

Biogeosciences Discuss., author comment AC1
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Reply on RC1

Boyi Liu et al.

Author comment on "Spatial and temporal variability of $p\text{CO}_2$ and CO_2 emissions from the Dong River in south China" by Boyi Liu et al., Biogeosciences Discuss.,
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RC: 1.1 The results show that $p\text{CO}_2$ (and in turn FCO_2) is higher in the larger rivers compared to the smaller rivers, which the authors interpret as resulting from proportional differences in C inputs (both CO_2 and DOC) and metabolism of allochthonous inputs. Since these are connected systems (i.e. the small rivers eventually flow into the larger ones), I'm a bit puzzled how CO_2 would increase downstream due to higher C inputs unless the study design somehow missed high CO_2 inputs from low order streams that directly joined the mainstream?

AC: Changes in riverine CO_2 can mainly result from the variation of two factors, external C input and in-stream metabolism processes. If the control mechanism in large and small rivers are the same, both are controlled by external C input. Then the higher CO_2 in the large river indicates more C input. Since the large river and the small river are connected, and the CO_2 of the large river comes from the small river, sampling bias could be responsible for the higher CO_2 concentration in large rivers. However, this theory cannot explain the seasonal changes in CO_2 concentration. For small rivers, the highest value of $p\text{CO}_2$ was observed in April, beginning of the flood season, when increased precipitation facilitates the transportation of the soil carbon from land to the river system. However, such an increase was not observed for large rivers in April, although an increase in DOC concentration suggesting more external C input. Instead, a significant increase in CO_2 concentration was observed in July, even though the DOC concentration was slightly lower compared with April. Therefore, we believe that external C input is not the controlling factor, and CO_2 increases downstream due to the high intensity of in-stream metabolism. Long water residence time combined with the high temperature in July facilitated OC decomposition and increased CO_2 concentration in large rivers. However, we do not have direct evidence to support our theory. We are considering using stable isotope to analyze the source of riverine C in the future. When sampling at the river basin scale, it is critical to reducing the error caused by the sampling process. In this study, small and large rivers from eight major sub-basins and different reaches of the mainstream have been sampled. We believe that this sampling strategy can represent the conditions of the basin nicely. There may be small rivers with high CO_2 concentration directly into the mainstream, but We believe that its impact on the CO_2 concentration of the mainstream is limited due to relatively small discharge.

RC: 1.2 Based on Figure 1, it appears that many of the smaller rivers were also at higher elevations. A bias towards higher altitude sites in the smaller rivers could explain the observed trends if these catchments had less vegetation/forest cover and, therefore, fewer C inputs (as both CO_2 and DOC). Indeed, the authors observed higher DOC concentrations in larger rivers, which they assume fuels higher respiration. Where does

this DOC come from if it doesn't pass through smaller rivers first? I suspect there is some sampling bias at hand.

AC: We agree that small rivers sampled tend to have a slightly higher elevation than large rivers. It is also partially because those headwater streams tend to be distributed in higher elevation in the hill-dominated Dongjiang river basin. Land cover will indeed influence the C input, and we will address its impacts in the discussion. However, small catchments in higher elevations tend to have more forest cover, so less C input may not be responsible for the low CO₂ in small rivers. Even though a slightly higher average DOC concentration was observed in large rivers than small rivers, the difference is not statistically significant. The DOC concentrations of the two are similar. That is why we believe higher CO₂ concentration in large rivers is due to favorable decomposition conditions rather than more supply of OC. It is difficult for OC to convert into CO₂ in small rivers due to the high flow velocity and short water residence time; thus, it could be transported and fuel the heterotrophic respiration in large rivers. There may be small rivers with relatively high C concentrations that could directly join the mainstream, but the impact on C input should be minor due to relatively small discharge.

RC: 1.3 There are additionally more processes, such as photo-oxidation or titration of the carbonate equilibrium via organic acids (indeed, you see increasing CO₂ with decreasing alkalinity), that could impact some the observed downstream increase in CO₂. These aspects are not discussed in the manuscript and the authors conclude too strongly that they know the responsible drivers without data to support such claims. Since more highly productive vegetation in the catchment could result in both higher CO₂ inputs and higher DOC that fuels respiration, I think it would be useful to explore the relationship between C concentrations (pCO₂ and DOC) and catchment land-cover (perhaps as a fraction of wet area, similar to Rocher-Ros et al 2019, L&O Letters or % forest cover).

