

## RC1:

Comments from Referees:

The Ms explored chemical weathering drawdown  $\text{CO}_2$  rates, major ion sources, and contribution of anthropogenic acids in the chemical weathering in a most severe acid rain impacted region, China. This is interesting, and the Ms is well structured and well written overall. The Ms could be improved with consideration as follows.

1. The field trip was conducted in the high-flow period. Whether is one hydrological sampling representative or can it represent a hydrological year, which must be explicated.

Author's response:

The river water of the southeast coastal rivers is mainly recharged by rain, and the amount of precipitation in high-flow season accounts for more than 70% of the annual precipitation in the area. During the high-flow season, the abundant water recharging facilitates the weathering product entering river system. However, during the low-flow period, the ground water contribution to the surface water might be greater and overprint the weathering information in river system, which would bring more inaccuracies to the weathering and  $\text{CO}_2$  consumption estimation. Therefore, it could be more representative to investigate the rock weathering during the high-flow season in the subtropical monsoon climate watersheds in this study. Indeed, more detailed time series investigation of water chemistry would help to constrain the weathering flux and explore the mechanism aspects, which would be the direction of our further work.

2. Alkalinity is titrated using HCl, while in the dataset of Table there is no alkalinity. I guess that the  $\text{HCO}_3^-$  is from Alk, is it right? If yes, please demonstrate how to calculate the  $\text{HCO}_3^-$ .

Author's response:

The content of  $\text{HCO}_3^-$  was calculated. Alkalinity was determined by phenolphthalein and methyl orange end point titration with dilute HCl. The HCl consumption volumes for phenolphthalein and methyl orange end point titration were used to calculate the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . Actually, there were little phenolphthalein alkalinity for all the samples (i.e. the HCl consumption volume for phenolphthalein end point titration were almost zero). The method was given in the Sampling and analytical method section in the revised version.

3. Authors referred many studies of rock chemical weathering, while several studies in Asia, such as Han River in the Yangtze and Mekong River in the Southeast Asian were ignored.

Author's response:

According to the RC, we have cited these studies in the attached revision in both introduction and discussion sections in the revised MS.

4. Authors should inform the extent of CO<sub>2</sub> consumption rate in this study in contrast to the world rivers, particularly Asian rivers and highly-impacted rivers.

Author's response:

According to the RC, we have compared the CO<sub>2</sub> consumption rates of SECRB to the major rivers in the world and Asian. Please find it in Lines 377-391 in the attached revision in the supplement.

5. I have noted that the references is mostly old, some new citations should be included.

Author's response:

We have added recent studies in both the introduction and the discussion sections in the revised version.

6. L 65 Change stronger to intense

Author's response:

It is revised in the revision.

7. L 138 How many samples?

Author's response:

We have added the number of samples in the revision.

8. L232-L233 Very high proportion of SO<sub>4</sub> and NO<sub>3</sub> is from atmosphere, if correct, does it mean the estimated CO<sub>2</sub> consumption rate is still overestimated because of contribution of HNO<sub>3</sub>?

Author's response:

Yes, we do think the N deposition also plays a role in rock weathering and have impacts on CO<sub>2</sub> consumption. However, the sources of NO<sub>3</sub><sup>-</sup> in river waters are complicated, e.g. atmospheric deposition, fertilizer, industry and urban waste water, as well as nitrification and denitrification. Although it is difficult to determine the origin of nitrate in river waters, we can at least assume that nitrate from acid deposition is one of the providers of protons. We added the discussions about the effect of HNO<sub>3</sub> in section 5.4, and recalculated the CO<sub>2</sub> consumption in the SCERB in the revision.

9. L393-394 Please could you supply the chemical equations for these weathering by HCO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or both HCO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. This will be helpful for readers to quantify the end-members.

Author's response:

The chemical equations for carbonate and silicate weathering by  $\text{HCO}_3^-$  and  $\text{H}_2\text{SO}_4$  have been repetitively mentioned in many previous basin scale weathering studies (e.g. Li et al., 2008; Spence, and Telmer, 2005; Chetelat et al., 2008; Xu and Liu, 2010). In addition, we discussed the  $\delta^{13}\text{C}$  isotopic composition of the end-members in lines 435-441 in the attached revision. For the condensing of the whole manuscript, we did not provide the chemical equations for carbonate and silicate weathering by  $\text{HCO}_3^-$  and  $\text{H}_2\text{SO}_4$ .

