

Dear reviewer,

We are grateful to your comments on the manuscript. Based on your very constructive comments, we have thoroughly revised the manuscript. We have also responded below to all your comments. Please see below the details. Major revisions have also been highlighted in the revised manuscript in green color.

With best regards

Mingyang Tian, on behalf of the coauthors

The manuscript by Mingyang Tian and co-authors investigates the riverine partial pressure of CO<sub>2</sub> and CO<sub>2</sub> efflux in the source region of the Yellow River and differentiates between landscape types (glacier, permafrost, wetland and grassland). This approach is different than the most studies about CO<sub>2</sub> in rivers. Commonly studies compare streams/rivers by size or by climate zone (Marx et al. 2017, Lauerwald et al. 2015, Raymond et al. 2013). Thus, this study aims to improve the understanding of carbon dioxide emissions in alpine rivers, particularly in the Tibetan Plateau. Further, different methods to determine CO<sub>2</sub> degassing were applied: floating chambers and headspace equilibrium method. Unfortunately, the uncertainties of results from the different methods are hardly discussed.

Overall, in my opinion the work has a high potential to make a good contribution to the understanding of CO<sub>2</sub> emission in rivers. However, at present several aspects require extensive revision. That is why I cannot recommend this manuscript for publication in its present form. I recommend re-submission after thorough revision according to the points below.

Major comments:

(1) This promising paper is restricted to the Yellow River source regions and lacks moving beyond that. I recommend showing results in a global context.

Reply: We have added the discussion of global context into the revised manuscript.

Now it reads ‘While the Yellow River source region occupies 17.6% of the whole Yellow River basin, it accounts for only around 4% of the basin’s total CO<sub>2</sub> efflux (Ran et al., 2015a; 2015b). The CO<sub>2</sub> effluxes of the Yellow River source region is also small compared with the efflux from boreal river catchments (Teodoru et al., 2009; Butman and Raymond., 2011; Crawford et al., 2013; 2015; Kokic et al., 2015; Looman et al., 2016) or even smaller relative to the global CO<sub>2</sub> efflux (Aufdenkampe et al., 2011).’.

(2) The final version of the paper would benefit from editing for language. While it is generally understandable, several idiomatic expressions and mistakes hamper the readability. For instance, make sure the text is in past-tense and use “the” before plural and delete it if singular follows.

Reply: We have thoroughly polished the language throughout the text. Many thanks for your comments.

(3) I strongly recommend to discuss the reliability of your data. For instance, how were fluxes determined by chamber method compared to fluxes by equilibrium headspace method?

Reply: Thanks for your comments. We have discussed the reliability mainly through three parts. Firstly, we used two methods to evaluate riverine CO<sub>2</sub> emissions (i.e., determine *F*CO<sub>2</sub> with the floating chamber method and determine *p*CO<sub>2</sub> with Dickson et al. (2007)). Secondly, we discussed the calibrated *p*CO<sub>2</sub> against the *p*CO<sub>2</sub> based on CO2SYM. Finally, we discussed the reliability of two *k*<sub>600</sub> datasets (i.e., *k*<sub>600</sub> calculated with *p*CO<sub>2</sub> and *F*CO<sub>2</sub> data; *k*<sub>600</sub> determined by using the Model 5 of Raymond et al., (2012)).

Specific comments:

Abstract

Ln. 1: Don't use the same sentence to start the abstract and the introduction

Reply: This sentence has been rephrased.

Now it reads 'Under the context of climate change, studying CO<sub>2</sub> emissions in alpine rivers is important because of the huge carbon storage in these terrestrial ecosystems.'

Ln. 25: They mostly were a CO<sub>2</sub> source. I remember that you also showed negative fluxes.

Reply: This sentence has been reworded.

Now it reads 'The results showed that most of the rivers in the Yellow River source region were a net CO<sub>2</sub> source...'

Ln. 32: Be careful with "significant" as it indicates a statistical significance. Is that the case here? Otherwise replace.

Reply: Replaced with 'considerably'.

Ln. 32-33: Rephrase sentence it is difficult to understand.

Reply: Rephrased.

Now it reads 'Although the rivers in the Yellow River source region annually release little CO<sub>2</sub>, there is a high carbon evasion potential.'

Ln. 33-37: These sentences include general knowledge. Give some numbers or statements derived from your research, as this increases the impact of the paper.

Reply: Replaced, please see lines 34 to 37.