AC: Indeed, we have concluded too firmly about the responsible drivers without enough direct evidence. Other factors may affect the concentration of CO₂ and should be discussed. We will reduce certainty and explore the relationship between C concentration and land cover. We will also discuss the potential impact of more processes. For example, photo-oxidation may be responsible for some of the deviation of ΔCO₂:ΔO₂ stoichiometry line.

RC: 2.The discussion of spatial and temporal patterns is blended together and needs to be disambiguated a bit. It is hard for the reader to make sense of these various overlapping trends. I would suggest starting with one (spatial), then the other (temporal) before finishing on how they overlap to result in the observed pattern.

AC: Thank you for your advice. We will revise the discussion about spatial and temporal patterns and improve the referencing of figures and tables.

RC: 3.Increased precipitation can both increase the transport of terrestrial C (including CO₂) and dilute it. How do you know which process dominates?

AC: We estimate the intensity of those two effects by analyzing the temporal pattern of riverine CO₂. For example, precipitation and CO₂ concentration increased simultaneously from January to April in small rivers, suggesting that the increase of terrestrial C transportation is the dominant process. In comparison, precipitation was similar between April and July, but CO₂ concentration decreased during this period. The dilution and depletion effect caused by precipitation should be more important in this case.

RC: 4.Throughout the discussion, the authors fail to reference their figures or tables in many cases that would make it much easier to observe their explanations.

AC: Thank you for your advice. We will revise it in the manuscript.

RC: 5.Given the high resolution of the pCO₂ data, would it not be interesting to upscale outgassing for the whole basin? Perhaps it could be compared to DOC/POC export if those have been previously estimated (or even roughly estimated using your values). A the very

least, I think the authors' data could be nicely displayed on a map (Similar to Figure 1 of Rocher-Ros 2019, *Limnology and Oceanography Letters*)

AC: We are also very interested in the calculation of basin-wide CO₂ emission. After all, one of our objectives is to provide support for more accurate global CO₂ emissions estimates. The estimation of CO₂ emissions at the watershed scale is not only limited by the accuracy of the CO₂ data but also the accuracy of the river network extraction. Currently, we are working on a study about the basin-wide CO₂ emissions estimates in the Dongjiang river basin. We intend to perform higher-precision river network extraction and water area calculation by combining remote sensing images and DEM. A more accurate watershed-scale CO₂ emissions estimation will be carried out, and its relationship with lateral carbon transport and net ecosystem productivity. This study intends to focus on the difference in carbon emissions between large and small rivers.

RC: Overall, I think the discussion of the drivers of CO₂ variability is overstated. Specifically, there is no direct evidence of lateral soil CO₂ nor dilution effect caused by precipitation. There doesn't seem to be much of a difference in dCO₂ vs. dO₂ between large and small rivers (Figure 6), suggesting that metabolism is similar. At minimum, the current discussion would need to justify why simultaneously low DOC and CO₂ are not an artifact of altitude/land-cover.

AC: Indeed, we have concluded too strongly about the responsible drivers without enough direct evidence. Other factors may affect the concentration of CO₂ and should be discussed. We will reduce certainty and discuss the potentials impact of more processes. Regarding dCO₂ vs. dO₂, dO₂ is higher in small rivers than large rivers with the same dCO₂, suggesting that the impacts of factors other than metabolism should be more obvious in small rivers. As for the relationship between DOC and CO₂, we will further elaborate on why DOC may not be the controlling driver of the CO₂ changes and discuss the possible influence of altitude and land cover.

RC: 16-17 - what direct evidence of soil CO₂ and dilution is there to support this statement?

