

Dear Prof Chris Le, the Editors-in-Chief of the Journal of Biogeosciences

Dear Dr Park, Dr Sarma, Dr Abril and Dr Butman, the Editors of the Special issues
Human impacts on carbon fluxes in Asian river systems

Please find enclosed the revised manuscript: "*CO₂ partial pressure and CO₂ emissions from the lower Red River (Vietnam)*" to be submitted as an Original Research Article to the *Biogeosciences*. All co-authors know and agree with the contents of the revised manuscript and declare no competing financial interests.

We would like to thank you, the editors and the reviewers for the helpful comments for improving the quality of the manuscript. As required, we have highlighted all the changes in blue and provide point by point replies to the reviewers' comments. We do hope that this now fully revised manuscript is suitable for publication in your journal.

Thank you very much for your kind consideration.

Sincerely yours,

Dr Thi Phuong Quynh LE on behalf of the authors.

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Dear Authors,

Please note that I do not see a final version of the manuscript but it appears you have addressed the concerns of the reviewers quite well. A decision will be made once a final version of the manuscript is submitted and can be properly reviewed.

Sincerely,

David Butman

Interactive comment on “CO₂ partial pressure and CO₂ emissions from the lower Red River (Vietnam)” by Thi Phuong Quynh Le et al.

Anonymous Referee #1

Received and published: 19 January 2018

General Comments:

This paper provides some important quantification of CO₂ concentration, evasion rates, and temporal and spatial heterogeneity in an understudied Southeast Asian river system. Given the lack of data available on these systems, the concentration data presented in the paper is valuable on its own.

I am concerned, however, at the large discrepancy between calculated and measured CO₂ given the lack of a reasonable explanation aside from calculation error. Furthermore, along with what the other reviewer wrote, the reliance on wind-speed as the only determinant factor for k₆₀₀ is subject to large errors in flux estimation. Knowing this, it is nearly impossible to assess how well correlated CO₂ flux is with any of the environmental parameters used in the multi-variate analysis at the end of the paper. I think if the authors figured out why their calculated values are off, used a more broadly accepted model to estimate k₆₀₀ (or better yet, measured it directly), and simply presented the concentration and flux measurements from the Red River, it would be a valuable contribution to the literature.

Thank you very much for the helpful comments. We revised the paper taking into account your comments concerning k₆₀₀. k₆₀₀ now is calculated from the formula proposed by Raymond et al (2012), based on different variables such as river discharge, water velocity, slope. The values of k₆₀₀ are now considered more realistic and then CO₂ flux evasion was recalculated.

Specific Comments:

-How exactly does the data presented in this manuscript relate to anthropogenic impacts? The authors suggest that the Red River is “strongly” affected by human activities but do not provide results that suggest humans have altered the amount or way by which CO₂ is evaded from the river. The

“influence of dams” based simply on observing higher concentrations at that site is unconvincing – there is no direct evidence. Likewise, the ascribed influence of human population is equally weak.

Thank you for the comments. We revised the discussion about the human impact on pCO₂ and fCO₂ of the Red river in the section “4.2 Spatial variations of pCO₂ and fCO₂ outgassing in pages 11- 12. In this section, separated factors such as dam impoundment, population density and land-use were discussed.

- There are more accurate ways to calculate k₆₀₀ than from wind speed. As the other commenter suggested, instantaneous discharge, flow hydraulics, and even channel slope may provide better or more robust ways to model k₆₀₀ compared to wind speed.

The explanation that wind speed is driving the diel signature in CO₂ flux is circular. Wind speed is how the flux was calculated in the first place, so higher winds during the day will always yield a “higher flux” of CO₂ during the day. CO₂ might have a completely different diel pattern if modelled with something other than wind speed.

It’s hard to evaluate the seasonal variation of CO₂ fluxes generated from only wind speed and concentration

Thank you very much for the helpful comments. As mentioned above, k₆₀₀ value was determined by the method proposed by Raymond et al (2012), then the CO₂ outgassing fluxes were recalculated and discussed for their seasonal and spatial variations.

K₆₀₀ was calculated as presented in the section “2.5 CO₂ fluxes determination”, page 5-6:

“In this study, k₆₀₀ was calculated using the equation from Raymond et al. (2012) based on stream velocity (V, in m s⁻¹), slope (S, unitless), depth (D, in meters) and discharge (Q, in m³ s⁻¹), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

- Although the authors suggest that their direct and calculated pCO₂ values were well correlated, they do not seem to correspond very well at all. The y-axis in Figure 3 makes it impossible to appreciate the noise in this relationship. More importantly, there is no plausible explanation as to why the slope is not close to 1, but rather that calculated pCO₂ was nearly 1/5 of that measured directly by their equilibrator.