10. L477 No year for this citation

Author's response:

The year is at the end of the citation.

11. Fig. 5. Please add p value

Author's response:

We have added p value ( $p < 0.01$ ) in Fig. 5 in the attached revision.

## **RC2:**

Comments from Referees:

This study estimated the chemical weathering rates and atmospheric  $\text{CO}_2$  consumption rates in the coastal catchments of SE China, based on the chemistry and isotopes of dissolved inorganic carbon in the coastal rivers. The most important finding of this work is the sulfuric acid plays an unignored role in chemical weathering of carbonate and silicate rocks, which has to be more carefully considered in the calculation of weathering rates and carbon cycling in the catchments where strong human activities occur. Overall, the paper was well organized and structured, and the major research conclusion will increase our better understanding of weathering process in river catchments. I basically agree with the major research findings of these study based on the high data quality and interpretation. My minor concern is about the influence of extreme climate events on weathering processes. As some studies suggest, the SE China is subject to strong typhoon impact every year, which could significantly alter the river water chemistry and probably weathering process in the catchments during typhoon season. This impact could not be ignored in the discussion part.

Author's response:

Yes, extreme climate events do have impacts on weathering processes, especially the geochemistry signals of river water. The impact could be generally temporal and regional. In the sampling period, typhoon "Chanthu" have landed on Guangdong province in July 22, 2010. However its major impacting area is Guangdong, Guangxi

and Yunnan province, which are relatively far away from our study basins. So, extreme climate events are not considered in this study. To be more cautious, during the period of public discussion, we successfully applied for the open access to the Annual Hydrological Report P. R. China and have got more detailed data from different hydrology observation sites to get a more accurate estimation of weathering and CO<sub>2</sub> consumption fluxes.

More specific comments and suggestions:

1) L97-100: How did you define the sizes (small, medium, large) of these different rivers in SE China? Based on their catchment areas, lengths or riverwater and sediment discharges?

Author's response:

The sizes of the rivers are based on the length and the drainage area. We have added this information in the Natural setting of study area section in the revision.

2) On River settings: I suggest this part should include the mean water (and sediment) discharges of these rivers investigated.

Author's response:

As there are many rivers, we did not provide the discharge data one by one in the main text. For the condensing of the MS, the discharge and basin area information are provided in table 3 in the revision.

3) L109: Data source?

Author's response:

It is calculated by the population and the administrative area of these three provinces.

4) L126: No influence of the Pacific Plate?

Author's response:

After more investigation of the regional tectonic background, we have added Pacific plate in the introduction of Yanshanian granitic rocks formation collision events. It is the result of multiple collision events between Cathaysia, Yangtze blocks and Pacific plate.

5) L141-142: To my knowledge, the estuaries and lower reaches of most of these river studied are subject to strong tidal influence. Based on the sampling locations on the map of Figure 1, it seems that some river water samples were taken much closer to the river mouths. Please make sure that all these samples were not influenced by tidal pumped sea water, or you have some special method to correct this kind of influence.

Author's response:

Yes, the estuary samples might be affected by seawater. To avoid this, first, we selected the sampling sites carefully to make it as far as possible from the tidal impacted area and also we avoid sampling during tidal period. In addition, we double checked the salinity and water chemistry data to rule out the samples might be contaminated by seawater.

6) L177: change to “Compared”

Author's response:

It is modified in the revision.

7) L181-182: Where are these rivers located?

Author's response:

The locations of the rivers are given in the attached revision.

8) L248-249: Considering the sizes of these rivers investigated, it may be more reasonable to compare them with those small- or medium-sized river systems.

Author's response:

Data from Gaillardet et al. (1999) are cited here as global typical end-members and variation trend, to put the SECRB in a big picture instead of comparison. To avoid misunderstandings, “for comparison” was removed in the revision.

9) L271: Do you mean the source rock types? To my knowledge, the tectonic settings of these rivers are much different. The climate regimes and anthropogenic activities as well are also much variable among these river catchments.

Author's response:

Yes, we have modified ‘geological’ to ‘lithological’ to avoid misunderstanding in the attached revision.

10) L322-324: What are the major reasons for the different silicate weathering rates observed in these river catchments? If the monsoon climate dominates the weathering process, the Xijiang in the southernmost should have the highest silicate weathering rates while the Huanghe in the northernmost has the lowest?

