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Interactive comment on "Gas transfer velocities of CO_2 in subtropical monsoonal climate streams and small rivers" *by* Siyue Li et al.

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General comments: The paper "Gas transfer velocities of CO2 in subtropical monsoonal climate streams and small rivers" appears to be something of a companion piece to "Riverine CO2 supersaturation and outgassing in a subtropical monsoonal mountainous area (Three Gorges Reservoir Region) of China" https://doi.org/10.1016/j.jhydrol.2018.01.057 published in the Journal of Hydrology. In this current submission, the authors present k calculated from floating chamber flux measurements and using models, and discuss the implications of the differing approaches to k for making regional scale flux estimates. Using chambers to determine CO2 fluxes, the authors then use pCO2 to derive the gas transfer velocity. These flux-derived k values are compared to modeled k values. It is good to see the spatial

aspects of the gas transfer velocity addressed. However, I do not feel that there is an adequate consideration of the uncertainty in the estimates/calculations provided. For the flux-derived k values, there is little provided in terms of uncertainty assessments.

Response: We thanked the referee for the comment. In our previous article, we studied the pCO2 and emission rate as well as their controls from fluvial networks in the TGR area, which is based on two field works in the TGR region, and the diffusive models from other studies were used. In this study, we attempted to derive k levels and develop the gas transfer model in this area (mountainous streams and small rivers) for more accurate quantification of CO2 areal flux, and also to serve for the fluvial networks in the Yangtze River or others with similar hydrology and geomorphology. In addition, we did more detailed field study in the two contrasting rivers Daning and Qijiang for developing models (see the sampling locations map). This study clearly showed original contribution to the current literature and this study is different than the article published in the Journal of Hydrology. We clearly state the new contributions and significances in the last paragraph of the "Introduction" as follows.

"Our recent study preliminarily investigated pCO2 and air – water CO2 areal flux as well as their controls from fluvial networks in the Three Gorges Reservoir (TGR) area (Li et al., 2018). The past study was based on two field works, and the diffusive models from other continents were used. In this study, we attempted to derive k levels and develop the gas transfer model in this area (mountainous streams and small rivers) for more accurate quantification of CO2 areal flux, and also to serve for the fluvial networks in the Yangtze River or others with similar hydrology and geomorphology. Moreover, we did detailed field campaigns in the two contrasting rivers Daning and Qijiang for models (Fig. 1). The study thus clearly stated distinct differences than the previous study (Li et al., 2018) by the new contributions of specific objectives and data supplements, as well as wider significance."

We added a section (4.4.) for "Uncertainty assessment of pCO2 and flux-derived k values" in the part of "Discussion".

The uncertainty of flux-derived k values mainly stem from air–water gradient of CO2 (ΔpCO2 in ppm) and flux measurements (Golub et al., 2017; Lorke et al., 2015; Bodmer et al., 2016). Thus we provided uncertainty assessments caused by dominant sources of uncertainty from measurements of aquatic pCO2 and CO2 areal flux since uncertainty of atmospheric CO2 measurement could be neglected.

In our study, aquatic pCO2 was computed based on pH, alkalinity and water temperature rather than directly measured. Recent studies highlighted pCO2 uncertainty caused by systematic errors over empiric random errors (Golub et al., 2017). Systematic errors are mainly attributed to instrument limitations, i.e., sondes of pH and water temperature. The relative accuracy of temperature meters was ±0.1 0C according to manufacturers' specifications, thus the uncertainty of water T propagated on uncertainty in pCO2 was minor (Golub et al., 2017). Systematic errors therefore stem from pH, which has been proved to be a key parameter for biased pCO2 estimation calculated from aquatic C system (Li et al., 2013; Abril et al., 2015). We used a high accuracy of pH electrode and the pH meters were carefully calibrated using CRMs, and in situ measurements showed an uncertainty of ±0.01. We then run an uncertainty of ±0.01 pH to quantify the pCO2 uncertainty, and an uncertainty of ±3% was observed. Systematic errors thus seemed to show little effects on pCO2 errors in our study.

Random errors are from repeatability of carbonate measurements. Two replicates for each sample showed the uncertainty of within ±5%, indicating that uncertainty in pCO2 calculation from alkalinity measurements could be minor.