We apologize for the errors of pCO₂ calculation values in the previous version of the manuscript. Values were corrected in the revised manuscript (see table 2). Figure 2 (fig 3 old) was also corrected. A difference between pCO₂ calculated and measured was found and discussed in the revised manuscript page 7.

- No specific reasoning given as to why temperature was positively correlated with pCO₂ concentration except enhanced weathering rates. Did the authors consider instream respiration?

This is possibly related to enhanced decomposition rates of organic matter.

-What are the +/- values in any of the tables? Standard deviation?

They are standard deviation. We added the information in the table captions.

- There seems to be overall very little diel signature in any of the water chemistry data presented in the paper. All of the differences seem to fit within the error bars of each “average” measurement.

Yes, we fully agree with the reviewer, and the discussion concerning day-night variations (first paragraph of the Discussion) was rewritten. pCO₂ differences between night and day were really low, most probably because of low temperature difference and low photosynthetic activity due to the turbidity of the Red River.

Technical Corrections:

17: I would avoid the use of the word “good” when describing a river system

The word “good” was replaced by “representative”

19: Not sure what is meant by “carbon dynamic”

The sentence was revised “This study aims to quantify the spatial and seasonal variability of CO₂ partial pressure and CO₂ emission of the lower Red River system”

21-22: Do you mean “relative” rather than “in contrast”?

“Relative” was replaced as suggested

42-43: Unclear sentence summarizing Raymond 2013

The sentence was revised “Raymond et al. (2013) estimated a global evasion rate of 2.1 Pg C yr⁻¹ from inland waters, and that global hot spots in stream and rivers which occupy only 20 % of the global land surface represented 70 % of the emission. They emphasised that further studies are needed for identifying the mechanisms controlling CO₂ evasion at a global scale.”

113: How was alkalinity measured? There are no methods detailing this

The method for alkalinity determination was added in the revised manuscript (see page 4)

277: Discussion mixed in with results, difficult to follow

Results and discussion are now better separated, as suggested.

286: More discussion in the results section

This was separated between results and discussion as suggested

346: Results being presented in the “Discussion”

This was separated between results and discussion

359: Results being presented in the Discussion

Results were added in the “Discussion” in page 12.

Anonymous Referee #2

Received and published: 9 February 2018

General comments:

The authors reported new data on CO₂ partial pressure and CO₂ evasion from the lower Red River in Vietnam. This paper also provides useful water chemistry data of the river system. Considering that river systems in the Southeast Asia are underrepresented in the global budget of riverine carbon fluxes despite their large river discharge and carbon loads, this study could provide valuable datasets. However, the paper can be improved further by (1) strengthening the estimates of CO₂ evasions, (2) providing detailed discussion on the observed patterns, and (3) reorganizing the paragraphs (e.g. some paragraphs in results fit to discussion, and vice versa). I would also suggest that the paper receive a thorough editing for grammar and clarity by the authors. Specific comments are below, which the authors can consider when revising the manuscript.

Thank you very much for the comments. We revised the manuscript and checked the grammar as suggested.

Specific comments:

Lines 43–47: These are confusing because the first one (2.7 Pg C yr⁻¹) includes riverine carbon transport, mineralization, and deposition, while the second one (“a lower value” is for CO₂ evasion only. I don’t think the estimate of CO₂ evasion (2.1 Pg C yr⁻¹) from inland waters by Raymond et al. (2013) is a lower value than the previous estimate. Lauerwald et al. (2015) provided a lower estimate, though.

The paragraph was revised

“Natural hydrological processes and biogeochemistry of many rivers in the world have suffered from the influences of climate change and human activities in their drainage basins. Riverine carbon fluxes and outgassing are important parts of the carbon exchange among terrestrial, oceanic and atmospheric environment. Rivers and streams not only transfer various forms of carbon (dissolved and particulate) to oceans, but also evade a significant amount of carbon to the atmosphere (Battin et al., 2009; Richey et al., 2002). Due to CO₂ evasion, the flux of carbon that leaves the terrestrial biosphere through global fluvial network was suggested to be twice larger than the amount that ultimately reaches the coastal ocean (Bauer et al., 2013; Regnier et al., 2013). Raymond et al. (2013) estimated a global evasion rate of 2.1 Pg C yr⁻¹ from inland waters, and that global hot spots in stream and rivers which occupy only 20 % of the global land surface represented 70 % of the emission. They emphasised

that further studies are needed for identifying the mechanisms controlling CO₂ evasion at a global scale”.

