 6:** Thank you for your question.

(1) Explanation of background: As described in the Introduction, from the view of the global carbon cycle, the $CO_2$ consumption due to carbonate weathering is recognized the “temporary” sink, while the consumption of $CO_2$ during the chemical weathering of silicate rocks has been regard as the net sink of $CO_2$ and regulates the global carbon cycle. Thus in carbonate-silicate mixing catchment, it is essential to distinguish proportions of the two most important lithological groups, i.e., carbonates and silicates, and evaluate the net $CO_2$ sink due to chemical weathering of silicate. In addition to the chemical weathering induced by $H_2CO_3$, sulfuric acid ($H_2SO_4$) of anthropogenic origins produced by sulfide oxidation such as acid deposition caused by fossil fuel

burning and acid mining discharge (AMD) also becomes an important chemical weathering agent in the catchment scale. Depending on the fate of sulfate in the oceans, sulfide oxidation coupled with carbonate dissolution could facilitate a release of $CO_2$ to the atmosphere, the carbonate weathering by $H_2SO_4$ (sulfide oxidation) plays a very important role in quantifying and validating the ultimate $CO_2$ consumption rate. Thus, under the influence of human activities, the combination of silicate weathering by $H_2CO_3$ and carbonate weathering by $H_2SO_4$ controlled the net sink of atmospheric $CO_2$.

The Pearl River includes three principal rivers: the Xijiang, Beijiang, and Dongjiang Rivers. The three river basins have distinct geological conditions. The Xijiang River is characterized as the carbonate-dominated area and the Dongjiang River has silicate as the main rock type. While the Beijiang River, which is the second largest tributary of the Pearl River, is characterized as a typical carbonate-silicate mixing basin. In addition, as the serve acid deposition and active mining area, chemical weathering induced by sulfuric acid make the temporary and net sink of atmospheric $CO_2$ to be reevaluated. These two points make the study area is representative.

(2) About the “hyperactive region”

According to the work of (Meybeck et al., 2006), the global coastal catchments were classified into eight classes based on the yields of riverine material by the COSCAT data set. In order to facilitate the visualization, mapping and comparison of river fluxes for any given material, the authors normalize all yields (Yi) to their global average (Y*). If the values of normalized yields Yi/Y* is between 5 and 10, the catchment is called the “hyperactive region”. Based on the calculation (Meybeck et al., 2006), the Pearl River is the “hyperactive region”.

**Question 7**: I recognize that Beijiang River is a major tributary of the Pearl River, but this river is relatively small compared to other world major river such as Amazon or Changjiang River. How does this river contribute the global carbon cycle?

**Answer 7:** Thank you very much for your question. Although the Beijiang River is not as large as Amazon or Changjiang River, the study of chemical weathering and CO2 sink in the Beijiang River can represent the carbon source and sink of such a river basin to some extents. In addition, the information of chemical weathering and $CO_2$ sink in the Beijiang River can also provide scientific evidence for global carbon cycle. The reasons why we chose the Beijiang River for our study area are that (1) The Beijiang River is characterized as a typical carbonate-silicate mixing basin, however, little study investigated chemical weathering and $CO_2$ sink in such a mixing basin which has a different mechanism of chemical weathering compared to river basins with a simple lithology (carbonate or silicate dominant). (2) The Beijiang River is located in the subtropical area in South China, the warm and wet climatic conditions make the Beijiang River a hyperactive region in China. Water discharge and chemical weathering is highly seasonal due to the warm and humid summer monsoon and the cool and dry winter monsoon. (3) The Beijiang River is the second largest tributary of the Pearl River, and it covers a basin of 52 068 $km^2$. The study of chemical weathering and $CO_2$ sink of the Beijiang River Basin is a supplement to the study of carbon cycle of the Pearl River which is the second largest river in China in terms of discharge volume.

**Question 8**: In addition, I have no idea why the authors compared total chemical weathering rate with latitude.

**Answer 8:** Thank you very much for your question. Based on the work of (Meybeck et al., 2006) and other researchers, the chemical weathering rate shows significant spatial trend. Generally it is found that the riverine output of materials is large in the low latitude area due to large runoffs (Fig.C2). So in this study, we compared total chemical weathering rate with latitude to give further evidence to support the conclusion.

