

Dear reviewer,

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

The manuscript of Ran et al. analyzes the spatial and temporal dynamics of pH, alkalinity and calculated pCO₂ data in the Yellow River catchment (China). In order to explain the found dynamics, they use information about geology, soil characteristics and past anthropogenic activities. The found results underline the high spatial and temporal variability of the investigated variables. Furthermore, they found an interesting correlation between pCO₂ and total suspended solids (TSS) with a threshold of 100 kg m⁻³. It's a nice study and an interesting approach to consider the whole catchment instead of just the main stem of a river. The setup is mostly well thought and most of the needed analyses are done. Furthermore, I like how the influence of dams on TSS, pH, total alkalinity (TAlk) and pCO₂ is presented. The strength of the long-term data set is striking. These findings would make a good contribution to the literature and the subject matter is thus, of interest to a broad sweep of Biogeosciences readers. However, the discussion is a mixture of results and discussion (it includes 4 additional figures which are not mentioned in the results). I would suggest transferring all results integrated in the discussion into the results part, so the discussion gets less comprehensive and the manuscript would profit from a clearer red line. Moreover, the discussion is too wordy and should be written in a more rigorous manner. Furthermore, a comparison of the measured values to other river systems would be helpful. The conclusions consist mainly of a summary. In general the conclusions are too weak and ambiguous, some parts of the discussion should be added there (see specific comments). Finally, the manuscript should be thorough restructured. Below you will find some more specific comments which should be solved before publishing:

“Based on your comments, we have thoroughly restructured the manuscript. All results now have been moved to the result section to make the structure clearer. In particular, Figs. 6 and 7 in the original version have been transferred to the result section in the revised version (now Figs. 5 and 6), and have been discussed in more detail in the discussion section. There are now 5 figures in the result section and only 2 figures in the discussion section. We have also reworded the discussion section to make it more succinct. Comparison of pCO₂ with other rivers has also been discussed (please refer to below replies). In addition, the conclusion chapter has also been reworded based on your specific suggestions. Please refer to the highlighted sentences in the revised manuscript.”

Specific comments:

The title does not reflect completely the story and is only partly succinct. There is also a strong focus at the end of the discussion on TSS and man-made influences/human impacts. Also the story should be glued better together in respect of pCO₂, TSS and human impacts. A clear take home message should be elaborated. Furthermore, the use of the expressions total suspended solids (TSS) and total dissolved solids (TDS) should be clear and constant throughout the entire manuscript. Moreover the acronyms TSS/TDS and TAlk should be written out in full in every chapter.

“As suggested by the two reviewers, the title has been changed to ‘Long-term spatial and temporal variation of CO₂ partial pressure in the Yellow River, China’. For the manuscript, we

have thoroughly restructured it to make it more succinct when discussing $p\text{CO}_2$, TSS, and human activities. Use of the expressions of TSS, TDS, and TAlk and other acronyms has been carefully checked to be clear and constant throughout the manuscript. ”

Abstract:

Line 9/10: “This indicates a strong CO_2 outgassing across the water-air interface.” Since this was not measured in this study and is somehow redundant to the last sentence of the abstract, this sentence should get removed.

“Agreed and removed.”

Introduction:

In general the statements should be better underlined by references and I am missing a paragraph about the applied method in the manuscript. Furthermore, the background of TSS/TDS could be explained much more in detail. What are the consequences already known from such a high load (four times more than worldwide average)?

“Based on your comments, missing references have been added into the statements (please refer to below replies and highlighted sentences in the manuscript). A brief description of the method has been added into the introduction section ‘Using historical records throughout the watershed during the period 1950s–1984 and recent sampling along the mainstem, we calculated the riverine $p\text{CO}_2$ from alkalinity and pH’, and a detailed method description is provided in section 2.4. In addition, we have provided more details about the high TSS and TDS in the manuscript. High TSS and TDS concentrations in the Yellow River basin are primarily because of severe soil erosion and intensive chemical weathering and human activity within the watershed. This has caused the Yellow River to be at the severe level at five indexes out of the nine riverine syndromes of global change defined by Meybeck (2003)(Chen et al., 2005. Global Biogeochemical Cycles, 19, GB3016). Thanks.”

