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

**Major comments**

The procedure to compute $pCO_2$ with the equation in L202 from the headspace measurements (prior and after equilibration) is incorrect and does not correspond to the one described by Dickson et al. (2007) (as stated by the authors). The major problem in the approach proposed in this equation is that it does not take into account the buffering capacity (due to the presence of HCO$_3^-$, or alkalinity) in the water sample. So, for a same $pCO_2$ in water (true value) and a same $pCO_2$ in air (initial value prior to shaking), the final $pCO_2$ in the headspace will be very different depending on the alkalinity of the sample. If we imagine a theoretical case of a near-infinite alkalinity water sample, then the final $pCO_2$ in the headspace will be nearly quasi-identical to the $pCO_2$ in water: due to the near-infinite buffering capacity, the solution will be able to adjust for the equilibration of the headspace and the water sample. This will not be the case of a zero-alkalinity sample, for which the final $pCO_2$ in the headspace will be intermediate between the “true” value and the $pCO_2$ in air prior to shaking.

Dickson et al. (2007) give in SOP4 (Determination of $pCO_2$ in air that is in equilibrium with a discrete sample of sea water) a procedure that relies on the readjustment of DIC to take into account the change of $pCO_2$ in the headspace that allows to re-compute “initial” $pCO_2$ from DIC and alkalinity, once DIC is corrected. Since the authors have alkalinity data, they have all of the data to make these computations that are easily achievable with a software to compute the CO$_2$ speciation such as CO2SYS. Also, the procedure to compute $pCO_2$ should take into account temperature variations between in-situ temperature and the final temperature at which equilibrium was achieved. It’s unclear how this was done and at which temperature the K0 in the equation L202 was computed. As the paper stands, I do not fully trust the $pCO_2$ data presented due to unclear computation procedure. Indeed, a systematic over-estimation of $pCO_2$ values could explain a systematic underestimation in the computation of k600 values that could explain why the computed k600 values are lower than those modelled (based on a parameterisation derived from tracer experiments) (Fig. 2).

Reply: We apologize for using this ambiguous equation as stated to mislead readers. We have provided a more detailed description of the equations (Lines 200 to 209). In fact, we have already considered the influence of alkalinity and have cited the method developed by Dickson et al. (2007). We have also considered the salinity indicator of fresh-water river systems and the calibration procedures of water vapor pressure. The reactions that take place...
when carbon dioxide dissolves in water can be represented by the following equilibria:

\[ \text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq) \]  
(1)

\[ \text{CO}_2(aq) + H_2O \rightleftharpoons H_2\text{CO}_3(aq) \]  
(2)

\[ \text{H}_2\text{CO}_3(aq) \rightleftharpoons H^+(aq) + \text{HCO}_3^-(aq) \]  
(3)

\[ \text{HCO}_3^-(aq) \rightleftharpoons H^+(aq) + \text{CO}_3^{2-}(aq) \]  
(4)

The notations \((g)\), \((l)\), and \((aq)\) refer to the state of the species, \(i.e.,\) a gas, a liquid, and in aqueous solution, respectively. The sum of the \(\text{CO}_2(aq)\) and \(\text{H}_2\text{CO}_3(aq)\) concentrations is expressed as \(\text{CO}_2^*(aq)\).

Redefining (1), (2), and (3) in terms of this species gives (5) and (6)

\[ \text{CO}_2(g) \rightleftharpoons \text{CO}_2^*(aq) \]  
(5)

\[ \text{CO}_2^*(aq) + \text{H}_2O(l) \rightleftharpoons H^+(aq) + \text{HCO}_3^-(aq) \]  
(6)

The equilibrium relationships between the concentrations of these various species can then be written as

\[ K_0 = [\text{CO}_2^*]/p\text{CO}_2 \]  
(7)

\[ K_1 = [H^+][\text{HCO}_3^-]/[\text{CO}_2^*] \]  
(8)

\[ K_2 = [H^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \]  
(9)

