

## Referee #1

The paper by Liu et al. presents seasonal  $p\text{CO}_2$  concentrations and  $\text{CO}_2$  fluxes from the Dongjiang River basin. They found that concentrations and fluxes were higher in larger rivers relative to smaller ones and in the wet season (summer) compared to the dry season. They also contextualized some of these broader findings with auxiliary measurements of DO, DOC, alkalinity, and pH.

The paper is presents a good quantity of spatially and temporally resolved  $\text{CO}_2$  data, adheres to established methods, and is generally well written. I think the data alone is a useful contribution however I think much of the discussion surrounding the drivers and explanation of  $\text{CO}_2$  differences is either lacking or unsupported. I think that after some revisions of the discussion, the manuscript could warrant publication in Biogeosciences. Below are my primary criticisms, followed by line-specific minor comments.

### Primary criticisms

The results show that  $p\text{CO}_2$  (and in turn  $\text{FCO}_2$ ) is higher in the larger rivers compared to the smaller rivers, which the authors interpret as resulting from proportional differences in C inputs (both  $\text{CO}_2$  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  $\text{CO}_2$  would increase downstream due to higher C inputs unless the study design somehow missed high  $\text{CO}_2$  inputs from low order streams that directly joined the mainstream?

Based on Figure 1, it appears that many of the smaller rivers were also at higher elevation. 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 less C inputs (as both  $\text{CO}_2$  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.

Reply: We have observed higher  $p\text{CO}_2$  in large rivers compared with the smaller rivers (Figure 3a and Figure 4 in the revised manuscript) and interpreted it as resulting from stronger in-stream metabolism of allochthonous C inputs. However, stronger in-stream metabolism may caused by increased C inputs or more favorable conditions for OC decomposition. The latter is more likely to be responsible for the spatial pattern of  $p\text{CO}_2$  in this study. Small rivers located in hill-dominated Dongjiang River Basin (DJRB) tend to have high flow velocity and short water residence time, making it hard for terrestrial organic carbons to convert into  $\text{CO}_2$  (Hotchkiss et al., 2015). Meanwhile, long water residence time in large rivers could facilitate the decomposition of organic carbon within the water column (Denfeld et al., 2013). Several missed high  $\text{CO}_2$  inputs from low order streams that directly join the mainstream is unlikely to be responsible for the high  $p\text{CO}_2$  due to their relatively small discharge.

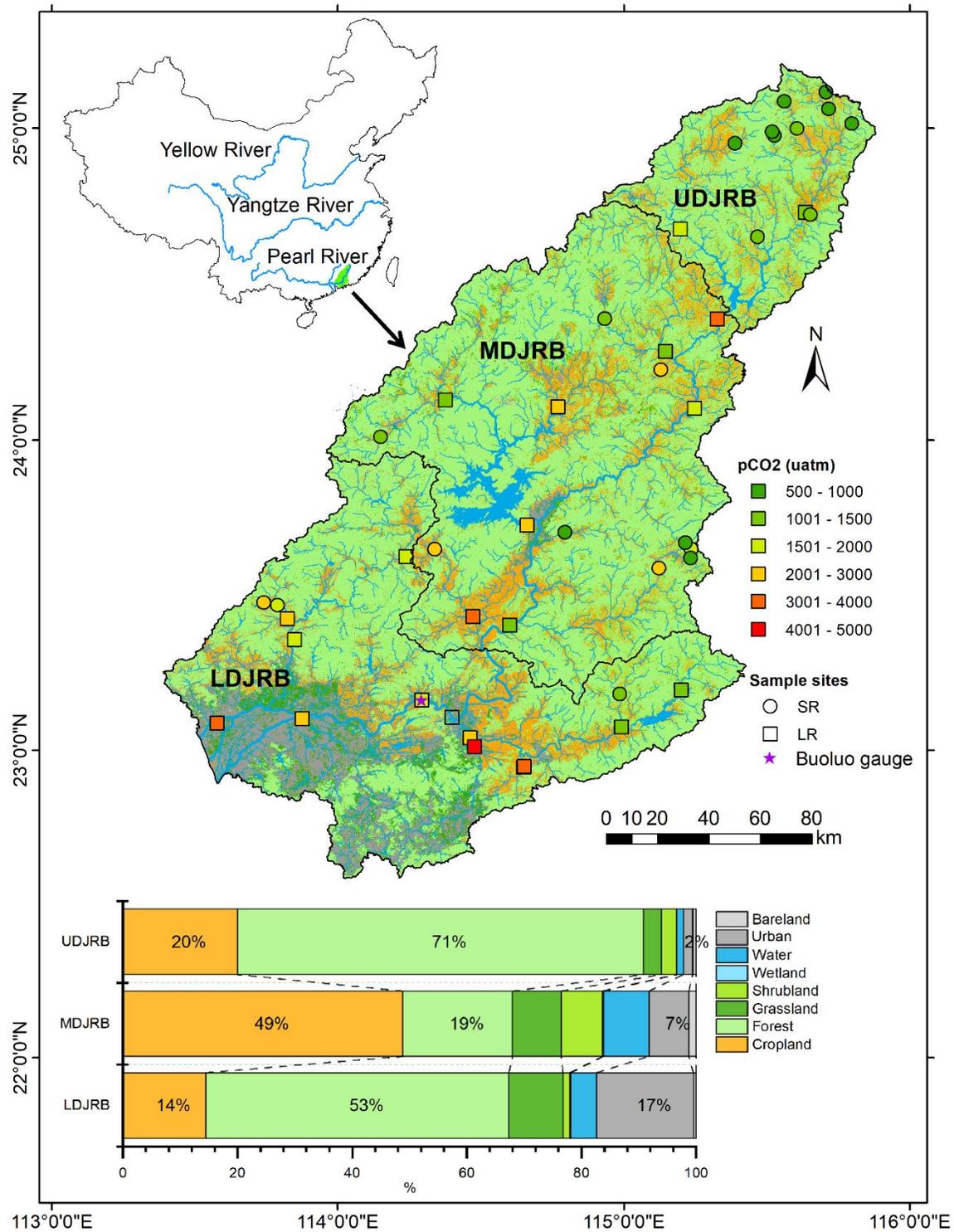
We realized the higher DOC in large rivers than that in upstream small rivers and suggested that there may have extra DOC inputs other than direct inputs from small rivers. Therefore, based on the referee's suggestion, we examined the impact of land use on riverine  $p\text{CO}_2$ . Our result showed increased  $p\text{CO}_2$  from forest-dominated streams in upper DRJB to Agricultural and urban impacted catchments in middle DJRB and lower DJRB (Figure 1 and Figure 3b). Agricultural

50 practices on cropland and domestic wastewater from the urban areas could contribute to the higher DOC and thus higher  $p\text{CO}_2$  as observed in large downstream rivers compared with small rivers. However, the effect of increased DOC on  $p\text{CO}_2$  is confined by other factors that control the OC decomposition. Our results showed that large rivers had similar DOC concentration but higher  $p\text{CO}_2$  compared with small rivers with similar land cover (Figure 7 in the revised version of manuscript), when the percentage of forest area was over 65% or when the percentage of the combined area of cropland and urban area was less than 30%, which was the case for the majority of our sample sites. This indicated that in-stream metabolism was stronger in large 55 rivers than in small rivers despite similar DOC concentrations. Less C inputs due to more forest cover is not enough to explain the lower  $p\text{CO}_2$  in small rivers. Please refer Line 240–244 and L305-330 in the revised version of the manuscript for the changes.

