

Dear Dr. Bouillon,

Thank you very much for the thoughtful review of our manuscript. Based on your and the reviewer's comments, we have further improved the manuscript. Please find below our point-by-point response (in bright blue) to the reviewer's comments. All changes have also been highlighted in yellow in the track change file of the manuscript. The line numbers refer to the lines in the revised version.

We hope that the revised manuscript will be acceptable for publication in Biogeosciences.

Thank you very much for your kind consideration.

With best regards

Lishan Ran, on behalf of all co-authors

Primary criticisms

The authors present a revised manuscript that now includes some analyses of the differences in river C by land-cover, which are welcomed. However, it is my view that the manuscript is still overly specific and confident about the origins and processes controlling CO₂ concentrations (*p*CO₂) when they do not have the data to rule out other explanations. Specifically, the authors still suggest that the spatial patterns observed are due primarily to in-stream metabolism.

Reply: Thank you very much for your comments. Based on your comments and suggestions, we have reframed the discussion on the drivers of the spatial pattern of the stream water *p*CO₂. Instead of focusing on the dominant role of in-stream metabolism, we now discuss how land-cover and catchment topography have affected the spatial pattern by influencing terrestrial carbon inputs and in-stream metabolism. Furthermore, based on your suggestions, we have reduced the certainty and discussed the potential impacts of other factors, including the higher soil respiration in cropland-impacted large river catchments, high gas exchange velocity in small rivers, and carbonate buffering. Please refer to Lines 293-361 in the revised version of the manuscript for the changes.

The land-use data they now present however, shows that the big and small rivers diverge in terms of %cropland/urban, with the larger rivers exhibiting higher proportions of impacted areas. The authors are correct that this could lead to higher inputs of labile DOC, but they do not provide evidence of this process. Further, higher soil respiration in these impacted zones could also generate higher soil CO₂, which is subsequently transported to the river.

Reply: Thank you very much for your suggestions. We have revised the discussion on the impact of land use on riverine *p*CO₂ by analyzing two processes that control the amount and lability of carbon transported from cropland to rivers. On one hand, cropland could provide a more favorable condition for soil erosion and the transfer of terrestrial carbon from land to rivers, contributing to a higher *p*CO₂. On the other hand, intensification of agricultural practices could promote the decomposition of soil organic matter, thereby increasing the concentration of CO₂ and labile DOC in the soil (Borges et al., 2018). The soil CO₂ could be easily transported to

45 rivers, while the liable DOC component could be decomposed rapidly after entering the rivers due to their sensitivity to in-stream metabolism (Lambert et al., 2017; Li et al., 2019). Therefore, we have discussed the possible impacts of both processes in explaining the high $p\text{CO}_2$ in cropland-impacted rivers in the revised manuscript and cited the references to support our arguments. Please refer to Lines 297-301 in the revised version of the manuscript for the changes.

50 In addition to land-use differences, the authors measured differences in k_{600} (gas transfer velocities) between the large and small rivers. It is well known that k_{600} and $p\text{CO}_2$ vary inversely (Rocher-Ros 2019, LOL), which also might explain the elevated $p\text{CO}_2$ concentrations in the larger rivers. In other words, in-stream metabolism might be very similar between
55 rivers/streams of all sizes, but simply the outgassing is higher in smaller and more turbulent streams, resulting in lower $p\text{CO}_2$. This seems in line with the similar $p\text{CO}_2/\text{O}_2$ trends the authors observed between the two size groups.

Reply: Thank you very much for your comment. We agree that the high k_{600} in small rivers could contribute to their relatively low $p\text{CO}_2$. Due to steeper slopes and higher flow velocities, small
60 rivers in the DJRB tend to have higher k_{600} . As a consequence, CO_2 in small rivers can emit into the atmosphere more rapidly, preventing the build-up of dissolved CO_2 and thus lower $p\text{CO}_2$. Therefore, based on your suggestions, we have discussed the impact of CO_2 emissions on riverine $p\text{CO}_2$ in small rivers. Please refer to Lines 317-321 in the revised manuscript for the changes. However, small rivers in the DJRB are much less turbulent than highly turbulent
65 streams (i.e., $k_{600} > 100 \text{ m d}^{-1}$) as reported by Rocher-Ros et al. (2019). The mean k_{600} values in small rivers of the DJRB were only $8.29 \pm 11.29 \text{ m d}^{-1}$ and $4.90 \pm 3.82 \text{ m d}^{-1}$ for the wet season and the dry season, respectively. Therefore, it is unlikely that the spatial pattern was primarily controlled by the outgassing of CO_2 from streams. Additional processes have facilitated the carbon transfer from small rivers to downstream large rivers, supporting the higher $p\text{CO}_2$ in large
70 rivers.