Lines 125–126: Alkalinity measurement is critical for the calculation of pCO₂ and CO₂ evasion. Please provide more detailed information on how the alkalinity was measured and double checked. Was there a difference in alkalinity between filtered and unfiltered samples? It seems the turbidity can go up sometimes and I wonder how this could influence the alkalinity of filtered water.

The method for alkalinity determination was added in the revised manuscript in page 4. “ Total alkalinity of the hourly samples was immediately determined on non-filtered water samples (30 ml water sample) in situ by titration method with 0.01M HCl (APHA, 1995). For each sample, triplicates were titrated and the analytical error was below 3 %”.

We also tried to test the difference in alkalinity between filtered and unfiltered samples at the Hanoi site in March 2018 and found that the alkalinity values were not so different in dry season when suspended solids was not so high .

Lines 138–: Have you measured CO₂ flux directly from the surface of the water and compared that with the calculated values? (e.g. Duc et al., 2013, Environmental Science & Technology, 47, 968-975)

Yes, we measured CO₂ flux directly from the surface of the water using a floating chamber method. We obtained an average CO₂ flux of 189 mmol.m⁻².d⁻¹ (with values ranging from 37.8 – 492.1 mmol.m⁻².day⁻¹). These values were lower than the values calculated from pCO₂ measured using equilibrator method and the equation provided by Frankignoulle et al. (2001) and Raymond and Cole (2011). This result was surprising since it is considered that when the water flow is higher than 0.2 m s⁻¹, the presence of the chamber induces artificial turbulence that results in elevated CO₂ fluxes.

Lines 143–: I agree with the other reviewers that using wind speed as a component in the equation may not appropriate. Detailed explanation is needed on why the equation was chosen.

As suggested by reviewers, we calculated k_{600} by other method proposed by Raymond et al (2012), basing on different variables such as river discharge, water velocity, depth and slope. The values of k_{600} now are ameliorated and then CO_2 flux evasion was recalculated.

K_{600} was calculated as presented in the section “2.5 CO_2 fluxes determination”, page 5-6:

“In this study, k_{600} was calculated using the equation from Raymond et al. (2012) based on stream velocity (V , in m s^{-1}), slope (S , unitless), depth (D , in meters) and discharge (Q , in $\text{m}^3 \text{s}^{-1}$), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

Lines 256–269: Detailed explanation is needed in “discussion” on why there is such a large difference in the measured and calculated pCO_2 .

We apologize for the errors of pCO_2 calculation. Values were corrected in the revised manuscript (see table 2). However, a difference between pCO_2 calculated and measured was found. An explanation concerning this difference was added in the manuscript revised in page 7 -8.

“3.3. Comparisons of the pCO_2 results obtained by the two methods

pCO_2 along the lower Red River (Vietnam) in the dry and the wet seasons were determined by two methods: i) direct measurements using an equilibrator connected to an IRGA, ii) calculated from pH and alkalinity using the CO_2 -SYS[®] software. The direct pCO_2 measurements gave slightly higher values than the calculated ones (Table 2), but the values of two methods were similar and presented the same trend of spatial and seasonal variations ($R^2 = 0.77$, Fig. 2; Table 2). Lower values of the calculated pCO_2 in this study may be caused by the analytical errors in pH or under-estimation of total alkalinity. Similarly, the CO_2 outgassing rates which were calculated from measured pCO_2 from equilibrator were higher than the ones derived from the calculated pCO_2 from CO_2 -SYS, however they are in the same orders and have similar variation trends (Table 3, Fig 2)”

Lines 299–312: This paragraph would belong to discussion rather than results.
Discussion: The results and discussion are mixed.

We revised the paragraph

Lines 400: Are the differences statistically significant?

Yes. The results from t-test showed that:

- *Seasonal (dry –wet) variation : difference appeared for all variables ($p < 0.05$)*
- *Day-night variation: difference for pH ($p < 0.05$) but no clear difference for other variables*

The results from t-test and ANOVA test showed that

Spatial variation (5 sites) : temperature was not different within 5 sites. Other variables were significant different ($p < 0.05$).

We added the difference statistics significant through the revised ms.

Lines 411–422: This sentence is too long. Extracting only essential information would be better than this long sentence.

This sentence is now revised and moved to the section “ 4.2 Spatial variations of pCO₂ and fCO₂ outgassing » in page 10 - 11

Tables: Is the “+/-” standard error or standard deviation? Please clarify it.