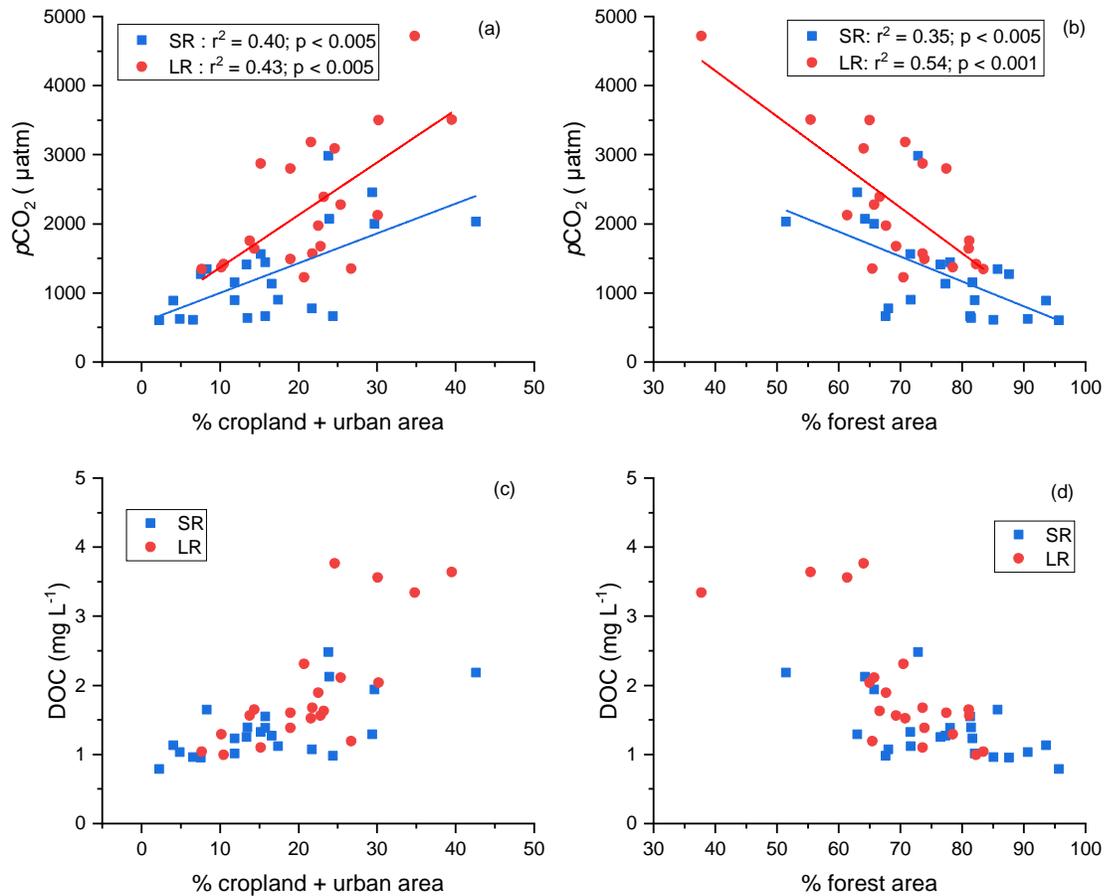
60 There are additionally more processes, such as photo-oxidation or titration of the carbonate equilibrium via organic acids (indeed you see increasing  $\text{CO}_2$  with decreasing alkalinity), that could impact some the observed downstream increase in  $\text{CO}_2$ . These aspects are not discussed 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  $\text{CO}_2$  inputs and higher DOC that fuels respiration, I think it would be 65 useful to explore the relationship between C concentrations ( $p\text{CO}_2$  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).

70 Reply: Thank you for your suggestion. We have examined the impact of land use on DOC input and riverine  $p\text{CO}_2$ . Our result showed that both DOC and  $p\text{CO}_2$  were negatively related to the percentage of forest area and positively related to the percentage of cropland and urban area combined (Figure 8 in the revised version of the manuscript). Agriculture practices on cropland and domestic wastewater from the urban area could contribute to the higher DOC and  $p\text{CO}_2$  as 75 observed in large downstream rivers compared to upstream small rivers. We also observed increased  $p\text{CO}_2$  from forest-dominated streams in UDJRB to the agricultural and urban impacted catchment in MDJRB and LDJRB (Figure 1 and Figure 3b in the revised manuscript). Moreover, our results showed that large rivers had similar DOC concentration but higher  $p\text{CO}_2$  compared with small rivers with similar land cover (Figure 7 in the revised manuscript), when the percentage of forest area was over 65% or when the percentage of the combined area of cropland and urban area was less than 30%, which was the case for the majority of our sample sites. This 80 suggests that in-stream metabolism was stronger in large rivers than in small rivers despite similar DOC concentrations, which also supported our arguments about the favorable condition for OC decomposition in large rivers. Please refer to Lines 307–359 in the revised version of the manuscript for the changes.

85 We have added two Figures (Figure 1 and Figure 7, Line 102 and Line 335 in the revised version of the manuscript) to support the discussion about the relationship between land cover and C concentration.



90 **Figure 1** Sample sites and land cover in the DJRB. Yearly average  $p\text{CO}_2$  at each sample site was displayed. Based on the land cover dataset: FROM-GLC10 (<http://data.ess.tsinghua.edu.cn>). Note, this figure has also been added into the revised version of the manuscript.



95

**Figure 7** (a) the relationship between yearly average  $p\text{CO}_2$  at each site and the percentage of cropland and urban area combined (b) the relationship between yearly average  $p\text{CO}_2$  at each site and the percentage of forest area (c) the relationship between yearly average DOC at each site and the percentage of cropland and urban area combined (d) the relationship between yearly average DOC at each site and the percentage of forest area. Note, this figure has also been added into the revised version of the manuscript.

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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.