Page 14065, first sentence: Please add a reference to that statement

“A reference (Aufdenkampe et al., 2011. *Frontiers in Ecology and the Environment*, 9, 53-60) has been added to the statement.”

Page 14065, line 9: Since the manuscript is not dealing with sedimentation I would remove this remark; the references should be reordered according to the year of publication

“The sedimentation remark has been removed and the references have been reordered. It now reads ‘a considerable fraction would be buried within the river network or returned to the atmosphere en route (Richey et al., 2002; Cole et al., 2007; Yao et al., 2007)’ (P1, line 45).”

Page 14065, line 11: Please add a reference to that statement and write CO_2 out in full

“ CO_2 has been written in full and two references (Cole et al., 2007; Butman and Raymond, 2011) have been inserted.”

Page 14065, line 13: References should be reordered according to the year of publication “Done”

Page 14065, line 18: This is a really ambiguous sentence, please rewrite and add a reference

“This sentence has been rewritten as: ‘Decomposition of terrestrially derived organic carbon and aquatic respiration are the primary sources of riverine CO₂’. A reference has also been added in.”

Page 14065, line 19: It’s ambiguous what refers to “its”, please rewrite

“Here it refers to riverine CO₂. To make it be clearer, it has been rewritten: ‘As an important parameter in estimating CO₂ outgassing, partial pressure of riverine CO₂ (*p*CO₂) indicates...’ (P2, Line 10).”

Page 14066, line 1: I do not understand the connection between strong turbulence and rapid mixing and turbulence and the biogeochemically activity. According to your arguments there is a stronger exchange with the atmosphere (because of a higher piston velocity), which is a physical process but not higher biogeochemically activity. Please specify.

“Yes, CO₂ outgassing fluxes from small streams are higher than those observed in larger rivers, mainly due to a higher gas transfer velocity as a result of strong turbulence and rapid mixing. In addition, the water the small streams convey has a great deal of contact with the benthic substrate and the atmosphere (Benstead and Leigh, 2012. *Nature Geoscience*, 5, 678-679), which would accelerate organic carbon decomposition and CO₂ emission. We have specified this in the text. (P2, Line 17-20).”

Page 14066, line 14: Please specify what you mean exactly with “hillslope ecosystem respiration”

“It has been reworded as: ‘Soil respiration in terrestrial ecosystems and...’.”

Page 14066, line 16: If there are few studies like that, please cite them and make sure that they not overlap with yours.

“As for the Yellow River, to our best knowledge, prior studies mainly investigate its carbon transport characteristics (e.g., Wang et al., 2012. *Global Biogeochemical Cycles*, 26, GB2025; Ran et al., 2013. *Journal of Hydrology*, 498, 76-88). In comparison, no studies on riverine *p*CO₂ changes have been conducted, in particular at the watershed scale. We have cited the studies on riverine carbon transport in the text. (P2, Line 35-37).”

Page 14066, line 20: Please add some explanations why this study is relevant and innovative and how it will contribute to the existing knowledge gap.

“A simple explanation about the study has been added into the manuscript. ‘The results will provide insights into the coupling between soil erosion and riverine *p*CO₂ and the impact of dam operation on downstream riverine *p*CO₂ changes’. (P2, Line 38-41).”

Materials and methods:

Page 14067, line 7: Ambiguous sentence. To which year refers the value of 49 km³ yr⁻¹?

“It refers to the period prior to the 1970s. It has been changed to ‘For comparison, the mean water discharge was only 49 km³ yr⁻¹ over the same period’.”

Page 14067, line 9-19: Nice informative paragraph “Thanks.”

