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Interactive comment on "High Riverine CO_2 Outgassing affected by Land Cover Types in the Yellow River Source Region" *by* Mingyang Tian et al.

Anonymous Referee #1

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Major comments

The procedure to compute pCO2 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 HCO3-, or alkalinity) in the water sample. So for a same pCO2 in water (true value) and a same pCO2 in air (initial value prior to shaking), the final pCO2 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 pCO2 in the headspace will be nearly quasi-identical to the pCO2 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 pCO2 in the headspace will be intermediate between the "true" value and the pCO2 in air prior to shaking.

Dickson et al. (2007) give in SOP4 (Determination of pCO2 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 pCO2 in the headspace that allows to re-compute "initial" pCO2 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 CO2 speciation such as CO2SYS.

Also, the procedure to compute pCO2 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 pCO2 data presented due to unclear computation procedure.

Indeed, a systematic over-estimation of pCO2 values could explain a systematic under-estimation 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). 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).

Specific comments

L 20 : I'm not sure that the large uncertainty on the estimate of riverine CO2 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.

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

L46: 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 difference sources of carbon for rivers.

L 55: Lauerwald et al. (2015) gives a global estimate of 0.65 PgC 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.

L 64: studies instead of studied

L78-79: can you please develop the differences of “underlying control mechanisms” for CO_2 emissions between alpine climate and other climates? For me it’s the same mechanisms, but it’s just colder.

L93-1002: 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.

L 155: The determination of end-point with Methylorange indicator seems a bit crude. Can you please state the estimated accuracy of the method ? Did you check the accuracy with standards made of $NaCO_3$?

L 245: You cannot conclude that the dampening effect of chambers is responsible for the lack of correlation between wind and K600. If k600 is overwhelmingly driven by other processes than wind, then you would also arrive at a lack of correlation irrespective of a dampening effect.

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.

L 303: the relationship between pCO_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.

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.

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.

L375: rephrase “Although groundwater is participated”

Legend of figure 2: On what grounds did you exclude k600 data above 70 m/d ? It is very awkward to exclude data without justification.

In figures 5-8 it could be useful to plot pCO_2 versus water temperature.

References

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Discussion paper