It's standard deviation. We added the information in the table captions

Figures: Is the error bar standard error or standard deviation? Please clarify it.

It is the standard deviation. We added the information in the figure captions

Figure captions needs to more detailed description of the figures including explanations on legends.

Figure captions were revised as suggested, and thus more detailed.

Anonymous Referee #3

Received and published: 13 February 2018

General Comments:

The manuscript entitled “CO₂ partial pressure and CO₂ emissions from the lower Red River (Vietnam)” by Le et al provides new and important data on CO₂ in the Lower Red River. The results are a good contribution for the understanding of the role of Asian rivers for the global carbon evasion from freshwater ecosystems. However, there are many technical problems that need to be address to increase the quality of the paper. I agree with the other reviewers that the estimate of the CO₂ evasion is the main problem in the paper and must be reworked. The figures and tables are clear and well designed. However, I suggested some changes in the number of figures and tables. In summary, the authors should review the flux calculation (see specific comments below); consider k600 calculations based on turbulence generated by water flow and; reorganize Results and Discussion sections. Specific comments and suggestions are below.

We thank you very much for the helpful comments and suggestions.

Specific comments:

66 – This sentence suggests that there is a “limited knowledge” about carbon flux. Does it mean that there are published information about carbon flux in the Red River, or not?

Yes, there are some published information about carbon fluxes for a peri-urban area in the Red River Delta (Trinh et al., 2012) and (Nguyen et al., 2018). We revised the sentence and add the references:

“However, there is a lack of data concerning CO₂ outgassing and carbon budget of the lower Red River (Trinh et al., 2012, Nguyen et al., 2018).”

79 – In the figure 1, the Ba Lat station does not seem to be located about 50 km from the sea. Please clarify.

We apologize for the error. The Ba Lat site is 13 km from the sea. The information was corrected in the text page 3.

Some references in the introduction are missing (e.g. lines 48, 56)

References were added in the revised manuscript

86 – I suggest removing the sentence “see below for the detail river discharge in 2014” and insert the correct reference - figure, table etc.

The sentence was removed, the word “table 1” was replaced

109 – The sentence “All solutions used for. . .” is unnecessary.

This sentence was deleted

151 – What is the “regulator”? You mean pump or a flux regulator? Please, clarify.

It was changed into “a flow regulator”.

162 – By convention k_{600} is the gas transfer velocity normalized to a Schmidt number of 600. And k is the gas transfer velocity. “ Sc ” should not be the “Schmidt number, normalized to Schmidt number of 600”. “ Sc ” should be the Schmidt number of a given gas (CO₂ in this case) at a given temperature. Please, clarify the calculation and check if the calculation is correct.

We revised the paper by recalculating the k_{600} proposed by (Raymond et al., 2012). Thus, Sc was removed from the new calculation.

K_{600} was calculated as presented in the section “2.5 CO₂ fluxes determination” , page 5-6:

“In this study, k_{600} was calculated using the equation from Raymond et al. (2012) based on stream velocity (V , in $m s^{-1}$), slope (S , unitless), depth (D , in meters) and discharge (Q , in $m^3 s^{-1}$), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

166 – I wonder why the authors did not consider the temperature variation measured by HOBO sensor to calculate “a”? Were temperature records not made at the same time? In addition, conductivity is much higher in Ba Lat station suggesting differences in salinity among stations. If “a” is a constant (line 167), the salinity variation seems not to be considered in the calculation.

We calculated the fCO_2 at 5 sites of the Red River with different α values : $\alpha = 3.941 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ at 24 °C for dry season and $\alpha = 3.138 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ at 27 °C for rainy season. The average flux of CO_2 outgassing was $525.7 \text{ mmol.m}^{-2}.\text{d}^{-1}$. Then, this value was very close with the one calculated from the constant $\alpha = 3.4 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ we used for both rainy and dry seasons of the Red River in this study, which resulted in the fCO_2 average of the whole Red River $530 \text{ mmol.m}^{-2}.\text{d}^{-1}$.

An explanation was added in page 6

“ α is the solubility coefficient of CO_2 for given temperature and salinity (Weiss, 1974) ($\text{mol L}^{-1} \text{ atm}^{-1}$). In this case, $\alpha = 0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$. In this study, salinity variations were low, except for the Ba Lat station. Temperature did not change a lot. We checked the influence of different α values in the dry ($\alpha = 3.941 \cdot 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 24 °C) and the wet season ($\alpha = 3.138 \cdot 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 27 °C) at the 5 sites and compared with the constant α value of $0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$. “

170 – Please, check the units of each element of the equation. The flux was calculated in $\mu\text{mol m}^{-2} \text{ s}^{-1}$ but the k , a and pCO_2 air is cm h^{-1} , $\text{mol L}^{-1} \text{ atm}^{-1}$ and ppm, respectively. Please reorganize the section 2.4.1 for clarification.