Page 14068, line 1: Please specify the major ions

“Major ions are Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , and SO_4^{2-} . The Yellow River Conservancy Commission that has a hydrological monitoring network publishes the ion concentrations for research use. These ions have been specified in the manuscript. (P3, Line 32).”

Page 14068, line 5+6: Please indicate the methods used to measure pH, discharge and TSS
“The pH was measured using a pH meter, water discharge was measured by multiplying cross-section area by flow velocity, and the TSS was determined by weighing the suspended solids after filtration. And a reference describing the sampling procedure has been inserted. (P3, Line 37; P4, Line 2-4).”

Page 14068, line 7-12: The timing of investigation is crucial (due to diurnal changes of pH). Were the water samples for pH taken in a similar time period? Please specify
“In each sampling event, 5 liters of water were sampled by buckets in the morning at 8 o'clock for both alkalinity analysis and pH measurement. Therefore, the water samples for pH were taken in the same time period. We have specified this in the text. (P3, Line 37-38; P4, line 1-4).”

Page 14069, line 14: Also here: Were the water samples for pH taken in a similar time period? Please specify
“Yes, the water samples for pH were taken at the same time period. It has been specified in the manuscript: ‘Concomitant determination of pH and water temperature was performed in situ using a Hanna HI9125 pH meter...’.”

Page 14070, line 5ff: Specify why this program was chosen and which pH scale was chosen
“The CO2SYS program proposed by Lewis and Wallace (1998) has been widely used to calculate $p\text{CO}_2$ in freshwater and seawater (e.g., Talmage and Gobler. 2010. PNAS, 107, 17246-17251; Hunt et al., 2011. Biogeosciences, 8, 3069-3076). In order to validate the program, we also calculate the $p\text{CO}_2$ using another program (PHREEQC). The calculated results are largely equal to that returned by the PHREEQC program, indicating the applicability. The pH scale ranges from 0 to 14. (P5, Line 16-19).”

Page 14070, 11+12: Please specify K1 and K2 (like done for KCO2) Chapter 2.4: The way the methods are presented is nearly identical to the method section of Li et al. 2012. Please try to present them in a more different way.

“K1 and K2 indicate the thermodynamic reaction constants for the 1st and 2nd dissociation of carbonic acid, respectively. We have rephrased the description about the $p\text{CO}_2$ calculation.”

Results: In general, the results should be accompanied by statistical tests wherever possible. This would increase the quality of the manuscript significantly.

“Thanks for your comment. When necessary, we have indicated the statistical tests (p value) in the manuscript or in the figures (e.g., Figs. 6 and 7; P5, 45-46).”

Page 14071, line 23: Please provide an exact number including standard deviation (avoid “about”)
“To be more exact, the standard deviation has been added, now the mean TALK is $3850 \pm 1000 \mu\text{mol l}^{-1}$.”

Page 14071, line 25: “but in the reverse direction with high TAlk coinciding with low pH” is not very clear for me. Please provide a correlation figure of these two variables in the supplement material and discuss this finding in more detail

“We have plotted the spatial variations of pH and TAlk within the Yellow River basin showing the correlation. Please see Fig. S1 in the Supporting Information.”

Page 14072, line 4-5: Can you please provide the p value for this non-significance? Which statistical test has been applied?

“We used ANOVA to analyze the temporal variation of TAlk. The $p=0.48$ indicates there is no significant change over the study period. The p value has been added into the text.”

Page 14072, line 26/27: “The seasonal ratio of $p\text{CO}_2$, defined as the ratio of $p\text{CO}_2$ in the dry season over that in the wet season, ranged from 0.8 to 2.3 with > 55% ratios between 0.9 and 1.5.” What is the knowledge gain of this ratio?

“The seasonal ratio of $p\text{CO}_2$ is used here to indicate its seasonal changes. Because it is recognized that riverine $p\text{CO}_2$ changes could be affected by delivery of terrestrial organic matter and soil CO_2 , for the Yellow River, this ratio indicates that much higher $p\text{CO}_2$ in the wet season relative to the dry season.”