Author's response:

Silicate weathering are complicated and affected by lithological setting, temperature and precipitation, etc. Silicate weathering rates in southeast coastal area is higher than the Xijiang and Huanghe but lower than Changjiang basin, which is the complicated results of silicate dominated bedrock (compared with Xijiang), high MAT and high runoff (compared with Huanghe and Changjiang basin). We have added some discussion with rivers in China and around the world in the following section (5.4

CO<sub>2</sub> consumption and the role of sulfuric acid) in the revision.

11) L401-402: How about the influence of seawater intrusion into the lower reaches of these rivers?

Author's response:

The sampling sites in the lower reaches are selected carefully: as far as possible to the estuaries to avoid the contamination of seawater. In addition, we carefully checked the salinity and water chemistry data before drafting the manuscript. The easily contaminated ions by seawater such as Cl<sup>-</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in the lower reach samples are in the normal range of fresh water.

12) On the spelling of river names: It always should keep in consistence in the text, figures and tables, e.g. Min, Jin, Han, Jiulong rivers, not “Minjiang, Jinjiang, Hanjiang”

Author's response:

We have improved this through the MS in the revision.

13) Table 1: The full names of TZ, EC, NICB and TDS should be given with the table. It's better to include the localities of these riverwater samples.

Author's response:

We have added the full names of TZ, EC, NICB and TDS in table1. The localities of the samples were given in Fig. 1. Pls find them in the attached revision. For the condensing of the table, we did not include the longitude and latitude information in it.

14) Table 3: Sources of riverwater discharges and runoff?

Author's response:

The data of basin area and annual discharge are from Annual Hydrological Report P. R. China, 2010, vol (7). The runoff was calculated by annual discharge and basin area. We have added the information in the revision.

15) Figure 1: You'd better to mark the major names of rivers, and geographic localities, and tectonic units you mentioned in the text, e.g. Huanghe, Cathaysia and Yangtze blocks, Zhejiang and Fujian Provinces.

Author's response:

We have modified this in the Fig. 1 in the revision.

16) Figure 4: Wrong spelling of “Contribution” in Y axis. Add a name of “Rivers” to X axis. The spelling of river names should be keep in consistence.

17) On all figures: The fonts used in the diagrams should be consistent.

Author's response to comment 16) and 17):

We have improved this in the revision.

**RC3:**

Comments from Referees:

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

Liu et al., Many papers on dissolved loads in rivers have been published, but the papers about anthropogenic impacts on chemical weathering and carbon sequestration are rare. Thus this is an interesting paper. Used the water chemistry data measured in many rivers in the Southeast coastal region of China, Liu et al. presented their study on geochemistry of the dissolved loads in the region with severe acid rain impacts. They sampled over 100 sites in the high-flow period in 2010, and employed the chemical compositions and carbon isotope ratio to quantify the associated atmospheric CO<sub>2</sub> consumption rates and the contribution of anthropogenic acids. This study found that sulfuric acid played an important role in in chemical weathering, and acid deposition should be considered in studies of chemical weathering and associated CO<sub>2</sub> consumption. In addition, this paper provides a valuable dataset on the water chemistry which can be used for carbon fluxes study. Thus, this paper fits well into the theme of this special volume on carbon fluxes in Asian river. I recommend to accept this manuscript after some minor revision.

1. Line 215-217, when the authors discuss the source of Cl<sup>-</sup>, they say “In pristine areas, the concentration of Cl<sup>-</sup> in river water is assumed to be entirely derived from the atmosphere, provided that the contribution of evaporates is negligible”. Please give a reference. In fact it was found that ground water was an important source of Cl<sup>-</sup> for rivers in many regions of China such as the Yarlung Tsangpo basin on the Qinghai-Tibetan Plateau.

Author's response:

The reference has been added in the attached revision. As the reviewer suggested, the Qinghai-Tibetan Plateau and arid area, groundwater play as an important source for Cl<sup>-</sup>. However, in humid and hot area like Southeast China, no salt-bearing rocks was found there. In addition, river water is mainly recharged by rain, but groundwater contribution is far more less than arid area. So, groundwater impact on river Cl<sup>-</sup> is not considered in this study.

2. L232-L233 High proportion of SO<sub>4</sub> and NO<sub>3</sub> were found in the study area, but the discussion mainly focused on the SO<sub>4</sub>. What was the role of NO<sub>3</sub> in the estimation of CO<sub>2</sub> consumption rate?