105

Reply: Thank you for your advice. We have revised the discussion about the drivers of spatial and temporal pattern. We started with analyzing the possible major controls of spatial pattern, then the temporal pattern, before finishing on other minor controlling factors. Please refer to Lines 293–380 in the revised version of the manuscript for the changes.

110

Increased precipitation can both increase the transport of terrestrial C (including CO<sub>2</sub>) and dilute it. How do you know which process dominates?

115

120 Reply: We estimated the impact of those effects by analyzing the temporal pattern of precipitation and riverine CO<sub>2</sub>. For example, precipitation and CO<sub>2</sub> concentration increased simultaneously from January to April in small rivers, which suggested that the increased terrestrial C transport was likely the dominant process in controlling the *p*CO<sub>2</sub> changes. In contrast, the precipitation was similar in April and July, but the CO<sub>2</sub> concentration decreased from April to July. Thus, the dilution and depletion effects caused by precipitation was more obvious. We also elaborated it in Lines 344–355 in the revised version of the manuscript.

125 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.

Reply: Thank you for your advice. We have improved the referencing of figures to support our arguments.

130 Given the high resolution of the *p*CO<sub>2</sub> 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). At 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)

135 Reply: We are also very interested in the calculation of basin-wide CO<sub>2</sub> emissions. One of our objectives was to provide support for more accurate global CO<sub>2</sub> emission estimates. Currently, the estimation of CO<sub>2</sub> emissions at the watershed scale is limited by the accuracy of the CO<sub>2</sub> data and the surface area accuracy of the river networks. We are now working on a parallel study about the estimates of basin-wide CO<sub>2</sub> emissions from the river network in the Dongjiang river basin. We intend to perform higher-precision river network extraction and water area calculations by combining remote sensing images and DEM (Wang et al., 2018; Wang et al., 2020). A more accurate watershed-scale carbon emissions estimation could then be carried out. Moreover, we will also compare it with lateral carbon export and NPP. In this study, we intend to focus on the factors that regulate the difference in CO<sub>2</sub> concentration and emissions between large and small rivers. Thank you for your advice about the data presentation. In addition, *p*CO<sub>2</sub> and land use cover have been displayed in Figure 1 (please refer to Line 101 in the revised version of manuscript for the changes)

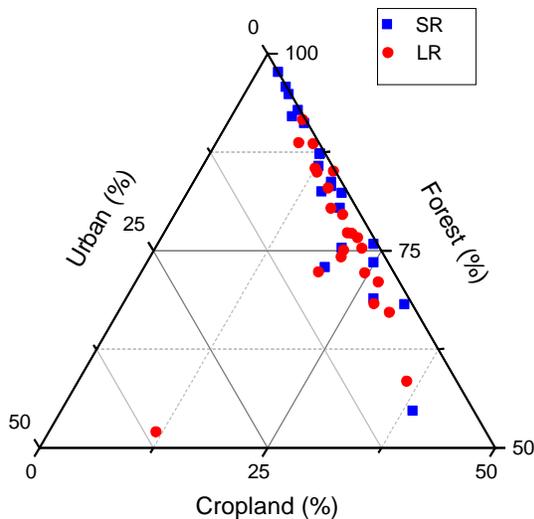
145 Overall, I think the discussion of the drivers of CO<sub>2</sub> variability is overstated. Specifically, there is no direct evidence of lateral soil CO<sub>2</sub> nor dilution effect caused by precipitation. There doesn't seem to be much of a difference in *d*CO<sub>2</sub> vs. *d*O<sub>2</sub> 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 CO<sub>2</sub> are not an artifact of altitude/land-cover.

150 Reply: Thank you very much for the comments and suggestions. We fully agree with the referee's comments. Based on your comments, we have substantially revised the manuscript by re-discussing the potential impact of other factors, including land use cover (Lines 305–334), , photo-oxidation and photosynthesis(Lines 375–380 in the revised version of the manuscript ).

165 Regarding the result of  $dCO_2$  vs.  $dO_2$ , a negative relation between  $dCO_2$  vs.  $dO_2$  was observed in both small and large rivers, suggesting that metabolism have occurred in both of them. However,  $dO_2$  is higher in small rivers compared with large rivers with similar  $dCO_2$ , suggesting that the impacts of other factors other than metabolism should be more important in small rivers, which is also supported by the higher  $pCO_2$  in large rivers than in small rivers with similar land cover and DOC concentration (Figure 8 in the revised version of the manuscript).

170 Based on the referee's suggestion, we have also examined the impact of land use on DOC input and riverine  $pCO_2$  (Lines 324–334 in the the revised version of the manuscript). Our results showed that large rivers had similar DOC concentration but higher  $pCO_2$  compared with small rivers with similar land cover (Figure 7 in the the revised version of the manuscript). This indicates that the higher  $pCO_2$  in large rivers is more likely the result of favorable conditions for OC decomposition, even though higher DOC could contribute to higher  $pCO_2$ .

175 Therefore, the observed spatial pattern is not the result of sampling bias. Moreover, both small and large rivers with a variety of land cover structures were sampled in this study to reduce the possible bias caused by the distribution of sample sites (Figure S4, also available in Supplementary).



180 **Figure S4** Forest, cropland, and urban cover respectively as a percentage of the total area of forest, cropland and urban area.

### 185 **Minor comments**

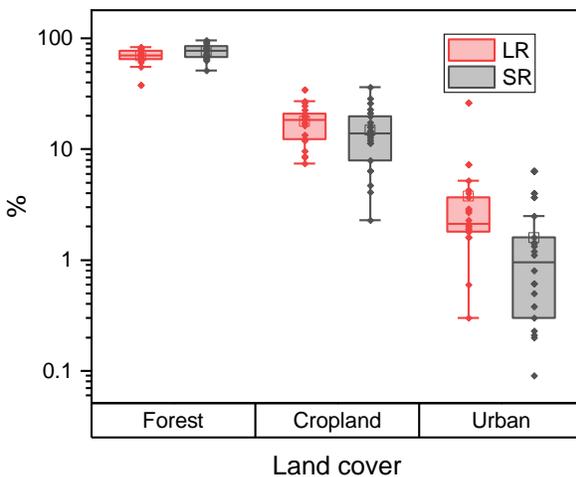
16-17 - what direct evidence of soil  $CO_2$  and dilution is there to support this statement?