Page 14073, line 4-8: Please provide standard deviation to the mean

“Standard deviation for each variable has been added into the text. (P6, Line 24-28).”

Discussion:

The discussion could be strengthened and more focused on the main outputs. In general, bring one paragraph at the beginning about your main findings and the connection of those.

Furthermore, try to bring your study in a bigger context, e.g. by answering questions like: how relevant is the high alkalinity in respect of rivers globally? Or is this phenomenon more catchment specific? How many similar rivers are existing and how is there the TSS transport? How representative is the Yellow River catchment?

“We have strengthened the discussion chapter to make it more focused on the results. In addition, we discussed the TAlk and $p\text{CO}_2$ of the Yellow River in relation to other large rivers in the world. The $p\text{CO}_2$ in the Yellow River waters is significantly higher than that in most of the world’s large rivers that generally ranges from 500 to 2600 μatm . High TAlk was probably the result of chemical weathering of loess which constitutes a large part of the drainage basin (Fig. 1). With the widespread carbonates in this region, chemical weathering of rocks and soils in the loess deposits has generated high dissolved solids with HCO_3^- being the dominant ion. Because TSS concentration in other rivers is usually quite low (i.e., $<10 \text{ kg m}^{-3}$), it is expected that their $p\text{CO}_2$ responds positively to TSS changes. While in the Yellow River, the TSS can exceed 400 kg m^{-3} due to the occurrence of gully erosion, the stable $p\text{CO}_2$ when the TSS is great than 100 kg m^{-3} may reflect the low organic carbon content of the soils mobilized by gully erosion.”

Page 14074, line 11-15: This paragraph should be reversed: highlight first your finding and discuss it afterwards with existing literature, not the other way around. Please consider this comment throughout the entire discussion.

“This paragraph has been rephrased to highlight our finding, and relevant reversions and changes have been made in the whole discussion section. Thanks for your comment. (Highlighted in P7).”

Page 14074, line 22-27+page 14075, line 1+2: Paragraphs which do not discuss results should be avoided, consequently this paragraph should be removed

“This paragraph has been removed from the manuscript. Thanks.”

Page 14075, line 16+17: This is a major finding and should be presented already in the results

“This finding, including Fig. 6, has been transferred to the result section.”

Page 14075, line 18+19: This exponential trend cannot be seen in figure 6 (there it is a linear trend). Please clarify this statement.

“Because the x-axis and y-axis in Fig. 6 have been log transformed, it shows a linear line, but it actually is an exponential trend, this can be seen from the regression equation inserted in Fig. 6.”

Page 14075+14076: Nice explanation of the TSS vs. $p\text{CO}_2$ relationship including the threshold of 100 kg m^{-3} “Thanks.”

Page 14076: In line 6 you talk about low $p\text{CO}_2$ caused by low TALK and high pH, in line 25 you talk about high $p\text{CO}_2$ resulted by high TALK. You stated that you used HCO_3^- as proxy for TALK (chapter 2.4). If you consider the classic DIC species vs. pH graph (Fig. 1; source: Wetzel, R.G. 2001. Limnology. Lake and River Ecosystems. Third Ed. Academic Press, San Diego. xvi, 1006 pp. ISBN 0-12-744760-1.): How can you explain your findings? Please discuss this aspect in more detail.

“In the Yellow River, the pH ranges from 7.4 to 8.6, indicating that the DIC species are mainly composed of HCO_3^- as shown in the figure. Meanwhile, the pH range suggests that CO_3^{2-} and free CO_2 account for a very small fraction of the DIC. The headwater region had a 25% lower TALK (or HCO_3^-) concentration and a 7% higher pH than the basin average, causing a lower $p\text{CO}_2$ based on the Eqs. (1-8). While in the QZ sub-basin, although the pH is lower ranging from 7.4 to 7.7 (Fig. 2a), the DIC species are still mainly composed of HCO_3^- . As a result of strong rock weathering, its TALK concentration is the highest, leading to the highest $p\text{CO}_2$ compared with other sub-basins. We have further discussed this in the manuscript. (P8, Line 6-27).”