Author's response:

Yes, we do think the N deposition also plays a role in rock weathering and have impacts on CO<sub>2</sub> consumption. However, the sources of NO<sub>3</sub><sup>-</sup> in river waters are complicated, e.g. atmospheric deposition, fertilizer, industry and urban waste water, as well as nitrification and denitrification. Although it is difficult to determine the origin of nitrate in river waters, we can at least assume that nitrate from acid deposition is one of the providers of protons. We added the discussions about the effect of HNO<sub>3</sub> in section 5.4, and recalculated the CO<sub>2</sub> consumption in the SCERB.

3. Line 321-324, The authors made a comparison between the studied rivers in east coastal region and other major/large rivers in China such as Changjiang, Huanghe and Xijiang river. It will be good to have a forward discussion explaining the major reasons for the difference.

Author's response:

Silicate weathering are complicated and affected by lithological setting, temperature and precipitation, etc. Silicate weathering rates in southeast coastal area is higher than the Xijiang and Huanghe but lower than Changjiang basin, which is the complicated results of silicate dominated bedrock (compared with Xijiang), high MAT and high runoff (compared with Huanghe and Changjiang basin). We added some discussion with rivers in Asia and the world in the following section (section 5.4) in the attached revision.

4. Line 386-387, "Carbonate rocks are generally derived from marine system and, typically, have 13C value close to zero", please add a reference

Author's response:

The reference has been added in the attached revision.

5. Table 1, how do you measure the HCO<sub>3</sub>? Are they calculated from the alkalinity? Please provide more info in the method section.

Author's response:

The content of HCO<sub>3</sub><sup>-</sup> was calculated. Alkalinity was determined by phenolphthalein and methyl orange end point titration with dilute HCl. The HCl consumption volumes for phenolphthalein and methyl orange end point titration were used to calculate the CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. Actually, there were little phenolphthalein alkalinity for all the samples (i.e. the HCl consumption volume for phenolphthalein end point titration were almost zero). The method was given in the Sampling and analytical method section in the revised version (Line 174-176).

6. Fig. 5. Please provide the p value.

Author's response:



P value is provided in the attached revision ( $p < 0.01$ ) in the supplement.

Other minor comments from referee 3:

Line 72-74 the sentence is not well structured, please re-phrase.

Author's response:

We have re-phrased it in the revision. pls find it in the attached revision in the supplement.

Line 195 lack space between “%” and “of”

Author's response:

Modified in the attached revision in the supplement.

### **EC1:**

The authors well responded to the reviewers and interactive comments and manuscript is in the good shape. However, I have few following queries:

1. How did you avoid sampling during tidal period - Please explain in detail about this.

This question was asked by Referee however the response is not satisfactory.

Author's response:

To avoid tidal effect on the river estuary samples, the sampling sites were selected carefully based on the following consideration. First, the sampling locations for the river low reach samples were chosen as far as possible from the tidal impacted area, normally further than 30 km. Second, we checked the local daily tidal time and conducted the sampling of river low reach during low tide period in the sampling day. Third, we also checked the salinity of the water by using salinometer (WS202, China) before sampling in the field. In addition, we double checked data before drafting the manuscript to make sure the river sample are not contaminated by seawater (e.g. all the water chemistry features of the samples were within the normal range of fresh water). These were noted in the Sampling and analytical method section in the revised manuscript (Line 158-164 in the revision)

2. The field trip was conducted during high-flow period hence the discussion represents to high-flow period only and this must be explicitly mentioned in the text as well in the title. ~70% of annual precipitation occurs during high-flow period, and high weathering expected, the processes during dry period (low-flow) is different. (This issue was also raised by RC1 - please explicitly mention about this).

Author's response:

Yes, the processes in low-flow season might be different in some extent due to the hydrologic and temperature effect. We have explicit this point in the title and in the text in the revised version (Line 469-477 in the revision).

3. How you could titrate only  $\text{HCO}_3^-$ ? Is it not TA and then calculated  $\text{HCO}_3^-$ ? It is not clear.

Author's response:

The content of  $\text{HCO}_3^-$  was calculated. Alkalinity was determined by phenolphthalein and methyl orange end point titration with dilute HCl. The HCl consumption volumes for phenolphthalein and methyl orange end point titration were used to calculate the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . Actually, there were little phenolphthalein alkalinity for all the samples (i.e. the HCl consumption volume for phenolphthalein end point titration were almost zero). The method was given in the Sampling and analytical method section in the revised version (Line 174-176).