190 Reply: We estimated the impact of those effects by analyzing the temporal pattern of DOC,  $CO_2$ , and precipitation. For example, DOC and  $CO_2$  concentration increased simultaneously from January to April in small rivers (Table 1 and Figure 4 in the revised version of the manuscript), suggesting an increase in terrestrial C inputs. However, an increase in  $pCO_2$  was not observed in large rivers during this period even though the DOC increased substantially, which means that

195 there are processes other than in-stream OC decomposition affecting the  $p\text{CO}_2$  changes in small rivers. Therefore, soil  $\text{CO}_2$  input is likely to be responsible for the changes since soil  $\text{CO}_2$  and in-stream metabolism are the two major sources of riverine  $\text{CO}_2$  (Yao et al., 2007). Meanwhile, an increase in discharge and decrease in  $p\text{CO}_2$  has been observed in small rivers from April to July, which indicates that the dilution effect caused by the increasing discharge and depletion effect could be responsible for the decrease. We have rephrased the statement and reduced the certainty. Please refer to Lines 344–355 in the revised version of the manuscript for the changes.

200 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.

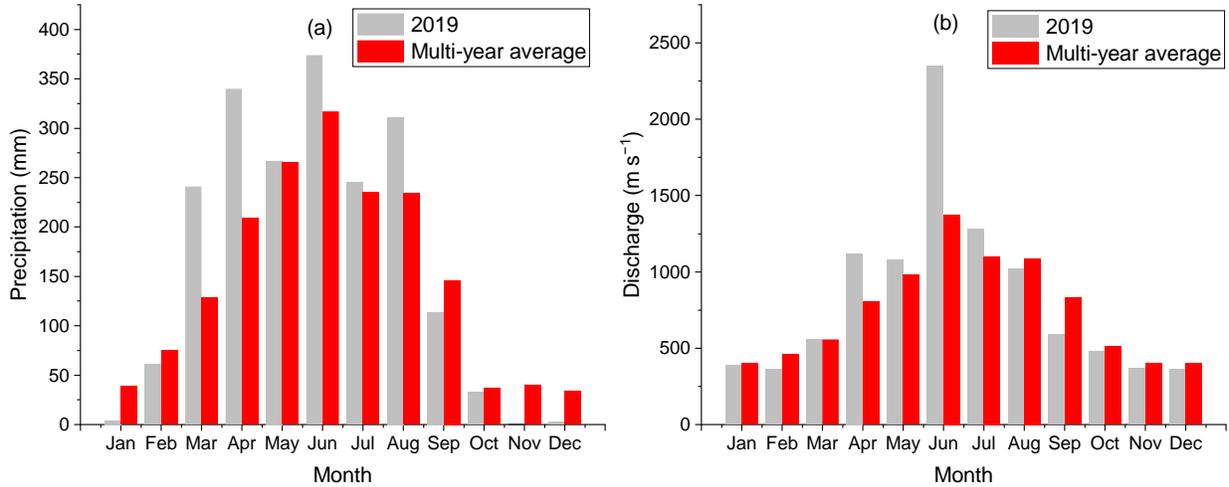
205 Reply: Thank you for your suggestion. We have added a land cover map (Figure 1) in revised version of the manuscript. It appears that the upstream small rivers in the DJRB are more covered with forest compared with the downstream large rivers, and are less impacted by human activities (Figure S3), which together have contributed to the lower  $p\text{CO}_2$  in small rivers. The impacts of land cover on the spatial pattern of  $p\text{CO}_2$  have been elaborated in revised manuscript. Please refer to Lines 305–330 in the revised version of the manuscript for the changes.



215 **Figure S3** Forest, cropland, and urban cover respectively as a percentage of the catchment area. The box mid-lines represent medians; the interquartile range (IQR) is represented by top and bottom of the box, respectively; whiskers indicate the range of 1.5 IQR; the white square symbols represent means, and the other symbols represent Forest, cropland, and urban cover respectively as a percentage of catchment area. Note, this figure has also been added into the Supplementary. Note, this figure has also been added into the Supplementary.

220 103 - Figure 2's data might be better suited for a bar graph?

Reply: Changed.



**Figure 2** Monthly variations in (a) precipitation of the DJRB and (b) water discharge at the Boluo hydrological gauge, based on data provided by the Hydrological Bureau of Guangdong Province. Note, this figure has also been added into the revised manuscript (Line 105).

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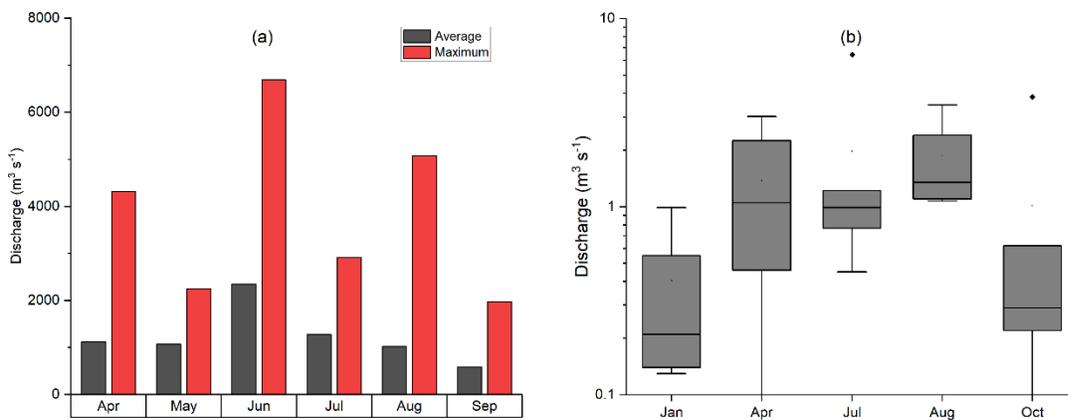
163 - I think the reference to equation 2 is incorrect here.

Reply: Changed.

230

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

Reply: Thank you for your advice. Related hydrologic data has been presented in Figure S1 in the supplementary.



235

**Figure S1** (a) Wet season discharge in Boluo station, based on data provided by the Hydrological Bureau of Guangdong Province. (b) discharge in first order streams

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

240

Reply: Thank you for your advice. Stream width has been presented in Table S1 in the supplementary.

