Interactive comment on "Dynamics of riverine CO$_2$ in the Yangtze River fluvial network and their implications for carbon evasion" *by* Lishan Ran et al.

Anonymous Referee #1

Received and published: 13 January 2017

Lishan Ran and colleagues present an anaylsis of the spatial pattern in riverine pCO2 in Yangtze River basin which is representative for the time before increased anthropogenic presure by river damming operations and land-use change since the 1980's. They anaylse the correlations between Ca and Si concentrations vs pCO2 and alkalinity for different stations. They also report the long-term decrease in pCO2 and the seasonality in riverin pCO2 in the mainstem of the Yangtze river for that time. The study is, to my knowledge, novel and of interest for the scientific community. The subject would fit well within the scope of Biogeosciences. The MS is well written in most of it's parts. Methods are clearly described, figures and tables are informative. I just feel that a few more anaylsis could easily be done to make the whole study complete. That

includes a more quantitaive analysis of environmental controls of the spatial patterns in riverine pCO2, which is the main subject of this paper (see major comment #1). I suggest publication after moderate revisions.

Major comment #1 One of the main objectives of the MS is to analyze the controls of the spatial patterns in riverine pCO2. This is mainly done quite coarsely by comparing catchments that are dominated by carbonate sedimentary rocks vs. catchments dominated by other lithologies. The MS features some plots of pCO2 vs. Si and Ca concentrations or discharge (Figs 5 and 6). However, these plots are made for distinct sampling locations and what is plotted are the different samples at this location. The differences between sampling locations are then discussed considering the different environmental characteristics of the catchments. In addition, in the MS, it is mentioned that these analyses have been done for plenty of sampling locations, but only a few examples are shown. And here I do not know why these examples have been chosen and in how far they are representative for the whole data set. I would like to encourage the authors to perform a more quantitative analysis of the spatial patterns in the riverine pCO2 and its environmental controls. They could plot the average pCO2 per sampling location vs. avg. concentrations of Ca and Si per sampling location (like Humborg et al., 2010 did for Sweden) or catchment properties like climate, lithology, terrain, land use, etc., (like Lauerwald et al., 2013, did for North America). Maybe they could perform these analysis separately for different stream orders.

General comments:

Abstract

L16: Here, and throughout the MS. The unit of alkalinity is unclear. I guess you mean μeq L-1. If you want to report alkalinity as molarity, then you will have to report it as molarity of e.g. the equivalent CaCO3. But it is more common to report alkalinity in μeq L-1.

L18: 'controlled by terrestrial ecosystem'. I think you would have to be a bit more

specific, like 'C inputs from terrestrial ecosystems'.

L25: Maybe you should change 'riverine carbon' to 'riverine CO2' to be more specific and consistent with the title of the MS.

Introduction

L46: Raymond et al and Lauerwald et al. have used the same data base: GloRiCh. However, while Raymond et al. used all the calculated pCO2 values, Lauerwald et al. used only the data from 18% of the sampling locations which were selected based on a minimum number of CO2 values per sampling location.

L60-62: Is this mainly due to high soil erosion and export of particulate organic carbon? Please, clarify.

L80: Maybe add a 'the' before 'riverine carbon cycle'.

L92: 'Globally substantial' is a bit unclear to me. Maybe you could change this part of the sentence to something like 'its contribution to the global CO2 evasion from rivers is likely significant'.

L93: Maybe change 'to refine global CO2 evasion' to 'to refine estimates of global CO2 evasion'.

Methods and Materials L101-104 and Fig.1: When you talk about sedimentary rocks being mainly composed of carbonates, you should use a term like 'carbonate sedimentary rocks'. 'Carbonate' is the name of a group of minerals, but here you talk about the rocks, more precisely about the lithology. Same is true for 'Silicates'. Silicates are a group of minerals. Igneous rocks also consist mainly of silicates. And metamorphic rocks can contain silicates and/or carbonates. So, I suggest you rename the lithology to 'siliciclastic sedimentary rocks'.

L134-137: The selection of samples with a pH >6.5 itself can introduce some bias for the overall picture of spatial patterns in pCO2 and total CO2 evasion from the river

network, as some specific system might be completely excluded from the analyses. That might be inevitable, but should at some point be discussed. Here, it would be interesting how many samples have been discarded (as % of total), where the affected sampling locations are predominantly located (I see that large parts of that river system have a rather high pH, in particular where carbonate rocks are abundant), and if there are sampling locations which had to be discarded because they only have such a low pH. Note that Raymond et al., 2013 and Lauerwald et al., 2015 chose a minimum pH of 5.4. Can you argue that for so low pH values the calculation of pCO2 might already have introduced a bias in their studies?