Now it reads 'Our study suggested that the dissolved organic carbon (DOC) in permafrost rivers ( $5.0 \pm 2.4$  mg L<sup>-1</sup>) is equivalent to that in peatland covered rivers ( $5.1 \pm 3.7$  mg L<sup>-1</sup>), and the DOC is mainly derived from old carbon stored in frozen soils. In addition, for glacial rivers with limited supply of exogenous carbon, the intensity of CO<sub>2</sub> emissions is still considerable. Therefore, with rising temperature due to global warming, increased CO<sub>2</sub> emissions in these regions should not be ignored for a better assessment of global riverine CO<sub>2</sub> emissions.'

## Introduction

Ln. 45: Researcher should not believe. General agreement/ consensus/ ...?

Reply: Replaced with 'Many researchers have argued that'.

Ln. 48-52: Please revise sentence as it is hardly readable.

Reply: Rephrased.

Now it reads 'Therefore, to more accurately estimate riverine CO<sub>2</sub> outgassing and understand its driving factors, more studies focusing on rivers in particular climates (i.e., alpine climate) and regions (e.g., headwater region or intermitted rivers) are strongly needed to gain deeper insights into global carbon balance processes.'

Ln. 55-57: Check Swakuchi et al. 2017. They included lower reaches of the amazon to global estimate by Raymond et al. (2013). This led to values of 2.58 petagrams (Pg) CO<sub>2</sub> yr<sup>-1</sup> for rivers and streams. See also Marx et al. (2017).

Reply: Added. And we have not only added the Swakuchi et al. (2017) result, but also the Lauerwald et al. (2015) into the revised manuscript.

Now it reads 'For example, recent global CO<sub>2</sub> outgassing fluxes from rivers and streams range from 0.65 to 3.2 P g C yr<sup>-1</sup> (Raymond et al., 2013; Lauerwald et al., 2015; Swakuchi et al. 2017; Drake et al., 2017), which are considerably higher than earlier estimate by Cole et al. (2007) (i.e., 0.23 P g C yr<sup>-1</sup>).'

Ln 57-60: This sentence is not clear. Do you mean there is a lack of direct measurement data? That is true. The studies you mention calculate pCO<sub>2</sub> from DIC/Alkalinity, pH and T, as this is the common method. There is a decent database (Hartmann et al. 2014), that was basis for global CO<sub>2</sub> emission estimates (Raymond et al. 2013; Lauerwald et al. 2015).

Reply: Thanks for your comments.

Now it reads 'A major reason for huge range is because of the absence of a global CO<sub>2</sub> outgassing database which includes direct CO<sub>2</sub> emission measurements over different rivers...'

Ln. 61: What do you mean by global river systems?

Reply: To make the statement clearer, we have reworded the statement.

It now reads 'More direct field measurements are therefore strongly needed to better refine global CO<sub>2</sub> efflux estimates.'

Ln. 73: Wrong word. This was not "concluded" but determined/measured.

Reply: Thanks for your kind reminding.

We have changed the 'conclude' to 'determined'.

Ln. 86: Statistically significant? Can you give a number?

Reply: We have removed the wording. Not it reads 'significant'.

Ln. 87-88: Do you compare autumn values here?

Reply: Yes, the comparison is conducted by Zhang et al. (2009). We have rephrased the statement.

Now it reads 'Zhang et al. (2009) measured  $F_{CO_2}$  of the Yellow River and concluded that the Yellow River waters were a source of atmospheric  $CO_2$  during autumn and the flux was about 0.0174 Tg C, which was similar to that of the Ottawa River but far less than that of the Amazon in autumn.'

Ln. 102: In the alpine rivers of the Yellow River?

Reply: The source region is only the alpine part of Yellow River.

Ln. 107-112: Good!

Reply: Thanks for your comments.

Material and methods

Later in the text you mention carbonate rocks/limestone. I recommend to provide data on bedrock geology in this section.

Reply: We have added the related description to revised manuscript.

Now it reads 'Its lithology is homogeneous and predominantly composed of shale and granite rocks (Chen et al., 2005).'

Ln. 138: analyses?

Reply: We have changed the 'analysis' to 'analyses'.

Ln. Accuracy of 0.004 for pH measurements in the field. Is that really realistic?

Reply: The accuracy of the WTW pH probe is  $\pm 0.004$ . During our field *in situ* pH measurement of river water, we recorded the pH value when the reading of the pH probe is stable, usually 2 minutes after being put into the river water. The recorded stable pH was used to represent the river water pH.

Ln. 150: This is basic knowledge: inorganic carbon species distribution dependency on pH (and temperature).

Reply: Yes, we consider most of the inorganic carbon as  $HCO_3^-$  when calculating the dissolved inorganic carbon species from alkalinity.

Ln. 153: Be consistent and add the country behind the company.