Stream size	Stream order	Stream width (m)						
		January	April	July	August	October	Wet season	Dry season
small		13.5 ± 9.9	16.9 ± 10.1	17.1 ± 10.6	15.1 ± 9.7	14.5 ± 10.9	16.3 ± 10.0	14.0 ± 10.3
	1	2.9 ± 1.5	4.7 ± 2.7	6.0 ± 2.1	5.6 ± 2.7	4.7 ± 2.0	5.4 ± 2.4	3.8 ± 1.9
	2	8.3 ± 5.2	12.7 ± 7.8	12.5 ± 7.2	10.1 ± 2.8	8.4 ± 3.2	11.8 ± 6.1	8.4 ± 4.1
	3	21.1 ± 7.4	24.7 ± 5.5	24.6 ± 8.5	22.1 ± 8.8	22.2 ± 10.3	23.8 ± 7.6	21.7 ± 8.8
large		173.9 ± 161.7	184.4 ± 164.0	187.2 ± 158.5	181.1 ± 162.4	175.1 ± 165.1	184.2 ± 159.1	174.5 ± 161.4
	4	67.6 ± 38.5	73.0 ± 47.1	87.0 ± 54.7	82.3 ± 64.4	66.2 ± 54.3	80.7 ± 54.2	66.9 ± 45.8
	5	164.3 ± 46.4	187.7 ± 69.6	166.6 ± 37.6	157.0 ± 54.9	164.6 ± 45.4	170.4 ± 53.2	164.5 ± 43.3
	6	226.5 ± 23.3	235.5 ± 37.5	241.3 ± 45.7	231.5 ± 44.5	243.9 ± 38.4	236.1 ± 33.4	235.2 ± 27.6
	7	425.2 ± 207.3	433.4 ± 200.0	436.5 ± 192.3	433.3 ± 196.8	426.2 ± 206.8	434.4 ± 177.6	425.7 ± 191.7

245 **Table S1** Seasonal variation in stream width for streams from first to seventh order.

202 - U10 is undefined.

250 Reply: U10 has been defined in the revised version of the manuscript. Now it reads “while wind speed at 1.5 m above the water surface was measured with a Kestrel 2500 handheld anemometer and normalized to a height of 10 m (U10) using the equation from Alin et al. (2011).” (Lines 138–139)

275 - DOC and CO<sub>2</sub> can simultaneously be transported from terrestrial systems, which also might explain their correlation.

260 Reply: Because DOC and CO<sub>2</sub> can be simultaneously transported from terrestrial systems, changes in DOC concentration could alter OC decomposition but not necessarily leads to the pCO<sub>2</sub> pattern. However, the positive relation between river water pCO<sub>2</sub> and DOC combined with the negative relation between pCO<sub>2</sub> and DO demonstrate that metabolic processes are important for CO<sub>2</sub> variation. This is also supported by the inverse relationship between ΔCO<sub>2</sub> and ΔO<sub>2</sub> (Figure 8 in the revised version of the manuscript).

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.

Reply: Thank you for your advice. We have rephrased the discussion to reduce the certainty (Please also refer to Lines 293–380 in the revised version of the manuscript), and discussed the potential impact of other factors, including land cover (Lines 305–334 in the revised version of

270 the manuscript), photo-oxidation, and photosynthesis (Lines 374–380 in the revised version of the manuscript).

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

275 Reply: Thank you for your advice. We have rephrased the discussion to reduce the certainty. Now it reads

280 “The difference in seasonal pattern can be explained by the drivers of  $p\text{CO}_2$  variability as the seasonal variation of riverine  $p\text{CO}_2$  is likely resulting from the changes of external carbon input, internal production of  $\text{CO}_2$  (Yao et al., 2007), and the dilution effect caused by precipitation (Johnson et al., 2007). For rivers where  $p\text{CO}_2$  is lower in summer than in winter, the dilution effect overrides the effect of increased carbon inputs and internal  $\text{CO}_2$  production (Luo et al., 2019). In contrast, for rivers like the Dongjiang river, although the dilution effect remains, increased  $\text{CO}_2$  input and metabolism are more significant factors in controlling  $p\text{CO}_2$ , thus leading to higher summer  $p\text{CO}_2$ .” Please refer to Lines 425–431 in the revised version of the manuscript for changes.

390 - Respiration and photosynthesis can occur simultaneously.

290 Reply: We agree that respiration and photosynthesis can occur simultaneously. We are interested in the impact of those two processes on  $p\text{CO}_2$  in our study area. In the nearby Xijiang River (a large river basin in south China with similar climate and landscape as the Dongjiang River basin), high DO and  $\text{CO}_2$  occurred simultaneously in summer, indicating that photosynthesis is dominant and C source other than respiration should be responsible for high  $\text{CO}_2$  concentration (Yao et al., 2007). In comparison, DO and riverine  $\text{CO}_2$  were negatively correlated (Figure 6 in the revised version of the manuscript), and oversaturated  $\text{CO}_2$  was observed at most sample sites (Figure 8 in the revised version of the manuscript), indicating that the effect of respiration is more obvious. The possible impact of photosynthesis has also been discussed in Lines 124–126 and Lines 376–379 in the revised version of the manuscript.

300 L13. 405 - The units for  $p\text{CO}_2$  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  $p\text{CO}_2$  data. Lastly, is the Mississippi River really a subtropical basin?

305 Reply: We apologized for the inconsistent use of units. In some studies, the results of  $p\text{CO}_2$  were only provided in ppm, and air pressure, an essential for unit transformation, was not provided. Therefore, we have added notes under the table to explain the inconsistent use of units. Thank you for the recommendation. In addition, we have added the data from rivers in Africa (Borges et al., 2015a; Borges et al., 2015b) into the revised version of the manuscript (Table 3, Line 440). For comparison, we try to include data collected under different hydrological conditions. According to the Köppen Climate Classification system, the lower Mississippi river basin belongs to humid subtropical climate zone (Chen and Chen, 2013).

315 L13. 409-412 - Again, I don't think these conclusions are justified

Reply: We have rephrased the sentences. Now it reads

320 “Spatial and temporal patterns of  $p\text{CO}_2$  were mainly affected by terrestrial carbon inputs and in-stream metabolism, both of which varied due to differential catchment settings, land cover, and hydrological conditions.” (Lines 455–457 in the revised version of the manuscript)

L13. 417- Still don't really see how depletion would only affect small streams and not the larger ones they flow into?

325 Reply: This may result from their different primary controlling process in small and large rivers.  $p\text{CO}_2$  in small rivers was more affected by soil  $\text{CO}_2$  input, so as the depletion of soil  $\text{CO}_2$ . For small rivers, the highest value of  $p\text{CO}_2$  was observed in April (Figure 4), which is consistent with the rapid surge of terrestrial C input, usually occurring at the beginning of the wet season (Hope et al., 2004; Yao et al., 2007; Johnson et al., 2008). However, such an increase in  $p\text{CO}_2$  was not observed in large rivers (Figure 4), even though DOC in large rivers, increased during the same period, similar to small rivers (Table 1). A possible explanation is that observed  $p\text{CO}_2$  rise was mainly originated from soil  $\text{CO}_2$ , which was readily emitted from the small rivers into the air, with little reaching the larger rivers downstream (Denfeld et al., 2013; Drake et al., 335 2018). Differences in  $p\text{CO}_2$  dynamic in July and August also reflected differential controlling processes in small and large rivers. A decline in  $p\text{CO}_2$  in July in small rivers suggested that it might have experienced the depletion effect occurring at middle and late wet season (Hope et al., 2004), during which soil  $\text{CO}_2$  decreased due to the continual precipitation. In contrast, the increase in  $p\text{CO}_2$  occurring in large rivers in July indicated that the depletion in soil  $\text{CO}_2$  input could hardly affect the  $p\text{CO}_2$  in large rivers during this period. Instead, stronger in-stream metabolism caused by OC input and favorable conditions for OC decomposition is more likely to be responsible for the rising  $p\text{CO}_2$ . Please also refer to Lines 344–359 in the revised version of the manuscript for changes.