The measured pH ranges also exhibited great effects on pCO2 uncertainty (Hunt et al., 2011; Abril et al., 2014). At low pH, pCO2 can be overestimated when calculated from pH and alkalinity (Abril et al., 2014). Samples for CO2 fluxes estimated from pH and alkalinity showed pH average of 8.39±0.29 (median 8.46 with quartiles of 8.24-8.56) (n=115). Thus, overestimation of calculated CO2 areal flux from pH and alkalinity is likely to be minor. Further, contribution of organic matter to non-carbonate alkalinity is likely to be neglected because of low DOC (mean 6.67 mg/L; median 2.51 mg/L) (Hunt

et al., 2011; Li et al., 2013).

Recent study reported fundamental differences in CO2 emission rates between anchored chambers (ACs) and freely drifting chambers (DFs) (Lorke et al., 2015), i.e., ACs biased the gas areal flux higher. However, some studies observed that ACs showed reasonable agreement with other flux measurement techniques (Crawford et al., 2013; Galfalk et al., 2013), and this straightforward, inexpensive and relatively simple method AC was widely used (Ran et al., 2017). Water-air interface CO2 flux measurements were made using ACs in our studied streams and small rivers because of relatively high current velocity; otherwise, floating chambers will travel far during the measurement period. In addition, inflatable rings were used for sealing the chamber headspace and submergence of ACs was minimal, therefore, our measurements were potentially overestimated but reasonable.

pCO2 was not measured, but rather was computed based on pH, alkalinity and temperature. This would have large uncertainties that then propagate into k estimates. Golub et al. (2017, doi: 10.1002/2017JG003794) note that "freshwater researchers must make significant efforts to standardize and reduce errors in pCO2 predictions". I encourage the authors to undertake a more systematic uncertainty analysis for their pCO2 values and propagate this error into uncertainty estimates for k.

Response: Thanks for the comment. We reported the quality control such as systematic errors and random errors of pH and alkalinity, water temperature, as well as non-carbonate alkalinity effects. Please refer to the response above.

Further, the authors here excluded deriving k values for samples that did not have a very large gradient in CO2 across the air-water interface. The authors chose 110 uatm as the threshold for excluding data, but this was presented without any indication of choice of threshold, making it appear rather arbitrary. Given the pH of the rivers sampled and the pCO2 that was at times undersaturated, this appears rather problematic in that it introduces bias that carries through to the regional estimates provided.

Response: We addressed this issue as follows. “Prior to statistical analysis, we excluded k600 data for samples with the air-water pCO2 gradient <110 μatm, since the error in the k600 calculations drastically enhances when âŰşpCO2 approaches zero (Borges et al., 2004), and datasets with âŰşpCO2 >110 μatm provide an error of <10% on k600 computation (see Fig. 1 as follows)”

The additional section 4.4 Uncertainty assessment of pCO2 and flux-derived k values included uncertainty of pH and scaling-up estimation, for example, effects of chemical enhancement for quite high pH values.

The authors in this paper refer to their k values as “observed”, but these are in fact derived, and so need to have uncertainty better characterized. Upscaling from X floating chamber measurements to a river network draining 58000 km2. How many flux measurements were made with floating chambers is not clearly stated, but it appears to be about 100 all made during summer 2016. Going from summer measurements for 100 points to annual estimates for 58000 km2 also requires some consideration of error propagation and bias. Fluxes were only retained when the floating chambers yielded linearly increasing CO2 against time, which again biases against low flux locations.

Response: We have changed “observed, or measured” to “flux-derived or derived”, and discussed the uncertainty of k values as mentioned above. We agreed that more samples could improve the CO2 estimates, while our sampling locations were much more or at least comparable to the other publications.

A total of 115 discrete grab samples were collected (each sample consisted of three replicates). Floating chambers with replicates were deployed in 101 sites (32 sampling sites in Daning, 37 sites in TGR river networks and 32 sites in Qijiang). The sampling period covers spring and summer season, our sampling points are reasonable considering a water area of 433 km2. For example, 16 sites were collected for Yangtze system to examine hydrological and geomorphological controls on pCO2 (i.e., Liu et al., 2017), and 17 sites for dynamic biogeochemical controls on riverine pCO2 in the

Yangtze basin (Liu et al., 2016, Global Biogeochemical Cycles).