Indeed, we have observed a pronounced presence of in-stream metabolism in both small and large rivers. However, the difference in the $\Delta\text{CO}_2:\Delta\text{O}_2$ stoichiometry between small and large
75 rivers suggested the different strength of in-stream metabolism (Rasera et al., 2013). The $\Delta\text{CO}_2:\Delta\text{O}_2$ stoichiometry in large rivers is closer to the 1:1 line than that in small rivers, indicating that large rivers are more affected by the metabolic processes (Jeffrey et al., 2018; Amaral et al., 2020). For large rivers, the linear regression is $\Delta\text{CO}_2 = -0.999 (\pm 0.081) \Delta\text{O}_2 + 18.020 (\pm 5.995)$ ($r^2 = 0.62$, $p < 0.001$). When the CO_2 concentration increases in large rivers, a similar magnitude of decrease in dissolved O_2 concentration occurs, indicating that in-stream
80 metabolism is the primary control on $p\text{CO}_2$. In contrast, the linear regression for small rivers is $\Delta\text{CO}_2 = -0.868 (\pm 0.098) \Delta\text{O}_2 + 21.42 (\pm 4.175)$ ($r^2 = 0.41$, $p < 0.001$), which means that with the CO_2 concentration increasing by $1 \mu\text{mol L}^{-1}$, the O_2 concentration decreases by only $0.868 \mu\text{mol L}^{-1}$. Therefore, extra CO_2 inputs have contributed to the changes in $p\text{CO}_2$ despite the strong presence of in-stream metabolism. We have revised the manuscript by discussing the similarity
85 and differences between the two size groups regarding in-stream metabolism. Please refer to Lines 341-361 in the revised manuscript for the changes.

90 Lastly, alkalinity has been shown to buffer and create CO₂ over saturation in natural waters (Stets 2017). Based on the aggregated table 1, it seems like the larger rivers do indeed have higher alkalinity.

95 Reply: Thank you very much for your comment. We agree that alkalinity could buffer and create CO₂ oversaturation in natural waters. Carbonate buffering could decrease the CO₂ emissions in small rivers by increasing the ionization of CO₂, resulting in increased transfer of DIC and higher pCO₂ in downstream large rivers (Stets et al., 2017). However, strong carbonate buffering usually occurs in high-alkalinity (>2500 μmol L⁻¹) streams with high pH (>8), while in low-alkalinity waters, the pool of ionized CO₂ is relatively small, indicating a weak carbonate buffering (Stets et al., 2017). Since the streams in the DJRB are characterized by low alkalinity (726 ± 364 μmol L⁻¹ and 844 ± 409 μmol L⁻¹ for small and large rivers, respectively), carbonate buffering is unlikely a major contributor to the high pCO₂ in large rivers, even though slightly higher alkalinity has been observed in large rivers. We have discussed the possible impacts of carbonate buffering. Please refer to Lines 321-328 in the revised manuscript for the changes.

105 Ultimately, I think that some reframing is still needed, and the authors should be less certain with their interpretations around metabolism as the primary control given that a plethora of additional controls (listed above) could also affect pCO₂. Moreover, I'd recommend perhaps abandoning the artificially divide between small/large rivers and just use discharge to examine effects of river size.

110 Reply: Thank you very much for your comments and suggestions. We have revised the discussion on the drivers of the spatial and temporal patterns. We started with analyzing the impacts of land cover and catchment topography on the spatial pattern of pCO₂, then the temporal pattern and its responses to precipitation and temperature seasonality, before finishing on other minor controlling factors. Based on the referee's comment, we have further examined the impact of other factors, including k₆₀₀, carbonate buffering, and increased soil respiration in cropland. The interpretations around metabolism were also revised. Please refer to Lines 293-389 in the revised manuscript for the changes.

120 We fully agree with the reviewer that discharge could greatly alter pCO₂ and CO₂ emissions and is an important hydrological attribute to examine the effects of river size on stream water pCO₂ and CO₂ emissions. For the DJRB with a clear seasonal pattern in flow discharge, however, we noted that one river could be divided into different size groups in different seasons according to its discharge size. This may affect our discussion on the pCO₂ and CO₂ emission difference between small and large rivers. In addition, stream order has been commonly used as a parameter when upscaling CO₂ emissions from regional and global river networks (Butman and Raymond, 2011; Raymond et al., 2013; Marescaux et al., 2018). Consequently, the spatial and temporal distribution of pCO₂ and CO₂ emissions along the stream size spectrum have been widely used to estimate regional and global CO₂ emission flux. In this manuscript, we tend to retain the stream size based on the Strahler stream orders, but we will also consider the effect of discharge on pCO₂ and CO₂ emissions in our future studies. We are very grateful for your constructive and useful comments.

130 **Specific comments**

13 - Incorrect usage of "hinges"

Reply: Thank you for the comment. We have replaced the “hinges” with “prohibits”.

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16 - I still don't see the evidence for this claim in the paper

Reply: We have revised the discussion on the drivers of the spatial and temporal patterns. We started with analyzing the impacts of land cover and catchment topography on the spatial pattern of $p\text{CO}_2$, then the temporal pattern and its response to precipitation and temperature seasonality.

140 Please refer to Lines 292-388 in the revised manuscript for the changes.

24-25 - Is the lack of difference the total magnitude or the areal flux? Very different implications...