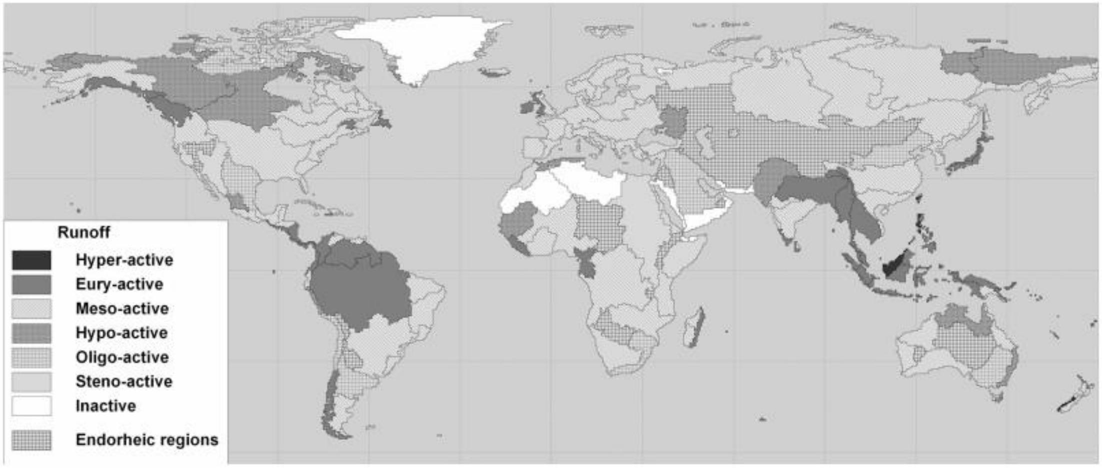


Fig.C2 Relative runoff for COSCATs related to mean annual runoff for the exorheic realm (Meybeck et al., 2006)

**Question 9**: Furthermore, there are also some previous studies about the Pearl River and its tributaries, some of which have already taken into consideration anthropogenic weathering in some way. Do the author's HCO3−-basis calculation methods and their results make a difference?

**Answer 9:** Thank you very much for your question. Based on our calculation method, the results in this study have compared with other Chinese rivers, as well as the Xijiang River which is the largest tributary of the Pearl River (see Lines 486-492 in Section 5.2.2). The total of $CO_2$ consumption rates CCR was $823.41\times10^3$ mol $km^{-2}$ $a^{-1}$ in the Beijiang River and was $960\times10^3$ mol $km^{-2}$ $a^{-1}$ in the Xijiang River. The total of $CO_2$ consumption rates in our study area showed little lower than that in the Xijiang River of the previous study.

In addition, some previous studies calculated the DIC apportionment based on the carbon isotope of DIC, however, our study calculated the DIC apportionment based on mass balance and $HCO_3^-$ concentration, the difference of these two methods will discuss in our other paper. Actually, this manuscript is focused on (1) the chemical weathering rate and the controlling factors on chemical weathering processes, and (2) the temporary sink of $CO_2$ and the influence of sulfide oxidation on net sink of CO2 by DIC apportionment procedure. Thank you very much for your attention to our studies, we hope our study can provide further information for global carbon cycle studies.

**Question 10**: I think the last section in discussion is too descriptive. I also have a concern that temporary and net sink of CO2 show large spatial variations, but in the discussion, the authors mentioned these values only in the SJs station (lowermost part).

**Answer 10:** Thank you very much for your suggestion. Actually, SJs station is the lowest station of the Beijiang River, which can represent the temporary and net sink of $CO_2$ of the whole river basin. 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. 1a), while the $SO_4^{2-}$ have negative correlation with the $CO_2$ net sink (Fig. 1b). It proved that human activities (sulfur acid deposition and AMD) dramatically decreased the $CO_2$ net sink and even make chemical weathering a $CO_2$ source to the atmosphere. We have added this part in the lines 521-524.

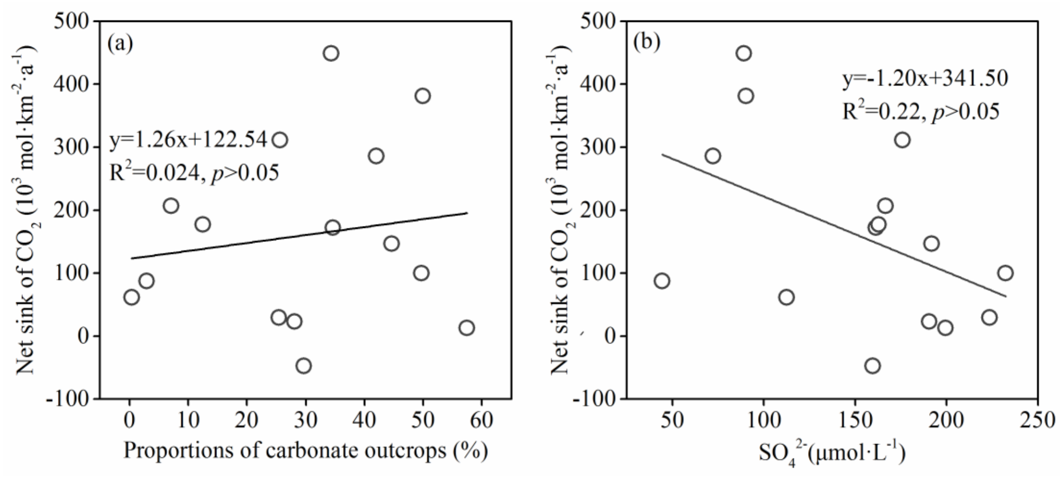


**Fig. 1 Correlations between $CO_2$ net sinks and proportions of proportions of carbonate (a) and correlations between $CO_2$ net sinks and $SO_4^{2-}$ (b)**

**Question 11**: As shown in equation (21), silicate weathering by sulfuric acid does not affect the concentrations of $HCO_3^-$ in the river. However, in equation (23) and (24), $[SO_4^{2-}]$ssw seemed to be described as αCSW×αSCW /αCCW × $[HCO_3^-]$riv. Would you please explain this calculation?