In our sampling points, all measured fluxes were retained since the floating chambers yielded linearly increasing CO2 against time following manufacturer’ specification.

Liu, S., Lu, X.X., Xia, X., Yang, X., Ran, L., 2017. Hydrological and geomorphological control on CO2 outgassing from low-gradient large rivers: An example of the Yangtze River system. Journal of Hydrology 550, 26-41.

Of the attempted flux measurements, what fraction was discarded?

Response: We revised as follows. “Prior to statistical analysis, we excluded k600 data for samples with the air-water pCO2 gradient <110 μatm, since the error in the k600 calculations drastically enhances when âŰşpCO2 approaches zero (Borges et al., 2004; Alin et al., 2011), and datasets with âŰşpCO2 >110 μatm provide an error of <10% on k600 computation. Thus, we discarded the samples (36.7% of sampling points with flux measurements) with âŰşpCO2 <110 μatm for k600 model development, while for the flux estimations from diffusive model and floating chambers, all samples were included.”

Finally, a minor point is that the authors state several times that theirs is the first determination of k for subtropical streams and small rivers. I would point the authors towards global syntheses on CO2 evasion as well as individual studies that include k estimates.

Response: We agree the comment, and addressed this issue. Several sentences for implication of k determination and comparison with other k studies were added in the part of Discussion. We also re-organised and added sub-headings of “Discussion”.

“4.1. Determined k values relative to world rivers; 4.2. Hydraulic controls of k600; 4.3. Implications for large scale estimation; 4.4. Uncertainty assessment of pCO2 and flux-derived k values”

Minor comments The figure S1 does not show the sample locations within the Daning or Qiijiang basins. These may be the same locations as Figure 1 in Li et al. (2018)

Journal of Hydrology doi: 10.1016/j.jhydrol.2018.01.057?

Response: The sampling sites and study aims are different than previous study (Please refer to the section of 2.1 and the last paragraph in the "Introduction"). In the revised Ms, we supplied the map of sampling locations in the main text as Fig. 1.

We added several sentences in the section of "INTRODUCTION" to highlight the differences between our study and previous study, as well as what is advanced by this study (please refer to the first Comment).

There are a number of grammatical issues throughout the paper that the authors should address.

Response: We carefully edited English, and also get helps from a native English scientist.

The additional Table was added to the Table S2 in SOM.

We also provided tracked PDF as supplement for your review.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-227/bg-2018-227-AC1-supplement.pdf

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Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-227, 2018.

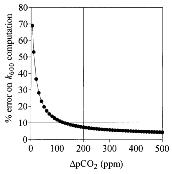

Fig. 1. Theoretical error (±%) on the computation of the gas transfer velocity of CO_2 (k600) as a function of the air–water gradient of CO_2 (ΔpCO_2 in ppm), assuming a constant uncertainty on ΔpCO_2 of ±3% (Borges et al., 2004).

Fig. 1.

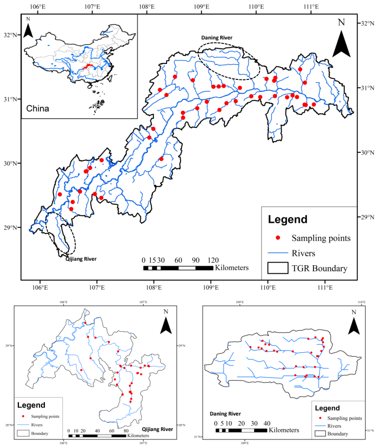

Fig. 1. Map of sampling locations of major rivers and streams in the Three Gorges Reservoir region, China (Please see in the main text).

Fig. 2.

The additional Table was added to the Table S2 in SOM.

	Current velocity m/s	Water depth m/s	Wind speed m/s	K600 cm/h	Reference
Mekong tributary	0.39±0.28	0.9±0.6	0.7±0.6	23.3±17.3	Alin et al., 2011
Yellow	1.8		1.8 (1.2-2.3)	42±17	Ran et al., 2015
Yangtze	1.2±1.5		1.2±1.1	38±40	Liu et al., 2017
Mekong stem	0.92±0.42		1.8±1.2	15±9	Alin et al., 2011

Fig. 3.