Reply: We apologize for the confusing statements. Small and large rivers have similar areal CO_2 fluxes. Small rivers have a higher gas transfer velocity (k) and lower $p\text{CO}_2$, while large rivers have a lower k value and higher $p\text{CO}_2$. We have further clarified this in the revised version of the manuscript, please refer to Line 24 for the change.

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56-57 - Is it necessarily runoff or could it be other seasonal factors (temp/plant seasonality/etc.)

Reply: Thank you very much for the comment. The rivers mentioned here are all located in the subtropical monsoon climate zone and have similar temperature and plant seasonality. The wet season has higher temperature and net primary productivity. Other factors may have affected the seasonal changes of $p\text{CO}_2$, but it is more likely that the increase of runoff during the wet season has contributed to the two distinct patterns of the $p\text{CO}_2$ dynamics. On one hand, recent studies have showed that the increased runoff could enhance external carbon inputs and thus CO_2 emissions in some rivers (Hope et al., 2004; Johnson et al., 2008). On the other hand, the increased runoff may result in a dilution of the dissolved CO_2 concentration in river waters (Ran et al., 2017; Li et al., 2018). We have further clarified this in the revised version of the manuscript, please refer to Lines 56-62 for the change.

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81-82 - I'd stick with either evasion or emission, for consistency

Reply: Thank you for your comment. We have replaced “evasion” with “emission” throughout the text.

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Figure 1 - The land-use areas do not make sense as currently displayed. Since this is one entire basin, the MDJRB should include the UDJRB areas and the LDJRB should include both since all upstream water flows into these lower parts of the basin... ultimately, the upstream land-cover should be calculated for each sampling point using the sub-catchment outlines.

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Reply: Thank you for your comment. The land-use area displayed in Figure 1 is mainly used to show the difference in land use from upstream to downstream. Considering most of our sample sites are located in tributaries, they are not under the influence of land use in the upper part of the basin. Thus, it may not be necessary to include the land cover in upper regions. For each sampling point, the upstream land cover has been calculated using the sub-catchment outlines as recommended by the referee.

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165 - Headspace is misspelled in the equation

Reply: Changed. Thank you very much for pointing this out.

297 - Do you mean decomposition here?

180 Reply: Yes, in the DJR, decomposition of OC is the primary form of in-stream metabolism. We have clarified this in the revised version of the manuscript. Please refer to Lines 383-388 for the changes.

185 297 - I don't think this is necessarily true! Many studies show higher rates of metabolism in small streams, which receive higher proportions of labile material from their proximity to recent terrestrial inputs.

190 Reply: Thank you very much for your comment. Indeed, DOC can be readily decomposed in some headwater streams, but it also depends on their setting. For example, the headwater streams in peatland or permafrost regions (Vonk et al., 2013; Dean et al., 2019) tend to have low gradients and more favourable conditions for DOC decomposition. In contrast, the headwater streams in the Dongjiang River basin usually have steep channel slopes and high flow velocities due to a predominantly hilly landscape. Therefore, it would be more difficult for DOC to be decomposed here. We have revised the discussion about OC decomposition in small rivers. Please refer to Lines 335-337 in the revised manuscript for the changes.

195 Also, I would use "Terrestrial organic carbon is" rather than the plural form.
Reply: Changed.

200 306 - I don't think it's appropriate to cite this reference in support of trends you are describing in your own study.

Reply: Thank you for your comment. We have removed the reference from the text.

205 307 - Here you cite Figure S3 but I think it should be Fig 7?

Reply: Changed. Thank you very much for pointing this out.

366- Should this be Figure 8?

Reply: Changed. Thank you very much for pointing this out.

210 371-374 - Are the y-intercepts statistically different? They are very close regardless...

Reply: Thank you very much for your comment. The p-value of the y-intercepts is 0.048, so they are statistically different. In order to clarify the differences between small and large rivers, we have substantially revised the discussion on the strength of in-stream metabolism in small and large rivers. Please refer to Lines 343-355 in the revised manuscript for the changes.

215 375- Abrupt transition after being so certain that metabolic processes govern $p\text{CO}_2$...

Reply: Thank you very much for your comment. Here we discussed why other factors are unlikely to be the primary process that govern the $p\text{CO}_2$ dynamics, which is consistent with our previous discussion about why the metabolic process is important for the $p\text{CO}_2$ dynamics.

220 377 - You do not have diel measurements so how do you know the effect of photosynthesis? Perhaps DO drops much lower at night?

225 Reply: Thank you very much for the comment. As the reviewer noted, because we did not conduct diel measurements, we cannot calculate the rates of aquatic photosynthesis and respiration in this manuscript. However, we can compare the effect of photosynthesis and in-stream metabolism based on the concentrations of DO and dissolved CO_2 . The unsaturated DO

indicates that the overall rate of respiration is higher than that of photosynthesis. Therefore, even if the DO drops much lower at night, it is unlikely that the rate of photosynthesis could be overwhelmingly higher than that of respiration at the daytime.

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