The calculation of \(\ln(K/k^o)\) is given by the expression (10) below (Weiss, 1974):

\[ \ln(K/k^o) = 93.4517 \left( \frac{100}{T/K} \right) - 60.2409 + 23.3585 \ln \left( \frac{T/K}{100} \right) 
+ S[0.023517 - 0.023656 \left( \frac{T/K}{100} \right) + 0.0047036 \left( \frac{T/K}{100} \right)^2] \]  
(10)

The calculation of \(\log_{10}(K_1/k^o)\) is given by the expression below (Lueker et al., 2000):

\[ \log_{10}(K_1/k^o) = - \frac{3633.86}{(T/K)} + 61.2172 - 9.67770 \ln(T/K) 
+ 0.011555S - 0.0001152S^2 \]  
(11)

The calculation of \(\log_{10}(K_2/k^o)\) is given by the expression below (Lueker et al., 2000):

\[ \log_{10}(K_2/k^o) = - \frac{471.78}{(T/K)} - 25.9290 + 3.169671\ln(T/K) 
+ 0.017815S - 0.0001122S^2 \]  
(12)

Where, \(k^o=1\) mol kg-soln\(^{-1}\), \(T\) is the temperature of the water, \(K\) is the kelvin of the water, \(S\) is the salinity.

The dissolved inorganic carbon content of water is defined as (13)

\[ C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]  
(13)

Redefining (7), (8), and (9) in terms of this species gives (13)
\[ pCO_2^{\text{headspace}, f} = pCO_2^{\text{headspace}, i} \times K_0 \times \left[ 1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} \right] \]  

(14)

Where, the brackets represent total concentrations of these constituents in solution (in mol kg\(^{-1}\)) and \([CO_2^*] \) represents the total concentration of all unionized carbon dioxide, whether present as H\(_2\)CO\(_3\) or as CO\(_2\).

The CO\(_2\) in water that emits into the headspace during the shaking process can be express:

\[ D_C = \frac{V_h}{V_w} \left( pCO_2^{\text{headspace}, f} - pCO_2^{\text{headspace}, i} \right)/(RT) \]  

(15)

Redefining (13), the original \(pCO_2\) of water could be calculated by (16)

\[ pCO_2 = \frac{C_T + D_C}{\left[ 1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} \right]} K_0 \]  

(16)

Finally, the \(pCO_2\) was corrected by water vapor pressure

\[ pCO_2^{\text{Correct}} = pCO_2^{\text{Dry}} \times (1 - pH_2O) \]  

(17)

Where, \(pCO_2^{\text{Dry}}\) is the corrected \(pCO_2\) value in dry air, \(pH_2O\) is the water vapor pressure over a water sample of given salinity at the temperature of equilibration, \(pCO_2^{\text{Correct}}\) is the final corrected \(pCO_2\).

Below is a screenshot of our calculation process shown as Figure 1.

Figure 1. The screenshot of raw \(pCO_2\) data calibration

Indeed, the exact contrary would be expected since floating chamber measurements with a fixed chamber lead to an enormous over-estimation of the flux measurements (Lorke et al. 2015).

Reply: Yes, there is an enormous over-estimation of the static chamber method. In fact, for large rivers with relatively favorable flow conditions (>2.5 m wide), we tied the chamber to a small rubber boat and freely drifted along the river course to measure the \(FCO_2\). Over the 36 sites, 32 (90%) of which we deployed the freely drifting chamber with a boat or pontoon. In contrast, we used the static chamber method to measurement the \(FCO_2\) in small and shallow rivers or streams (<2.5 m wide) which may have caused an overestimation of \(CO_2\) evasion to some extent (Lorke et al., 2015). Fortunately, we used the static chamber deployment method only at 4 sites, accounting for about 10% of the total sampling sites. To holistically analyze the \(CO_2\) dynamics from headwater small rivers/streams to the downstream large rivers, we have combined the \(FCO_2\) datasets from deployments of both freely drifting chamber and static chambers. We also realized the potential overestimation from the static chambers, therefore we have discussed the associated uncertainty in the revised manuscript.
**Specific comments**

L 20: I’m not sure that the large uncertainty on the estimate of riverine CO$_2$ emission is due to a lack of data “especially” in headwaters (as stated). There is a generalised lack of high-quality CO$_2$ data everywhere in rivers. Given that 80% of riverine emissions of CO$_2$ are in the tropics, I would assume that largest source of uncertainty is lack of data in tropical areas.

