

Dear reviewer,

We thank you very much for your comments on our manuscript.

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Review of "Spatial and temporal dynamics of CO<sub>2</sub> partial pressure in the Yellow River, China".

Summary: The manuscript entitled "Spatial and temporal dynamics of CO<sub>2</sub> partial pressure in the Yellow River, China " by Dr. Ran and Co-authors investigates how dynamics of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) varies along one of the world's large rivers, the yellow river in China. To reach this aim, long term time series are derived from modeling pCO<sub>2</sub> based on pH/alkalinity.

The main contribution of the manuscript is that it adds to the growing body of literature on the variation of pCO<sub>2</sub> in large fluvial systems. Earlier work has shown that other major rivers such as the Amazon (Richey et al., 2002), northern humid rivers (Butman & Raymond, 2011) or boreal streams (Campeau et al., 2014, Wallin et al., 2013) can overall greatly contribute to the evasion of pCO<sub>2</sub> from streams and rivers to the atmosphere (Aufdenkampe et al., 2011, Raymond et al., 2013). However, the current manuscript focuses on the Yellow river, a large fluvial system that, according to my knowledge has up to date received little attention. Furthermore, this river has some specific properties such as for example the high sediment loads, as it drains loess plateaus that make it an interesting and exceptional study system.

The manuscript uses reasonable and commonly used methods and derives compelling results. Furthermore, it puts them into context and is overall well prepared. Thus, I consider the manuscript as a valuable contribution to the journal 'Biogeosciences' and suggest that the manuscript is accepted for publication after some minor revision work that I have listed in my comments below.

General comments:

Comment: There is no evaluation of the uncertainties that arises from modeling pCO<sub>2</sub> based on pH and alkalinity. However, these uncertainties have been mentioned already in the early literature (see for example Cole & Caraco, 1998) and are one of the main reasons why pCO<sub>2</sub> is today more commonly measured by other methods (GC or in situ sensors). Thus, I suggest that at least a few sentences discussing these uncertainties are added to the manuscript. This will help the reader to understand the limitations of the study. Adding such a discussion most often increases the overall credibility of the work.

“We have added the uncertainty discussion into the manuscript: ‘To validate the simplification, we also estimated the pCO<sub>2</sub> using the program PHREEQC (Hunt et al., 2011). The pCO<sub>2</sub> results derived by PHREEQC are very close to that by CO<sub>2</sub>SYS with <3% differences. However, the calculated pCO<sub>2</sub> results may have slightly overestimated the actual values (Cole and Caraco, 1998)’. Thanks for your suggestion. (P5, Line 17-19).”

Comment: The language and the structure of the manuscript are generally good. However, the discussion is not as good as the other parts of the manuscript yet. I suggest some changes here (see detailed comments below) to clarify and correct the language.

“Based on your comments, we have carefully revised the discussion section. Please refer to the highlighted sentences in the manuscript.”

Minor comments and suggested changes:

Title: Good, but could be even more precise. Specifically I wonder about the term ‘dynamics’, and if it could be replaced by ‘variation’. Also the term ‘long term’ could be added, as this is part of this story.

“As suggested, the title has been changed to ‘Long-term spatial and temporal variation of CO<sub>2</sub> partial pressure in the Yellow River, China’.”

Abstract: Overall good. However, I would want the authors to state here explicitly that pCO<sub>2</sub> was determined from Alkalinity and pH, that is, from other variables.

“We have stated this in the revised manuscript. ‘By determining the pCO<sub>2</sub> from alkalinity and pH, we investigated its dynamics in the Yellow River watershed...’. (P1, Line 18-20).”

Last sentence: This is confusing as KCO<sub>2</sub> was not measured or modelled. I would suggest to reword a bit more carefully to something like “large potential for CO<sub>2</sub> evasion” instead.

Introduction: Overall good and very well referenced.

“The sentence has been reworded: ‘Given the high pCO<sub>2</sub> in the Yellow River waters, large potential for CO<sub>2</sub> evasion is expected and warrants further investigation’. (P1, Line 34-35).”

The only thing I found was: P 14065, L12 ff, where there is a bit too much listed on what topics were researched in the past. As a reader this doesn’t help much, if not at least little hints are given of what was found by these studies. Alternatively this section can be reduced.

“We have reworded these statements. ‘Comparative studies associated with lateral carbon fluxes have highlighted the significance of CO<sub>2</sub> evasion in assessing global carbon budget (Melack, 2011). For example, Richey et al. (2002) show that CO<sub>2</sub> emission in the Amazon River basin is an order of magnitude greater than fluvial export of organic carbon to the ocean’. In addition, the length has also been reduced. (P2, Line 4-7).”

Materials and Methods: Reads well - nothing to add. Historical records of water chemistry:

“Thanks.”

P 14068, L09 I am not sure if political chaos is the right term here, as it sounds valuing to me. May be good to rephrase. “We have removed this term.”