345 Referee #2:

350 My one main concern is in relation to the way the dataset was collected. It appears that the data was not collected with replicates and in a kind of snapshot approach across a large river basin. It is therefore very challenging to standardise for hydrological conditions, time of day etc. when co-ordinating sampling from such a large basin. However, there should be some analyses and discussion around this point to explore how this might impact the results as presented. One of the aims of the study is to “investigate the spatial and temporal pattern of  $p\text{CO}_2$  and  $\text{CO}_2$  emission along stream size spectrum” – how would different sampling conditions affect this? Not enough context is provided to reassure the reader that artefacts of the sampling process are not driving at least some of the variability observed in this dataset.

360 Reply: We thank the reviewer's comments. It is challenging to sample from such a large basin. However, we have put great efforts into reducing the artefacts when designing the sampling strategy (Please refer to Lines 109–124 in the revised version of the manuscript for changes. ). We have carefully chosen the location and time of our fieldwork campaigns. In total, there were 43 sampling sites from seven Strahler stream orders, including 21 large rivers (i.e., fourth

to seven order streams, including mainstem and major tributaries) and 22 small rivers (i.e., first to third order headwater streams). Those sampling sites were widely distributed in the mainstem and nine major sub-basins with different topographic features and land cover (Figure 1 in Line 101 of the manuscript and Figure S4 in the supplementary).

In order to investigate CO<sub>2</sub> emissions under different hydrological conditions, we performed five fieldwork campaigns from December 2018 to October 2019, including three in the wet season (early wet season - late April, middle wet season - early July, and late wet season - late August) and two in the dry season (middle dry season - December 2018 to early January 2019 and early dry season - late October 2019). Sample sites were measured during the daytime over two weeks in each field trip. Three rounds of campaigns in the wet season allow each sample site to be measured under different hydrological conditions, and the two-week duration of each campaign allowed streams with different orders and sizes to be measured under various discharges. As for the dry season, the hydrological condition was relatively stable due to low precipitation.

However, there are some artefacts that we were unable to avoid. The possible impacts have been discussed in the revised version of the manuscript (Lines 124–126). For example, our sample sites were measured in the daytime which may lead to underestimate in *p*CO<sub>2</sub> and CO<sub>2</sub> emission (Reiman and Xu, 2019). nocturnal CO<sub>2</sub> emission rates in rivers could be 27% greater than the daytime rates (Gómez-Gener et al., 2021). We admit that artefacts of sampling have affected our dataset, but they are unlikely to drive the spatial and temporal patterns. Thank you so much for your insightful comments.

L55. Please indicate which references refer to which so that the reader can use this as a pointer towards specific studies which observed one or the other pattern.

Reply: Thank you for your advice. References have been changed accordingly. Now it reads “In addition, different rivers in this region may have contrasting trends in CO<sub>2</sub> dynamic due to different underlying controlling factors. Some rivers have the highest CO<sub>2</sub> efflux in the wet season (Li et al., 2013; Le et al., 2018; Ni et al., 2019), while others have the highest CO<sub>2</sub> efflux in the dry season (Luo et al., 2019)”. Please refer to Lines 55–56 in the revised version of the manuscript for changes.

L96. What type of forest? Just to clarify, these “plains and hills” are predominantly covered by this forest? Please provide some more information on the extent of coverage.

Reply: The dominant land use of the catchment is highly diverse evergreen forests of broad-leaved and needle-leaved species (Ran et al., 2012; Chen et al., 2013), accounting for about 64% of the river basin area. Please refer to Lines 94–96 in the revised version of the manuscript for changes.

L127. Please provide details of the flow meter, including accuracy etc.

Reply: Flow velocity was determined using a Global Water Flow Probe FP111 with a precision of 0.1 m s<sup>-1</sup>. Please refer to Line 137 in the revised version of the manuscript.

L130. Can you provide an indication of how big this underestimation might be?

410 Reply: Flow velocity measured near the bank could be about 40% of the maximum flow velocity at the crosssection (Moramarco et al., 2004; Le Coz et al., 2008). Please refer to Lines 140–142 in the revised version of the manuscript.

415 L142-3. These volumes are larger than what are typically used for headspace extractions. Did you test this method for accuracy compared to smaller volume methods or can you provide a reference to back up this approach? Mostly to confirm that full equilibration between water and headspace is occurring within 1 min of shaking.

420 Reply: Thank you for your advice. A comparative analysis of the small and large volume headspace method has been conducted to evaluate the accuracy of the headspace extraction method used in this study (Supplementary text1). Now it reads

425 “Both large volume bottle and small volume syringe were used in headspace equilibration method (Yoon et al., 2016). In this study, a 625 mL reagent bottle and a 100 ml syringe equilibrators were chosen for headspace extraction to investigate the impact of headspace volume and shaking time on the result of  $p\text{CO}_2$  measurement. For the bottle equilibrator, 400 ml of sample water was collected with 225 ml ambient air, while 50 ml of sample water was collected with 50 ml of ambient air for the syringe equilibrator. According to Hope et al. (1995), equilibrium in the headspace could be achieved after 1 min of vigorous shaking when adapting the rapid headspace analysis technique developed by Kling et al. (1991). However, 5–10 min were also used for  $p\text{CO}_2$  determination (Abril et al., 2015). Therefore, we measured the  $p\text{CO}_2$  value in the headspace after shaking the equilibrator for 1–5 min at the one-minute interval. The average of triple replicates was then calculated for comparative analysis (Table S2). The experiment showed that syringe and bottle equilibrator gave very consistent results. Overall, the average  $p\text{CO}_2$  value of syringe headspace was 1.2% larger than that of the bottle headspace, which was less than the 1.5% error of Li-850. However, it could take more time for a large volume equilibrator to achieve equilibrium. The  $p\text{CO}_2$  results of the small volume syringe headspace are not significantly different after more than two minutes of shaking, while it took the large volume bottle equilibrator three minutes to achieve a similar  $p\text{CO}_2$  value. Therefore, for rapid field measurement of surface water  $p\text{CO}_2$ , shaking for two minutes when using syringe headspace and three minutes when using the bottle headspace could yield reliable test results (Figure S3). In this study, we vigorously shake the bottle equilibrator for at least 1 minute (usually 1-3 minutes), which might cause a 1–5% underestimate of the  $p\text{CO}_2$  result. Furthermore, Koschorreck et al. (2021) found that reducing the headspace ratio could significantly increase the accuracy of the headspace method. Therefore, a large volume equilibrator might be more suitable for the field measurement since a low headspace ratio could be easier to achieve.