Reply: Added, USA.

The full citation reads 'Whatman GF/F, GE Healthcare Life Sciences, USA'.

Ln. 57: "Specific bottle" be more precise! Brown glass bottle? Volume?

Reply: We have provided a more detailed description of the sampling procedure. They are 100 ml amber glass vials.

Now it reads ‘...the remaining filtered water was transferred into 100 ml amber glass vials...’.

Ln 159: Germany

Reply: Corrected.

Ln. 160: Not less. “... precision better than ...”

Reply: Thanks for your comments, we have changed it to ‘precision better than’.

Ln. 162: Use Determination instead of calculation here.

Reply: Thanks for your comments, we have changed it to ‘determination’.

Ln. 164-165: Can you give a precision of the Li-7000 analyzer?

Reply: A precision better than 1%, added.

Now it reads ‘...which has a precision better than 1%...’.

Ln. 175-176: Were 6-10 mins sufficient to get data for a linear flux estimation?

Reply: Yes, the 6-10 minutes of chamber deployment is enough to determine the flux. Below is a screenshot of the slope of CO<sub>2</sub> concentration against time. We can see that there is a stable increasing trend of CO<sub>2</sub> concentration after a short turbulence. Therefore, we used the this steadily increasing trend as the slope (R<sup>2</sup> usually higher than 0.97) to determine the CO<sub>2</sub> outgassing flux.

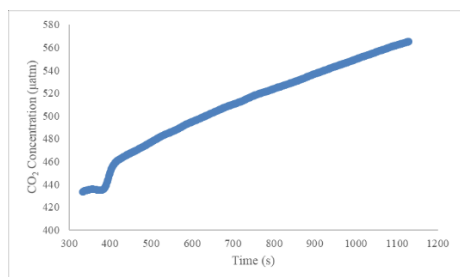


Figure. The screenshot of CO<sub>2</sub> concentration accumulation against time.

Ln. 181-190: A better description is needed here. The first equation is a linear approximation of CO<sub>2</sub> flux from chamber measurements. The second is mostly applied when *p*CO<sub>2</sub> is calculated from DIC/Alkalinity, pH and T. However, here it can be used to estimate *k*<sub>H</sub>.

Reply: Based on your comments, we have reworded the description. Firstly, we used the linear approximation of CO<sub>2</sub> flux from chamber measurements to calculate the CO<sub>2</sub> outgassing flux. Secondly, we used the Dickon et al., (2017) method to calibrate the headspace-based *p*CO<sub>2</sub>. Finally, we utilized the obtained CO<sub>2</sub> outgassing flux (i.e., *F*CO<sub>2</sub>) and river water *p*CO<sub>2</sub> to determine *K*<sub>600</sub>.

Ln. 200: “... blow±3

Reply: Thanks for your comments, we have corrected it to ‘analytical error below ±3%’.

Ln. 195-208: Good method. Did you ever apply chambers until equilibrium was reached? It would be interesting to see if results match.

Reply: Unfortunately, we did not apply chambers until equilibrium was reached because it would need around 1 hour for every chamber deployment. In our future field measurements, we will try to determine the river water  $p\text{CO}_2$  by waiting for the equilibrium and then compare the two methods. Many thanks for your suggestions.

## Results

Ln. 218-219: Please add the year.

Reply: We have added the year.

Now it reads 'The annual average air temperature in 2016 was  $16.7 \pm 6.3$  °C.'

Ln. 229: The last part of the sentence is interpretation and belongs to the discussion section.

Reply: Thanks for your comments, we have removed this sentence.

Ln. 244: This is new. You did not mention with in the MaterialMethods section! I thought you determined  $k_{600}$  by rearranging equation (2)? This belongs to the MaterialMethods section.

Reply: Thanks for your comments. We have added the description of citation of Raymond et al. (2012) method to the Section Material and Methods. In addition, we have moved this discussion part to the discussion section.

Ln. 245: Computed? From what? Chamber measurements? I guess with model results you refer to model 5 by Raymond et al. (2012).

Reply: Thanks for your comments. We have added the material methods about this.

Now it reads 'We also predicting the  $K_{600}$  ( $\text{m d}^{-1}$ ) through the Model 5 given by Raymond et al. (2012).

$$K_{600} = VS \times 2841 \pm 107 + 2.02 \pm 0.209$$

Where, V is the stream velocity ( $\text{m s}^{-1}$ ), S is the slope of rivers (unitless).