P14069, L7: Was the abbreviation introduced? I may have missed it, but check that they are all introduced correctly.

“Yes, the abbreviation ‘TALK’ has already been introduced (P4, Line 2). In addition, we have checked all abbreviations in the whole manuscript to ensure they are correctly introduced.”

P14070, L5, remove ‘the’ before Henrys law. “Done”

L17: may be better to write the pK = -lg K out in words, as this is easier to grasp. “Agreed and changed”

L21: 'indicative of natural processes' needs more explanation. There are streams with pH 4-10, all based on natural processes...

"The pH in the Yellow River is generally in the range of pH7.4-8.6 (Chen et al., 2005. Global Biogeochemical Cycles, 19, GB3016), except additional human pollution that could lead to lower or higher pH values. We have indicated this in the manuscript. (P5, Line 13-15)."

Results: P 14072, L6-9 this section should maybe still go into the methods; these are not strictly results.

"Just as the reviewer commented, division of the basin into 7 sub-basins is not strictly results. Because Fig. 2 is mainly used to shows the spatial variations of pH and  $p\text{CO}_2$  superimposed on the sub-basin division boundaries, it possibly needs another figure to show only the division map if this section is moved to the methods. Therefore, we retain it here for simplicity. Thanks."

L10 how is the variation significant? Was this tested?

"The  $p\text{CO}_2$  changed with two orders of magnitude from about 200  $\mu\text{atm}$  to more than 30,000  $\mu\text{atm}$ . This variation is based on comparison of the  $p\text{CO}_2$  values at the 129 stations."

P14073, L10: Can a stream exhibit something? Suggest to reword.

"The tributary streams are characterized by pronounced seasonal variation. This statement has been reworded as 'Compared with tributary streams showing pronounced seasonal variation, the mainstem exhibited more complicated seasonal patterns'. (P6, Line 18-22; 30-31)."

Discussion: The discussion is overall not as strong as the other sections, even though well referenced. Make sure the main line of argumentation is not lost.

"According to your comments and suggestions, we have carefully revised the discussion section. Please refer to the highlighted sentences in the manuscript."

P14074, L22ff: reads nicely. "Thanks."

P14075, L9 not sure about the term 'abnormal', suggest rewording.

"The term 'abnormal changes' has been changed to 'anomalous observations'."

L15: this hypothesis can't stand by itself like this. Is there any more support for this?

"Hortonian overland flow has been found to be the dominant runoff process on the Loess Plateau (e.g., Kang et al., 2001. Hydrological Processes, 15, 977-988; Liu and Singh, 2004. Journal of Hydrologic Engineering, 9, 375-382). Thus, the generated overland flow may have diluted the TALK and caused the reduced riverine  $p\text{CO}_2$ . (P7, Line 33-36)."

L25: not sure about the use of 'since then' here. Maybe 'thereafter'? "Agreed and changed."

P14076, L4: What is meant with lower organic matter composition? This remains unclear. Lower quality of organic matter? If so, please write that. Also, does any data support this? Here some more clarification is needed.

"Here it means lower organic carbon quantity for decomposition because the mobilized subsoils have lower organic carbon content. We have revised this statement in the manuscript. The lower

organic carbon quantity is resulting from the lower organic carbon content (0.2-0.3%) compared with the topsoils (0.5-1.5%). Thanks. (P8, Line 1-4).”

L16: Ice melt or snow melt? Seems strange to melt so much ice that fast. Or is it ice dams?

“It is ice melt that forms ice dams, causing flooding in the upper Yellow River in Inner Mongolia, usually starting from early spring (early March) with rising temperature (please refer to Chen and Ji. 2005. Hydrological Sciences Journal. 50, 319-330).”

L18-22: Also here, is there any data or other study to support this? I’ve seen this in other ecosystems, but those were closer to the arctic circle than this one. I have my doubts, that the ice cover could completely exclude the exchange with the atmosphere, as long as the river is still flowing. Even in boreal regions, this is not very common for streams.

“The surface water in the reach of the Yellow River from QTX to Toudaoguai (please refer to Fig. 1 in the manuscript) would be completely frozen up during the period from late November to early March (temperature: -10~ -20 °C). Our latest preliminary study shows that, during this period, the ice cover could almost completely prevent the exchange with the atmosphere during this reach, although the water underneath is still flowing. Below are two photos showing our recent fieldwork on the Yellow River (near Toudaoguai on Nov 28, 2014) measuring riverine  $p\text{CO}_2$  and outgassing by digging a hole into the water. The ice is about 10-13 cm thick, so that we can safely walk and stand above the ice.”



L24: ‘more research...’ this statement is not needed here and should be removed. “Agreed and changed.”

P14077, L1: rephrase as ‘bitter tasting streams’ as this is what is meant. Also, this is a bit funny – I like it. “Done”

L3: ‘will not only result in’; L4: ‘but also the elevated’ “Done”

L10-20: this read better. “Thanks”

L23: is alkalinity really ‘produced’?