”

450 **Table S2** Comparison of measured  $p\text{CO}_2$  using two headspace extraction methods.

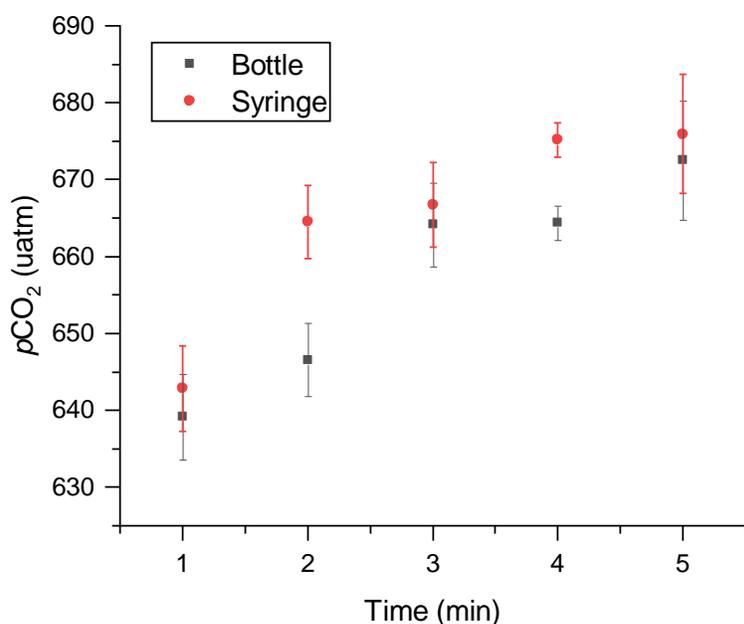
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Equilibrator	Shaking time
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		1 min	2 min	3 min	4 min	5 min
Bottle	test 1	637.9	642.3	669.1	664.6	673.1
	tes 2	645.3	651.7	658.2	666.5	680.0
	tese 3	634.4	645.8	665.2	662.1	664.6
	Average	639.2	646.6	664.2	664.4	672.6
Syringe	tes 1	640.6	662.7	664.9	681.5	681.5
	tes 2	639.5	670.4	670.4	674.8	680.3
	tes 3	648.4	660.5	664.9	669.3	666.0
	Average	642.8	664.5	666.7	675.2	675.9

Note, this table has also been added into the Supplementary.



455 **Figure S2** Measured  $p\text{CO}_2$  in headspace after shaking for 1-5 minutes. Note, this figure has also been added into the Supplementary.

L162. Think this is supposed to be eq 3.

Reply: Changed.

460 L189. Does this include replicates at any sites? Or were single measurements only of  $\text{FCO}_2$  and  $p\text{CO}_2$  undertaken at each site? It seems strange to omit any kind of replication at each

measurement site, so I would encourage the authors to explain why and discuss whether this lack of replication had any major impact on their findings.

465 Further, were sites measured all in the same day or over multiple days? If so, how might time of day or hydrologic conditions varied across these measurements within each campaign? I know you can't go back and fix any of these potential issues after the fact, but some discussion of potential issues here would be useful to convince the reader that these decisions made when designing the sampling strategy have not substantially impacted the data that is presented here.  
470 This is most concerning when I look at Table 1. The values appear very consistent across all the sites, yet the standard deviation compared to the means are very large in some cases.

475 Reply: The measurements of  $p\text{CO}_2$  at each site were repeated twice, and the average was then calculated to represent the surface  $p\text{CO}_2$ . The variation between the two measurements is less than 5%, and the accuracy of Li-850 is within 1.5% of the reading (Lines 158–160 in the revised version of the manuscript). However, for most sites, only one successful measurement of  $\text{FCO}_2$  was conducted. A successful chamber measurement could take several deployments because chamber could encounter obstacles or got stranded on underwater banks, especially in small rivers. Therefore chamber was deployed for multiple times until it can drift freely without being  
480 stopped by obstacles. We do conduct more than one successful measurement in several sites and the results were consistent. The drifting allowed chamber to measure the  $\text{FCO}_2$  along the reach, which could reduce the possible bias of conducting measurement at a single location. We understand that this is not an ideal sampling strategy, but it is unlikely having substantial impacts on the result. Considering that the chamber measurement is mainly used for the comparison of  
485  $k_{600}$  and  $\text{FCO}_2$  between dry and wet season and between small and large rivers, five measurements at each site (three in wet season and two in dry season) could still reflect  $\text{CO}_2$  emission under different hydrological conditions in streams with different sizes. For small rivers, 33 and 52 measurements were conducted in dry and wet season, respectively. For large river, 42 and 61 measurements were conducted in dry and wet season, respectively.

490 In order to investigate  $\text{CO}_2$  emissions under different hydrological conditions, we performed five fieldwork campaigns from December 2018 to October 2019, including three in the wet season (early wet season - late April, middle wet season - early July, and late wet season - late August) and two in the dry season (middle dry season - December 2018 to early January 2019 and early  
495 dry season - late October 2019). Sample sites were measured in the daytime over two weeks for each field trip. Three rounds of campaigns in the wet season allow each sample site to be measured under different hydrological conditions, and the two-week duration of each campaign allowed streams with different orders and sizes to be measured under various discharges. As for the dry season, the hydrological condition was relatively stable due to low precipitation.  
500 However, field measurements conducted during the daytime could lead to underestimate in  $p\text{CO}_2$  and  $\text{CO}_2$  emission (Reiman and Xu, 2019). nocturnal  $\text{CO}_2$  emission rates in rivers could be 27% greater than the daytime rates (Gómez-Gener et al., 2021).

505 L197. Change Q to “discharge”

Reply: Changed.

510 L225. What did this “strongest increase” actually relate to? Stream order is just a proxy for many things, including discharge, catchment characteristics etc. This is not fully discussed or addressed in the discussion.

515 Reply: Initially, we expected a gradual decrease or increase in  $p\text{CO}_2$  from low order to high order streams. However, we only observed a strong increase in  $p\text{CO}_2$  from the third order stream to the fourth order stream, it was stronger than any other two consecutive stream orders. Meanwhile, the first to third order streams have similar  $p\text{CO}_2$  values, and the fourth to seventh order streams have similar  $p\text{CO}_2$  values. As such, we discussed the underlying mechanisms that regulate the differences in the  $p\text{CO}_2$  between small rivers (the first to third order streams) and large rivers (the fourth to seventh order streams).