**Answer 11:** Thank you very much for your question. Firstly, we are very sorry for that there are two equations numbered (23). We have changed numbers in the revision manuscript. In other to explain clearly for this question, we present some of equations as followed.

$$\mathrm{CCW:}(\mathrm{Ca}_{2-x}\mathrm{Mg}_x)(\mathrm{CO}_3)_2 + 2\mathrm{H}_2\mathrm{CO}_3 \rightarrow (2-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+} + 4\mathrm{HCO}_3^- \quad (18)$$

$$\mathrm{SCW:}(\mathrm{Ca}_{2-x}\mathrm{Mg}_x)(\mathrm{CO}_3)_2 + \mathrm{H}_2\mathrm{SO}_4 \rightarrow (2-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+} + 2\mathrm{HCO}_3^- + \mathrm{SO}_4^{2-} \quad (19)$$

$$\mathrm{CSW:CaSiO}_3 + 2\mathrm{H}_2\mathrm{CO}_3 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Ca}^{2+} + \mathrm{H}_4\mathrm{SiO}_4 + 2\mathrm{HCO}_3^- \quad (20)$$

$$\mathrm{SSW:CaSiO}_3 + \mathrm{H}_2\mathrm{SO}_4 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Ca}^{2+} + \mathrm{H}_4\mathrm{SiO}_4 + \mathrm{SO}_4^{2-} \quad (21)$$

Where $CaSiO_3$ represents an arbitrary silicate.

(1) If we do not use the equation (22) and (23) as followed, just two equations (24) and (26) can get based on mass balance, however, we have three unknowns ($\alpha_{CCW}$， $\alpha_{SCW}$ and $\alpha_{CSW}$). Thus, we have a hypothesis, according to the studies of (Galy and France-Lanord, 1999) and (Spence

and Telmer, 2005), carbonate and silicate weathering by carbonic acid in the same ratio as carbonate and silicate weathering by sulfuric acid, the mass balance equations are followed:

$$[SO_4^{2-}]_{riv} - [SO_4^{2-}]_{pre} = [SO_4^{2-}]_{SCW} + [SO_4^{2-}]_{SSW} \quad (22)$$

$$[SO_4^{2-}]_{riv} - [SO_4^{2-}]_{pre} = \alpha_{SCW} \times [HCO_3^-]_{riv} \times 0.5 + \frac{\alpha_{CSW} \times \alpha_{SCW}}{\alpha_{CCW}} \times [HCO_3^-]_{riv} \quad (23)$$

Where the subscripts CCW, SCW, CSW and SSW denotes the four end-members defined by carbonate weathering by carbonic acid, carbonate weathering by sulfuric acid, silicate weathering by carbonic acid and silicate weathering by sulfuric acid, respectively. The parameter α denotes the proportion of DIC derived from each end-member processes.

(2) According to the above equations (22) and (23), we can get a further equation (25) as followed.

$$[Ca^{2+}]_{car} + [Mg^{2+}]_{car} = \alpha_{CCW} \times [HCO_3^-]_{riv} \times 0.5 + \alpha_{SCW} \times [HCO_3^-]_{riv} \quad (24)$$

$$[SO_4^{2-}]_{SCW} + [SO_4^{2-}]_{SSW} = \alpha_{SCW} \times [HCO_3^-]_{riv} \times 0.5 + \frac{\alpha_{CSW} \times \alpha_{SCW}}{\alpha_{CCW}} \times [HCO_3^-]_{riv} \quad (25)$$

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

(3) Combing the equations (24), (25) and (26), the proportions of $HCO_3^-$ derived from three end-members (CCW, SCW and CSW) can be calculated, and the DIC (equivalent to $HCO_3^-$) fluxes by different chemical weathering processes are calculated by following equations.

$$DIC_{CCW} = \alpha_{CCW} \times [HCO_3^-]_{riv} \quad (27)$$

$$DIC_{SCW} = \alpha_{SCW} \times [HCO_3^-]_{riv} \quad (28)$$

$$DIC_{CSW} = \alpha_{CSW} \times [HCO_3^-]_{riv} \quad (29)$$

**Reference:**

Appelo, C.A.J., Postma, D., 2004. Geochemistry, groundwater and pollution. CRC press.

Meybeck, M., Dürr, H.H., Vörösmarty, C.J., 2006. Global coastal segmentation and its river catchment contributors: A new look at land - ocean linkage. Global Biogeochemical Cycles, 20(1).