In addition, the large values we excluded are mostly concentrated on the modeled part. There are many factors affecting the  $K_{600}$ , such as wind speed, slope, flow velocity, depth, and discharge as mentioned above. Thus, using only flow velocity and slope of river channels would have caused overestimation for mountainous rivers due to their relatively high channel slope and thus higher flow velocity. Therefore, we have removed the extremely high  $K_{600}$  data points from analysis.'

Ln. 246: This belongs to the discussion, not results.

Reply: Thanks for your comments, we have moved this section to the discussion section.

Now it reads 'With respect to the  $k_{600}$ , the computed  $k_{600}$  showed statistically significant but weak correlation with the modeled results when the high  $k_{600}$  values ( $>70 \text{ m d}^{-1}$ ) were removed from analysis. Given the chamber's dampening effect of wind (Matthews et al., 2003), there was no any statistically significant relationship between wind and  $k_{600}$  for streams. Instead, flow

velocity is a relatively good predictor of  $k_{600}$  and can approximately explain 15% of its variability. Although we deployed the floating chamber very carefully, the statistical analysis could not reflect the complex interactions of various environment factors except the four land cover types through our 36 sampling sites. Additionally, it is worth noting that the Model 5 of Raymond et al. (2012) has overestimated the  $k_{600}$ , especially for mountainous rivers. This is probably because of low water temperature that has constrained CO<sub>2</sub> degassing although the steeper channel slope has caused stronger flow turbulence (Battin et al., 2008). A low temperature will limit the rate of Brownian motion and reduce the CO<sub>2</sub> exchange with the atmosphere. Meanwhile, a low temperature will increase the solubility of dissolved CO<sub>2</sub>, thus reducing the outgassing of CO<sub>2</sub>.

Ln. 249-251: This sentence is not understandable. Please rephrase. Be more precise: did you apply a statistical approach to determine relationships?

Reply: Yes, we did a linear statistical analysis of flow velocity and  $K_{600}$ , and conclude that it could represented 15% of  $K_{600}$  ( $r^2=0.15$ ).

Ln. 251-255: This belongs to the discussion, not results.

Reply: Thanks for your comments. We have moved this section to the discussion section.

Ln. 279: Statistically significant? Otherwise don't use "significant".

Reply: Thanks for your comments. We have removed this unappreciated word.

#### Discussion

Ln. 294: This is a poor beginning. Better describe the key result in a larger context "This study shows/demonstrates..." to create a red line for the forthcoming discussion.

Reply: Corrected.

It now reads 'This study shows that the lowest  $F_{CO_2}$  appeared in the permafrost covered region...'

Ln. 295: Be aware that not all the riverine CO<sub>2</sub> is derived from land. Your statement is not correct.

Reply: Yes, the aquatic plants and glacier water or groundwater support amount of river CO<sub>2</sub> in alpine river. Corrected.

It now reads 'It is well known that a large quantity of riverine CO<sub>2</sub> is derived from land...'

Ln. 310-312: Please revise this sentence.

Reply: Revised.

Now it reads 'One potential explanation is that its low temperature (i.e., annual average water temperature: 9.9 °C) because of high elevation may have constrained soil respiration and riverine organic matter degradation.'

Ln.314: Replace "not easy".

Reply: Replaced.

Now it reads 'it may be difficult for CO<sub>2</sub> to degas ...'.

Ln. 325-326: This sentence is vague and insignificant. Rephrase with details.

Reply: Rephrased.

Now it reads 'Wang (1998) discovered that these rivers are predominantly supplied by glacier melting that is characterized by significant seasonal variability.'

Ln. 326: Use past-tense.

Reply: Rephrased.

Now it reads 'The sampled glacier rivers showed the lowest annual average DOC concentration...'

Ln. 327-329: Rephrase sentence to increase readability.

Reply: Rephrased.

Now it reads 'This is probably because the sub-catchments around the Aemye Ma-chhen Range do not have sufficient vegetation coverage as a result of high elevation and low temperature, limiting the terrestrial source of DOC.'

Ln. 335: "highlights"

Reply: Rephrased.

Now it reads 'This suggests that the...'

Ln. 341-344: Rephrase this sentence.

Reply: Rephrased.

Now it reads 'Our observations found that, with increasing distance from the glaciers, the riverine pCO<sub>2</sub> exhibited a decreasing trend, which is likely caused by the dilution of glacier-related pCO<sub>2</sub>.'

Ln. 346-...: Use past-tense.

Reply: Corrected.

Now it reads 'The river FCO<sub>2</sub> was the highest in the peatland coverage area...'

Ln. 355: Sufficient for what?

Reply: Rephrased.

Now it reads '...which can provide enough riverine CO<sub>2</sub>.'

Ln. 366: "Analyses"

Reply: Thanks for your comments. We have changed 'analysis' to 'analyses'.