520 L245. Clarify the sentence here: “indicating that the majority of the river network is a carbon source”.

Reply: Changed.

525 L259. Not sure what this means, between wet vs dry seasons?

530 Reply: Thank you for your comment. Among five fieldwork campaigns, two of them were performed in dry season and three of them were performed in wet season. Here we compare the result between different campaigns in the same hydrological season. We have clarified it in the revised version of the manuscript. now it reads  
“However, comparisons between different phases in the same hydrological period (e.g., early, middle, and later wet season) did not differ significantly (paired sample t test,  $p > 0.05$ ) for both river size classes.” (Lines 278–280)

535 L264. High compared to what?

Reply: It is higher than other months.

540 L273. This too broad a statement to really be useful. This is dependent on the river and its setting etc. Perhaps rethink the purpose of this opening sentence and target it more directly to the immediate discussion.

545 Reply: Thank you so much for your advice. Based on your suggestion, we have reworded the statement to make it more specific and relevant to this study. Now it reads “The spatial pattern of  $p\text{CO}_2$  in the DJRB is likely resulting from changes in the intensity of in-stream metabolism.”. Then, we immediately started the discussion about how in-stream metabolism could differ in small and large rivers. Please also refer to Lines 293–294 in the revised version of the manuscript for the changes.

550 L310. Which “should” lead to a decrease? Because you then observed  $p\text{CO}_2$  to increase, rather than be diluted.

555 Reply: In small rivers, a decrease in  $p\text{CO}_2$  in July was observed, and it was likely the result of the  $\text{CO}_2$  depletion effect in soils combined with the dilution effect of precipitation. The dilution effect leads to a decrease in  $p\text{CO}_2$ . We have rephrased it in the revised version of the manuscript (Lines 353-355) Now it reads

560 “A decline in  $p\text{CO}_2$  in July in small rivers suggested that it might have experienced the depletion effect occurring at middle and late wet season (Hope et al., 2004), during which soil  $\text{CO}_2$  decreased due to the continual precipitation.”

RC: L322. Decomposition of organic carbon “within the water column” (internal DOC decomposition)?

565 Reply: Changed.

L331. Plenty of studies have indicated that DOC can be readily decomposed in headwater streams, e.g. Vonk et al. 2013 (doi: 10.1002/grl.50348), Dean et al. 2019 (doi:10.1029/2018JG004650).

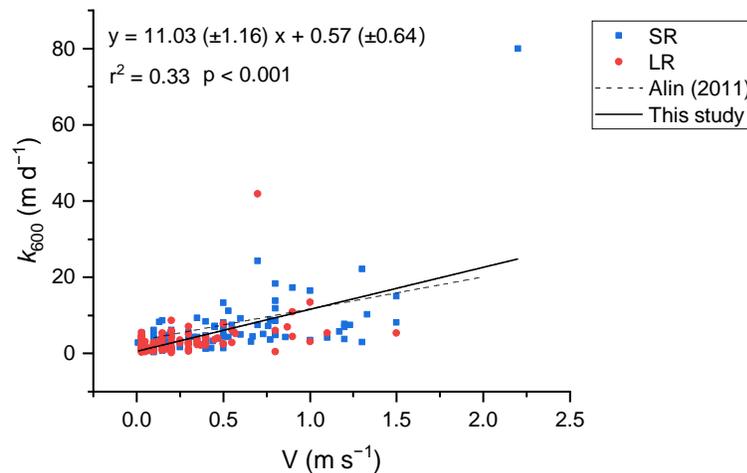
570 Reply: Thank you for your recommendation. Indeed, DOC can be readily decomposed in some headwater streams, but it also depends on their setting. Headwater streams in peatland or permafrost regions (Vonk et al., 2013; Dean et al., 2019) tend to have low gradients and more favorable conditions for DOC decomposition. In contrast, the headwater streams in the  
575 Dongjiang River basin usually have high channel gradient and high flow velocity due to a predominantly hilly landscape. Therefore, it will be more difficult for DOC to be decomposed here.

L334. Should you not then see a correlation between DOC and  $p\text{CO}_2$ ?

580 Reply: We have observed a positive relation between river water  $p\text{CO}_2$  and DOC (Figure 6b in the revised version of manuscript). Moreover, the discrepancy in seasonal changes of DOC and  $p\text{CO}_2$  was also observed in our data. Increased DOC in large rivers from January to April did not  
585 lead to the increase in  $p\text{CO}_2$ . A possible explanation for such phenomenon is that the effect of increasing DOC on  $p\text{CO}_2$  is confined by other factors that control the intensity of in-stream metabolism. For large rivers, relatively low temperature and short water residence time due to high flow velocity may have led to the low  $p\text{CO}_2$  in April despite increased DOC. Therefore, even though the higher  $p\text{CO}_2$  in large rivers relative to small rivers was associated with stronger  
590 in-stream metabolism, it might not be controlled by DOC concentration.

L343. In line with previous studies, e.g. Long et al. 2015 (doi: 10.1002/2015JG002955). Fig 8. I suggest repositioning the legend so that single blue dot is more obvious.

Reply: Thank you for your advice. The legend has been repositioned.



595

**Figure 9** Relationship between  $k_{600}$  and flow velocity. The dashed line represents the parameterization of (Alin et al., 2011).

600

L393. For all rivers? Or large rivers? Because the earlier discussion suggested internal production of  $\text{CO}_2$  was more important for the larger rivers.

605

Reply: A negative relationship between DO and  $p\text{CO}_2$  has been observed in both small and large rivers (Figure 6 in the revised manuscript), which suggests that internal production of  $\text{CO}_2$  occurs in both of them. Undersaturation of DO and supersaturation of  $p\text{CO}_2$  have been observed in both small and large rivers, which means that internal production of  $\text{CO}_2$  occurs in both small and large rivers, even though in-stream metabolism was more important for the large rivers (Figure 6 in the revised manuscript). In contrast, supersaturation DO and supersaturation  $\text{CO}_2$  occurred simultaneously in summer in the nearby Xijiang river (Yao et al., 2007), indicating that photosynthesis is stronger than respiration and other C sources should be responsible for high  $p\text{CO}_2$  concentration. Therefore, compared with Xijiang River, the contribution of internal production of  $\text{CO}_2$  on  $p\text{CO}_2$  is more obvious for both small and large rivers in the Dongjiang River Basin. Even though small rivers were also under the influence of lateral soil  $\text{CO}_2$  input.

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