Page 14076, line 29: This sentence is scientifically not relevant, please remove

“Agreed and removed.”

Page 14077, line 10-12: This finding should be presented already in the result part

“Agreed and transferred to the result section.”

Page 14077, line 13: Do you have evidences for that? Please underline this statement with data if possible

“The Yellow River basin is located in a semiarid-arid climate with low precipitation and groundwater table. Arid climate is found to be conducive to chemical weathering (McFadden, 1982. The impacts of temporal and spatial climatic changes on alluvial soils genesis in southern California). The dry climate allows the deeper soil horizons to interact with the atmosphere in most time of a full hydrological year. Our recent study shows that HCO_3^- concentration in the dry season with lower groundwater table is much higher than that in the wet season (Ran et al., 2014. Geomorphology, in press). This may be partly due to the relatively enhanced exposure to

weathering during the low groundwater table period. We have revised this statement in the text. (P8, Line 23-34).”

Page 14077, line 22-26: Please avoid paragraphs where you do not discuss your results directly
“We have thoroughly revised these paragraphs throughout the discussion section to avoid irrelevant statements. Thanks.”

Page 14078, line 16-18: I am not convinced from this argumentation and I doubt that the indicated references support the made statement sufficiently. Why it cannot be the other way around? Extended residence time combined with sufficient organic carbon availability may lead to a higher $p\text{CO}_2$. Please revise, precise and extend this argumentation.

“As the reviewer commented, extended water residence time would also lead to a higher $p\text{CO}_2$, although the decreased suspended solids and turbidity and increased water residence time would promote photosynthesis. Therefore, the balance between photosynthesis and respiration/decomposition in the reservoir water column determines the impact of dams on riverine $p\text{CO}_2$. We have revised the discussion as: ‘Extended residence time combined with sufficient organic matter availability may enhance CO_2 production, causing a higher $p\text{CO}_2$. This is particularly true for tropical reservoirs into which organic matter inputs are sufficient, especially in the initial years after impoundment (Roland et al., 2010; Raymond et al., 2013). On the other hand, reduced flow turbulence and increases in water residence time would promote photosynthesis of aquatic plants and reduce aqueous CO_2 concentration (Teodoru et al., 2009; Wang et al., 2011)’. (P9, Line 22-29).”

Page 14078, line 18: Please avoid starting sentences beginning with “Figure X presents...”
“It has been revised: ‘An example about the impact of dams on downstream $p\text{CO}_2$ changes was presented in Fig. 8’.”

Page 14079, line 17-23: This conclusion paragraph should be moved to the conclusions part
“This conclusion paragraph has been moved to the final conclusion section. Thanks.”

Page 14079, line 27+28: This sentence is too ambiguous and not correct like that. Please specify or remove
“This sentence has been removed from the text.”

Page 14080, line 2-11: If you discuss CO_2 outgassing you must consider the piston velocity (k). Beside the $p\text{CO}_2$ value this is a crucial factor and must be taken into account here.
“Yes, the piston velocity (k) is a very important factor in estimating CO_2 outgassing flux. ”

Page 14080, line 17-26: May put a shortened and concise version of this paragraph in the conclusions
“A shortened version of this paragraph has been added into the conclusion section: ‘Considerably high riverine $p\text{CO}_2$ in the Yellow River waters with respect to the overlying atmosphere indicates that substantial amounts of CO_2 are emitted into the atmosphere. Given the huge human impacts on flow, TSS, and carbon fluxes, future efforts to estimate CO_2 outgassing flux and assess its importance in the global carbon cycle are urgently needed.’ (P11, Line 17-25).”

Conclusions:

The conclusion consists mainly of a summary. In general the conclusions are too weak and ambiguous. The conclusion would profit from a shortened summary of the highlights and the addition of the concluding parts of the discussion (see my comments above).