Reply: We completely agree with you. The largest proportion of riverine CO$_2$ emissions are in the tropics and it is critical for us to do more work in these regions. But for future research on the feedback of alpine riverine CO$_2$ emissions to global warming, it is also essential for us to investigate the current riverine CO$_2$ outgassing in this region. The studies on CO$_2$ emissions from the Yellow River were mainly confined to its middle and lower reaches and the estuary. In contrast, little has been done in its upper reaches, especially the source region on the Tibetan Plateau. The Yellow River source region is located in an alpine zone with the mainstream and its tributaries flowing through a variety of land cover types, including grassland, wetland, glacier, and permafrost. Affected by increasing temperature due to global warming, these alpine rivers have become hot spots of riverine carbon cycle studies and warrant a thorough understanding of their implications in the context of global climate change (Ulseth et al., 2018; Peter et al., 2014; Hood et al., 2015). In particular, although Ran et al., (2015a; b) have used compiled water chemistry data to estimate $p$CO$_2$ and $F$CO$_2$, there are no field-based direct measurements of CO$_2$ emissions from these alpine rivers.

L 45: Please rephrase. Researchers do not “believe”. They build theories and test hypotheses.

Reply: Rephrased.

Now it reads “Many researchers have argued that…”.

L 46: Emerging evidence (Abril et al. 2014) points to the importance of wetlands in driving riverine CO$_2$ emissions rather than “terrestrial ecosystems”, as these are conceptually different sources of carbon for rivers.

Reply: Thanks for your comments. We have added the related description into the revised manuscript.

Now it reads ‘Abril et al. (2014) pointed that wetlands are the primary source of riverine CO$_2$ emissions in the Amazon river…’.

L 55: Lauerwald et al. (2015) gives a global estimate of 0.65 Pg C yr$^{-1}$.

Reply: We have added this result to our revised manuscript.

Now it reads ‘…recent global CO$_2$ outgassing fluxes from rivers and streams range from 0.65 to 3.2 Pg C yr$^{-1}$…’.

L55: The value of 0.7 PgC/yr from Cole et al. (2007) is for all inland waters. Cole et al. (2007) give a value of 0.2 PgC/yr for rivers alone.

Reply: Thanks for your kind reminder. We have corrected the ‘0.75’ to ‘0.23’.

Now it reads ‘…higher than the earlier estimate by Cole et al. (2007) (i.e., 0.23 Pg C yr$^{-1}$).’.
L 64: studies instead of studied

Reply: Thanks for your suggestions. We have changed ‘studied’ to ‘studies’.
Now it reads ‘…there are limited studies on CO2 effluxes of rivers in extreme geographical and climatic conditions…’.

L78-79: can you please develop the differences of “underlying control mechanisms” for CO2 emissions between alpine climate and other climates? For me it’s the same mechanisms, but it’s just colder.

Reply: We agree with you. The lower temperature is one of the characteristics of the alpine climate. In addition, it has many other environmental characteristics, such as stronger sunshine, lower air pressure, and lower precipitation compared with other climates, which are the essential conditions for affecting riverine carbon transport.

Furthermore, export of DOC is important to riverine CO2 outgassing, and the sources of DOC are different. For example, in tropical wetland of the Amazon River system, Mayorga et al. (2005) find that respiration of contemporary organic matter (less than five years old) originating on land and near rivers is the dominant source of CO2 that drives outgassing in medium to large rivers. Abril et al. (2014) further showed that the flooded forests and floating vegetation export large amounts of carbon to river waters and the Amazonian wetlands export half of their gross primary production to river waters as dissolved CO2 and organic carbon. For the Wuding River flowing through arid and semi-arid Loess Plateau in north China, Ran et al. (2017) concluded that lateral carbon derived from soil respiration and chemical weathering played a central role in controlling the variability of riverine pCO2. For the Wuding River, Ran et al. (2018) also showed that enhanced organic matter inputs from agricultural tillage in spring and from terrestrial ecosystems in summer are the major sources of riverine carbon, and radiocarbon analysis suggests the release of old carbon previously stored in soil horizons.