Ln. 367-368: The relationship between pCO<sub>2</sub> and pH is well known. This sentence is not correct, as the pH (and T) determines the species of inorganic carbon in water.



Reply: Thanks for your comments. We have corrected the unappreciated description.

Now it reads 'This also shows that  $p\text{CO}_2$  is partially affected by the water pH.'

Ln. 375-381: What makes you think that groundwater input is higher in grassland regions? If you give a statement like this, you need references. Groundwater samples are not sufficient evidence for this statement, as groundwater  $p\text{CO}_2$  typically are higher than stream  $p\text{CO}_2$ .

Reply: Rephrased.

Now it reads 'While stream DIC source are highly variable across space and time (Smits et al., 2017), most of the  $\text{HCO}_3^-$  in the Yellow River source region is derived from carbonate and silicate weathering (Wu et al., 2005; Wu et al., 2008; Wu et al., 2008), which largely reflects the contribution of groundwater inflow (Marx et al., 2017).'

Ln. 384: see comment Ln. 294:

Reply: Rephrased.

Now it reads 'This study demonstrates that the annual average  $p\text{CO}_2$  is...'

Ln. 401-403: There are several other potential reasons. How about pH changes (higher pH means less carbon in the form of  $\text{CO}_2$ )(Stets et al. 2017)? And how about decreasing proportion of groundwater distribution with increasing stream/river size (Marx et al. 2017)?

Reply: Thanks for your comments. We have added these potential reasons into the manuscript. It is common that a higher pH suggests a lower proportion of dissolved  $\text{CO}_2$  in the DIC species. There is usually an overestimation when using the pH-Alk system to determine the  $p\text{CO}_2$  (Abril et al., 2015). The pH values in our study area ranges from 7.89 to 9.02. Therefore, it should not be the reason for the underestimated  $p\text{CO}_2$ .

Ln. 411: "Easily neglected"?

Reply: Rephrased.

Now it reads 'Obviously, it is considerably challenging to detect the impact of groundwater inflow without high-resolution sampling.'

Conclusions

Ln. 445: Revise sentence. Verb missing?

Reply: Revised.

Now it reads 'In the permafrost region, the large amounts of terrestrially-derived DOC supported its high  $p\text{CO}_2$  levels. While in the glacier region, the glacial DOC and  $\text{CO}_2$  may have played an essential role in determining  $\text{CO}_2$  outgassing. In the peatland and grassland regions, decomposition of plant-derived organic matter is an important source of riverine  $\text{CO}_2$ . Finally, the ground water and chemical weathering are also played an important role in supporting riverine  $\text{CO}_2$  in the whole Yellow River source region.'

Ln. 451: Is this flux for the study area or the whole Yellow River?

Reply: Yes, corrected.

Now it reads ‘the riverine CO<sub>2</sub> efflux of the Yellow River source region was estimated...’.

Ln. 452: What is the number in Ran et al.? Is the number for the whole Yellow River?

Reply: The number determined by Ran et al., (2015 a, b) was  $-0.168 \pm 0.084 \text{ T g C yr}^{-1}$ . It is the estimated flux for the source region of the Yellow River only.

Table

Add the year somewhere. The table has to be understandable for itself. Revise subscripts and superscripts, as there are many mistakes.

Reply: We have added the year and corrected the subscripts and superscripts. Please see Table 1 for the additions.

Figure

Figure 1: Good!

Reply: Thanks for your comment.

Figure 2: (a) Are these mean values for all your data? Add a small paragraph in the Material Methods section where you explain your values? Use same names in the Figure title than for the axes labels. Add reference for modeled k<sub>600</sub> (Raymond?).

Reply: We have rephrased the title and added a reference of Raymond et al. (2012) into the revised manuscript.

(b) Which k<sub>600</sub> did you display here? Measured or modeled ones? Please clarify. The last sentence in your Figure title should be explained in the Material Methods section.

Reply: It is the *K*<sub>600</sub> measurements based on in situ *p*CO<sub>2</sub> and *F*CO<sub>2</sub>. We also add some explanation into material method section.

Figure 3: Add the dimension for fluxes. What for is the box (red, green) under the legend? Delete?

Reply: Deleted the box and the legend are easier to understand.

Figure 4: Write “Figure” with a capital letter at the beginning. Add the year in the Figure title.

Reply: Corrected and added the year.

Figure 5 and 6: Be consistent with brackets: Dimensions either inside or outside brackets.

Reply: Corrected, thanks for your comments.

Figure 7: (d) the a-axis label is not correct.

Reply: Corrected, thanks for your comments.

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