“We have rephrased the conclusion section. The summary of the major findings have been shortened and the concluding parts, mainly in Sections 4.1 and 4.2, have been transferred into the conclusion chapter. Thanks. Please refer to the highlighted text in the manuscript. (Highlighted in P10-11).”

Figures:

Fig. 2: Add in the figure legend the division of the 7 sub-basins and indicate the acronyms

“Legend for the 7 sub-basins has been added and the acronyms have been indicated into the figure.”

Fig. 3a: This is not the optimal way to present the data. May show it better as a boxplot or a bar figure (including SD); I do not understand what “Raw sampling data were added to the left.” exactly means, please specify

“We have re-plotted Fig. 3a using a bar plot and SD. The raw TALK data added to the left in Fig. 3b are to show the distribution of data points.”

Fig. 4: Only one legend and x-axis needed, please revise

“Only one legend in (a) has been retained. However, for the x-axis, because the sampling period at Lijin (05/07/2011-15/07/2012) is a little different from at Toudaoguai and Tongguan (05/07/2011-05/07/2012). Thus, we retain the x-axis for each plot.”

Fig. 5: Please standardize the layout of the 3 subfigures and indicate the p value of the regression

“The layout of the 3 subfigures has been standardized and the p value for each regression has been inserted into the figures.”

Fig. 6: Please indicate the meaning of the two different trend lines in the figure text. Bring data from other studies into this figure. It would be awesome to see still a correlation.

“Based on your suggestion, the meaning of the two trend lines have been indicated in the figure caption: ‘The solid line denotes the regressed line for the TSS concentration ranging from 0 to 100 kg m^{-3} , and the dashed line indicates the stable trend of $p\text{CO}_2$ when the TSS concentration is higher than 100 kg m^{-3} .’”

Fig. 8: Indicate the acronyms

“The acronym QTX has been indicated in the figure.”

References:

The references in the text are not arranged properly (not chronologically in respect to the year). Additionally: Wu et al., 2008 and Lewis and Wallace, 1998 are cited in the text but do not appear in the references. Furthermore, Hu et al., 1982 is in the references but not mentioned elsewhere. Please revise the references carefully.

“All the references in the manuscript have been chronologically arranged. We have also carefully corrected the reference list. Thanks.”

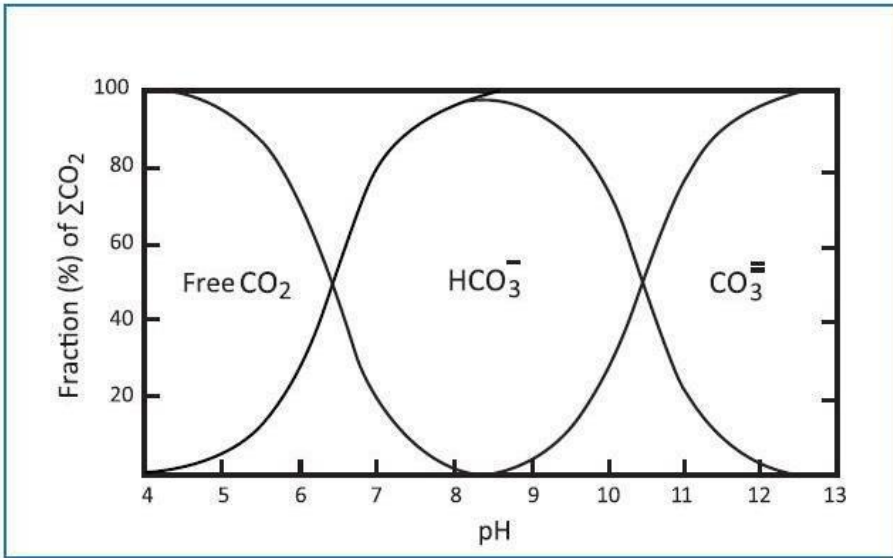


Fig. 1. DIC species vs. pH graph