Globally, approximately 13% of the annual flux of glacier dissolved organic carbon is a result of glacier mass loss. These losses are expected to accelerate, leading to a cumulative loss of roughly 15 teragrams (Tg) of glacial dissolved organic carbon by 2050 (Hood et al., 2015). The storage of soil organic carbon in the Arctic and subarctic regions is about 1672 Pg, accounting for about half of the global soil carbon storage (Ping et al., 2008, Tarnocai et al., 2009). And the DOC transported from the permafrost to the Arctic Ocean by large rivers accounts for 11% of the global river DOC flux (Finlay et al., 2006). Unlike other areas, the glacier and frozen soils are important DOC sources in boreal regions which could have strong response to global warming.

L93-102: Ran et al. (2017) reports very extensive data-set in the Wuding River (part of the Yellow river basin) with data obtained at altitudes up to 1340m. So, some information is already available.

Reply: Thanks for your comments. The carbon dynamics in the semi-arid Wuding catchment
has been compared to that in the Yellow River source region. We have added a comparative analysis into the revised manuscript.

Now it reads ‘Ran et al. (2017) further studied the Wuding River, a tributary of the middle Yellow River, and concluded that lateral carbon derived from soil respiration and chemical weathering played a central role in controlling the riverine $\rho$CO$_2$. In addition, radiocarbon analyses of the degassed CO$_2$ suggest the release of old carbon previously stored in soil horizons (Ran et al., 2018).

L 155: The determination of end-point with Methyl orange indicator seems a bit crude. Can you please state the estimated accuracy of the method? Did you check the accuracy with standards made of NaCO$_3$?

Reply: Yes, we have checked the accuracy with NaCO$_3$ standards before each experiment. Total alkalinity was determined by triplicate titrations in the field with 0.1 M HCl, and methyl orange was used as the indicator, following the standards as suggested by APHA (1999, Standard Methods for the Examination of Water and Wastewater). Our field triplicate titration results are highly consistent with the difference between the three results generally less than 3%. Thus, we expected that the obtained alkalinity results are reliable with high confidence. Finally, DIC was calculated from total alkalinity, pH, and temperature by using the program CO$_2$calc. Because the measured pH varied from 7.0 to 9.0, the calculated DIC was approximately equal to alkalinity, with >96% of the alkalinity composed of HCO$_3^-$, consistent with the relative speciation (%) of CO$_2$, HCO$_3^-$, and CO$_3^{2-}$ in water as a function of pH (please refer to Figure 2 below). In fact, the concentration of required HCl we prepared was usually not exactly 0.1M because of manmade errors. In this case, we used NaNO$_3$ standards to calibrate the HCl concentration prior to titration. Therefore, the actual HCl concentration was usually 0.098 or 0.099 M, and we used this number (0.098 or 0.099), instead of 0.1, for the titration calculation.

Figure 2: Relative concentrations of the different inorganic carbon compounds against pH.

L 245: You cannot conclude that the dampening effect of chambers is responsible for the lack of correlation between wind and K600. If $k_600$ is overwhelmingly driven by other processes than wind, then you would also arrive at a lack of correlation irrespective of a dampening effect.

Reply: There are many factors affecting the gas transfer velocity, e.g., wind speed, flow velocity, depth, slope, discharge etc (Wanninkhof et al., 1992; Zappa et al., 2007; Raymond et
al., 2012). Below are the linear relations between these factors and $K_{600}$.