AC: Due to the lack of stable isotope analysis, we do not have direct evidence pointing to the source of carbon. We can only estimate the effects of soil CO₂ input and dilution by analyzing the temporal pattern of riverine CO₂. For example, precipitation and CO₂ concentration increased simultaneously from January to April in small rivers, suggesting an increase in terrestrial C transportation. Meanwhile, a more rapid response of riverine CO₂ to terrestrial C input in small rivers comparing with large rivers in April suggests different C sources controlling the CO₂ changes. We will reduce certainty and discuss the limitation of our estimation.

RC: 96 - Figure 1 could be supplemented with a land-cover map. Many of the smaller rivers appear to be at higher elevations and I am curious if they are less forested.

AC: We will add a land-cover map along with the spatial pattern of CO₂ concentration. Actually, catchment at higher elevation in the Dongjiang river basin is more forested, we will evaluate the impact of land cover on riverine CO₂ concentration in the discussion.

RC: 103 - Figure 2's data might be better suited for a bar graph?

AC: Thank you for your advice. We will revise it in the manuscript.

RC: 163 - I think the reference to equation 2 is incorrect here.

AC: Thank you for your advice. We will revise it in the manuscript.

RC: 195 - There is no hydrologic data in Table 1. Discharge should be presented.

AC: Thank you for your advice. We will provide related hydrologic data in the supplement.

RC: 197 - Again there is no stream width or discharge data presented anywhere in the manuscript besides these lines of text.

AC: Thank you for your advice. We will present stream width in the supplement.

RC: 202 - U10 is undefined.

AC: Thank you for your advice. U10 has been defined in L125.

RC: 275 - DOC and CO₂ can simultaneously be transported from terrestrial systems, which also might explain their correlation.

AC: We agree that DOC and soil CO₂ can simultaneously be transported from terrestrial systems. However, a discrepancy in the temporal pattern of DOC and riverine CO₂ was observed, which suggests that DOC input might not be the controlling factor. That's also why we discuss the impacts of internal metabolism according to the result of dCO₂ vs. dO₂.

RC: 297-318 - This section is very overstated and not the only way to interpret these data. I recommend revising and rephrasing to reduce certainty and include alternative explanations.

AC: Thank you for your advice. We will rephrase to reduce certainty and discuss the possible impacts of land cover.

RC: 381-382 - This is possible, but not certain.

AC: Thank you for your comment. We will reduce certainty here.

RC: 390 - Respiration and photosynthesis can occur simultaneously.

AC: We agree that respiration and photosynthesis can occur simultaneously, And we are interested in the intensity of those two processes in the Dongjiang River. In the nearby Xijiang River, high DO and CO₂ occurred simultaneously in summer, indicating that photosynthesis is dominant and C source other than respiration should be responsible for high CO₂ concentration observed. In contrast, DO and riverine CO₂ were negatively correlated, and supersaturated CO₂ was observed in the Dongjiang River, indicating that the effect of respiration is more obvious.

RC: 405 - The units for pCO₂ are not consistent (sometimes uatm sometimes ppm). What about Borges 2015, nature geoscience that includes a significant amount of data for rivers in central Africa? Also Mann et al. 2014 JGR-Biogeosciences has additional pCO₂ data.

Lastly, is the Mississippi River really a subtropical basin?

AC: In some studies, the results of pCO₂ were only provided in ppm. We will add notes under the table. Thank you for the recommendation. We will add extra data from Africa. According to the Köppen Climate Classification system, sampled lower Mississippi river basin belongs to the Humid subtropical climate zone.

RC: 409-412 - Again, I don't think these conclusions are justified

AC: Thank you for your comment. We will reduce certainty here.

RC: 417- Still don't really see how depletion would only affect small streams and not the larger ones they flow into?

AC: If lateral C input is the primary driver of riverine CO₂ in small and large rivers, depletion should affect both small and large rivers. However, the decrease in riverine CO₂ during the wet season was only observed in the small rivers, not the large rivers, indicating different controlling factors. One possible explanation is that, for large rivers, DOC concentrations in April and July are both more than enough to support the requirement of respiration. Therefore, the intensity of in-stream metabolism rather than DOC concentration controls the temporal pattern of riverine CO₂ in large rivers. We understand that this is only one possible explanation without enough direct evidence. Therefore, the limitation of this explanation will be discussed in the manuscript.