L164: What is the conventional method? I see later that you used CO2SYS, Raymond et al., 2013 and Lauerwald et al., 2015 used PhreeqC. Would there be any systematic difference in calculated pCO2 using CO2SYS or PhreeqC? That could be answered maybe later in the discussion section.

L164-168: For what do you need the concentration of bicarbonates? Please, clarify.

Results L179-180: Maybe change to 'relatively lower' to 'relatively low'.

L182-186: Like I mentioned in the abstract, you should report your alkalinity in μeq L-1.

L193-195: If you consider the downstream decrease in pCO2 from headwaters to the lower reach of the main river, which you highlighted in the abstract, this method does not make much sense at this scale, because you ignore the stream orders of the sampled river reaches. It would make more sense if you would only interpolate the pCO2 of small headwater rivers.

L228-232: I think you are talking about lithology rather than mineralogy. See my comment in method section. L232-240: When you plot Ca or SiO2 concentrations against pCO2 per sample for distinct stations separately, then these Ca and SiO2 concentrations would represent tracers for the relative contribution of ground water inputs, which are diluted by the contributions of surface runoff (+shallow sub-surface runoff). SiO2

is likely the better tracer, because it is less reactive then Ca (which can be subject to carbonate precipitation and adsorption in the soil). Maybe you could discuss these plots a bit along those lines.

Discussion L267-276: If you exclude stream and rivers with low pH for methodological reasons, then you will systematically exclude some natural systems and have a biased estimated for the whole river network (Wallin et al. 2014, GBC). You should discuss that here as well. If you exclude form one sampling location that has pH values higher and lower 6.5, and exclude all the lower values, then you would get a biased average pCO2 at that station, in particular if you assume high pCO2 to coincide with low pH.

L296-316: Following my comment on L232-240, you could discuss the SiO2 vs pCO2 plots in Fig 6 as indication of higher CO2 concentration in ground water in Wusheng and Xiajiang catchment. For these two catchments, do you have a negative correlation between discharge and pCO2? That would be consistent with the assumption that SiO2 is a tracer for baseflow contribution vs. dilution by surface runoff. Then, these two catchments would show a different discharge-pCO2 relation than the Yunxian station. If that's the case, it would be interesting to discuss the differences. Are there riparian wetlands present upstream of Yunxian? See e.g. Teodoru et al., 2015, Biogeosciences.

L311-316: Another potential explanation is the large catchment implying a long traveling time of soil derived carbon, maybe combined with the absence of riparian wetlands around the main stem (if that is the case?). Then, direct inputs of CO2 from soil respiration and inputs of labile DOC from adjacent soils and vegetation would be relatively low. And higher inputs far upstream might have already been lost to the atmosphere.

L325-329: I do not really understand that, sorry. Could you please explain that argument in a bit more detail?

L325-334: Humborg et al., 2010 (also cited in your paper) also looked at correlations between Ca2+ and SiO2 vs pCO2. Maybe it would be good to discuss your findings with that of Humborg et al., 2010.

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L345: Here, I stumbled over the term 'heterotrophic ecosystem'. Maybe you should rephrase it to 'more pronounced net-heterotrophy', or something similar.

L361: Do you mean 'km-3 yr-1', i.e. mass per year instead of area per year?

L363-365: Did soil respiration increase in response to soil erosion?

L368-370: If floodplains would be present, you would also have a positive correlation of discharge vs pCO2 in the main channel (see Mayorga et al., 2005, and Richey et al., 2002, Nature and maybe also Teodoru et al., 2015, Biogeosciences, see comment on L296-316).

L375-378: For the Amazon, Richey et al.(2002, Nature) assumes higher gas exchange velocities from large, open rivers due to wind effects. Similarly, the gas exchange velocity reported by Alin et al., 2011 for the Amazon and the Mekong basins are not generally lower for the main channel, which offers a long fetch for the wind, while smaller tributaries are more protected against wind. But these are low gradient systems (low relief). It might be different if the main control on gas exchange velocities would be the channel slope (see Raymond et al., 2012, Limnology and Oceanography). But also for larger rivers in the US it was found that gas exchange velocities were rather high and to a substantial proportion supported by wind (e.g. Beaulieu et al., 2012, JGR).

L384-385: Here you could also cite Butman and Raymond, 2011, Nat Geosc.

Conclusion L426-431: That is not the conclusion of this study but a repetition from the introduction. In the conclusion, you should simply summarize your results in order to answer the main research questions that you have worked out in the introduction.

L429-437: Here you should explain how the riverine pCO2 3 to 5 decades before today can be important for refining estimates of CO2 evasion. I guess someone estimating CO2 evasion would do it for the most recent period. Will you use these estimates in a future study to compare it to a more recent state of this system, in order to quantify the anthropogenic perturbation of the river-atmosphere CO2 fluxes due to damming and

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land-use change. That would be an important outlook.

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