The results show that, slope and flow velocity show a relatively positive relationship with the $K_{600}$. This means that all these factors did not overwhelm the flow velocity in affecting the gas transfer velocity. Previous studies indicate that there are two main reasons for the overlooking in the relationships between gas transfer and wind speed. Firstly, the short-term monitoring of wind speed is less stable than long-term averaged winds to estimate gas transfer velocities. Another factor frequently overlooked is that the chemical enhancement of CO$_2$ exchange will increase CO$_2$ fluxes at low wind speeds (Wanninkhof et al., 1992). Small-scale waves have been suggested as a dominant mechanism for $k_{600}$ (Bock et al., 1999). Surface contamination by thin organic films measured in the field has also been shown to dampen high frequency waves and leads to reduced gas exchange (Frew et al., 2004). Less dependence of $k$ is observed on wind speed under conditions when buoyancy dominates the production of turbulence in the near-surface layer (McGillis et al., 2004). During very low winds, gas exchange is controlled by tide-driven surface turbulence within the aqueous surface boundary layer in rivers and estuaries. (Zappa et al., 2007). Overall, the dampening effect is likely the
reason for the obscure linear relationship between wind velocity and $k_{600}$.

L 252: clarify statement “mainly due to the water temperature played a crucial role in limiting CO$_2$ transfer between the air-water interface”. Since the gas transfer is normalized to Schmidt number of 600, this automatically removes the effect of water temperature. 
Reply: Here we argue that a low temperature condition will have two effects on the CO$_2$ emission from river water. Firstly, the low temperature conditions limit the rate of Brownian motion and reduce the exchange of CO$_2$ across the water-air interface. Secondly, low temperatures will increase the solubility of the gas in water, which reduces the outgassing of CO$_2$. A clearer description has been replaced in the manuscript. Now it reads ‘A low temperature will limit the rate of Brownian motion and reduce the CO$_2$ exchange with the atmosphere. Meanwhile, a low temperature will increase the solubility of dissolved CO$_2$, thus reducing the outgassing of CO$_2’.”.

L 303: the relationship between $p$CO$_2$ and DOC can also indicate that both have a common origin such as (simultaneous) inputs from soils. It does not imply that DOC “supports” CO$_2$ production as stated. 
Reply: Thanks for your comments. The unappreciated description has been removed because we did not perform related experiments about riverine CO$_2$ source.

L 349: Abril et al. (2014) report on the influence of floodplain lakes on CO$_2$ dynamics in the Amazon rivers, not "peatland rivers" as stated. 
Reply: Thanks for your comments. The uncorrected citation has been removed.

L 349: Hu et al. 2015 is missing from the reference list. I assume it’s Hu 2005, that seems to correspond to a PhD thesis from one of the co-authors, possibly based on part of the data reported in this paper, so corresponding to circular auto-citation. 
Reply: Sorry for having listed the reference Hu (2005) in an incorrect order. The Hu (2005) is a Master thesis work in the same research area and does not belong to any co-authors. The corrected order has been listed in the reference.

L375: rephrase “Although groundwater is participated” 
Reply: Rephrased. 
Now it reads ‘In addition, DIC is an important source of riverine CO$_2$ for grassland rivers. While stream DIC source are highly variable across space and time (Smits et al., 2017), most of the 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).’.

Legend of figure 2: On what grounds did you exclude $k_{600}$ data above 70 m/d? It is very awkward to exclude data without justification. 
Reply: The large values we excluded are mostly concentrated on the modeled part. There are
a number of 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. We have provided a detailed justification in the revised manuscript, and now it reads '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, the extremely high $k_{600}$ values calculated from Raymond et al. (2012) Equation (18) were excluded from the comparison between our calculated $k_{600}$ and the modeled $k_{600}$.

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

(18)

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

In figures 5-8 it could be useful to plot $p$CO$_2$ versus water temperature.

Reply: Below is the linear relation between water temperature and $p$CO$_2$.

![Graph showing the linear relation between water temperature and $p$CO$_2$.]

It is known that water temperature could play an important role in controlling riverine organic matter degradation (Battin et al., 2008), but the analysis in complex river network structures and land cover types (i.e., glacier, permafrost, wetland, and grassland) did not showed a statistically significant linear relationship. Thus, we did not add this figure into our revised manuscript.

References