“Alkalinity indicates the quantitative capacity of an aqueous solution to neutralize an acid. Terrestrial carbonate alkalinity can be produced through chemical weathering (Raymond and

Cole, 2003. Science, 301, 88-91). In addition, alkalinity can also be produced by microbial activity (Logan et al., 2005. Water Research, 39, 4537-4551). ”

L24: ‘human induced rainfall acidification’ seems a strange term. Suggest rewrite to: “Significant decreases in pH in the middle... have been detected and are hypothesized to result from acid rain that is likely caused by anthropogenically induced sulfur emissions to the atmosphere.” or similar. Also, Figure 3 actually shows no indication for this happening, but rather the opposite.

“As suggested, the sentence has been rewritten. Water sources for the Yellow River are spatially highly uneven. About 60% of the water discharge comes from the upper reaches, in particular the HR and HT sub-basins (please refer to Fig. 1 and Wang et al., 2007. Global and Planetary Change, 57, 331-354). Fig. 3 thus shows mainly the pH changes in water originating from the upper reaches, and the water from the middle reaches (<40%) may only partly affect the pH changes. (P9, Line 5-8).”

P14079, L13 remove ‘aggressive’, as this is subjective. “Removed.”

L3-4: ‘Riverine pCO<sub>2</sub>...’ this sentence does not make any sense, as it is the gas transfer velocity that does that, but pCO<sub>2</sub> can be a result of a myriad of different processes.

“This sentence has been removed. Thanks.”

P14080, L9-11, this sentence also doesn’t really make sense and needs language editing. If the uncertainties are so ‘great’, what does your study then add to this? Right now it doesn’t make sense to me. What is meant by a ‘diagnosis’? A robust estimate?

“An uncertainty regarding previous outgassing estimates is because those studies only involve mainstem channels due to lack of a spatially resolved pCO<sub>2</sub> database on small streams. We have reworded this sentence as: ‘Given the existing uncertainties, quantifying pCO<sub>2</sub> in different orders of streams of a complete river network is critical to resolve a robust estimate of riverine CO<sub>2</sub> evasion’. (P10, Line 21-23).”

Conclusions:

P14081, L11 replace resulted with resulting. “Done”

Tables:

1) ok. “Thanks”

2) how about replacing ‘item’ with ‘variable’. Also you could add river kilometers to each of the stations named here, just as a rough reference (for example below the station name).

“Changed. The river kilometers indicating the channel length to the river mouth have been added into the table.”

Figures:

Fig. 1-4) all ok. “Thanks.”

Fig. 5) please give station names, or other indications of the locations as it is unclear where a, b and c are in Fig.1.

“The station names have been added into the 3 subfigures, and their locations have also been highlighted in Fig.1.”

Fig. 6) it may be reasonable to refer to the discussion or the references given to indicate why a step function is used here. Without this additional knowledge it just looks like there is ‘more scatter’ at the highest values.

“We have indicated the meaning of the two trend lines in the figure caption to explain why a step function is used here: ‘The solid line denotes the fitted line for the TSS concentration ranging from 0 to 100 kg m<sup>-3</sup>, and the dashed line indicates the stable trend of pCO<sub>2</sub> independent of increasing TSS concentration when it is higher than 100 kg m<sup>-3</sup>’. Many thanks. (P16, Line 23-25).”

All following o.k. “Thanks.”

Refs: Please check again, that all of them are there and formatted correctly. There seem to be a few missing(?).

“We have carefully checked the references and formatted them based on the instructions for authors. Missing references have been added into the manuscript. Thanks.”

References cited here:

Aufdenkampe AK, Mayorga E, Raymond PA et al. (2011) Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment*, 9, 53-60.

Butman D, Raymond PA (2011) Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience*, 4, 839-842.

Campeau A, Lapierre J-F, Vachon D, Del Giorgio PA (2014) Regional contribution of CO<sub>2</sub> and CH<sub>4</sub> fluxes from the fluvial network in a lowland boreal landscape of Québec. *Global Biogeochemical Cycles*, 28, 2013GB004685.

Cole JJ, Caraco NF (1998) Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF<sub>6</sub>. *LIMNOLOGY AND OCEANOGRAPHY*, 43, 647-656.

Raymond PA, Hartmann J, Lauerwald R et al. (2013) Global carbon dioxide emissions from inland waters. *Nature*, 503, 355-359.

Richey JE, Melack JM, Aufdenkampe AK, Ballester VM, Hess LL (2002) Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO<sub>2</sub>. *Nature*, 416, 617-620.

Wallin MB, Grabs T, Buffam I, Laudon H, Ågren A, Öquist MG, Bishop K (2013) Evasion of CO<sub>2</sub> from streams - The dominant component of the carbon export through the aquatic conduit in a boreal landscape. *Global Change Biology*, 19, 785-797.

“Thanks a lot for providing these helpful references.”