Thank you for the comments. The flux is now calculated from different variables taking into account different units. We added the explanation for converting the final unit of flux calculation in $\text{mmol m}^{-2} \text{ d}^{-1}$ in the section 2.4 CO_2 fluxes determination in page 5

183 – If k_{600} values are closely related to flow velocity and channel gradient, why author used k_{600} values calculated from wind speed? The authors should present a convincing explanation or review the calculation and values.

Thank you for the comment. We now calculate the k_{600} by the formula proposed by Raymond et al (2012) which is based on river flow velocity, river discharge, depth, slope in pages 5 and 6:

“ k_{600} , was gas transfer velocity of CO_2 or piston velocity (cm h^{-1}). Some studies indicate that k_{600} values are closely related to flow velocity and channel gradient for rivers (Alin et al., 2011). In this study, k_{600} was calculated using the equation from Raymond et al. (2012) based on stream velocity (V , in m s^{-1}), slope (S , unitless), depth (D , in meters) and discharge (Q , in $\text{m}^3 \text{s}^{-1}$), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}''$$

220 – The same results are presented in Table 2 and Figure 2. Please, remove the table or the figure.

Figure 2 was removed as suggested.

223 – I suggest add Alkalinity values in the table or figure 2.

Alkalinity values are presented in the table 2, in the column named “TAlk”.

257 – Change “monsoon” to “wet”.

It was changed

263-269 – Abril et al., 2015 discuss overestimation of pCO_2 using total alkalinity in acidic, organic-rich freshwaters. However, if this water condition is not the case of Red River, the find of Abril is not an explanation for the opposite (lower calculate values when compared with the measured values). These values should be similar or, please, provide a clear and convincing explanation.

Thank you for the suggestion. We removed the sentence from the revised manuscript.

276 – Discussion inside the Results section. Results and Discussion are mixed in several parts of these sections. I suggest re-write and reorganize these sections.

Thank you for the suggestion. We re-writed and reorganized the Results and Discussion sections

Table 1 – Please double check the station location. I plot the station locations and there are some inconsistencies (e.g. Ba Lat is located in the ocean and not in the Red River).

There was a mistake for the location of the Ba Lat site. This was corrected in table 1 and in the text. Other sites were also checked.

Table 2 and Figure 2 – Why the values after +/- in table 2 and the error bar in Figure 2 are different? What does they mean?

We checked the table 2. The figure 2 was removed in the revised manuscript.

Figure 6 – What the gray and dark circles mean. Dry and wet season? Insert these information in the figure caption.

The figure 4 demonstrates the Relationship between environmental variables and pCO₂ at the five sites of the lower Red River in the wet (Sept) and the dry season (Nov) 2014. The figure and caption were revised.

Anonymous Referee #4

Received and published: 14 February 2018

GENERAL COMMENTS

Le et al. report a valuable and potentially interesting data-set of CO₂ data measured with an equilibrator at several stations of the Red River. This is a valuable data-set as CO₂ data directly measured are lacking worldwide, and in particular in sub-tropical and tropical environments.

However, the paper suffers from a poor writing (English phrasing and syntax) that absolutely needs to be improved.

Also, the presentation and discussion of the results are extremely convoluted. The authors make a list of numerous possible hypothesis but do not really provide a convincing interpretation of the data (a clear and solid “story-line”).

Some of the comparisons in the discussion are out of scope and irrelevant such as comparisons with mangroves, beaver ponds, sea-ice and the Southern Ocean.

Thank you for the comments and suggestions. We revised the manuscript in taking into account all comments/suggestions from the reviewers.

MAJOR COMMENTS

The discussion is extremely convoluted and goes in all sorts of directions but nothing really conclusive comes out of it. By looking at the pCO₂ plot in Figure 2, we can conclude:

- Differences between night and day are not statistically different whatever the site. The authors should try to explain this by comparing with other **river** sites where night-day pCO₂ differences have been reported. The low phytoplankton biomass as indicated by chlorophyll-a content and the low differences in night-day temperature that induce low variations in CO₂ solubility probably explain the low daily variations in pCO₂. Anyway the low daily variations of pCO₂ are an interesting aspect of the paper that deserves a longer discussion. Possibly make a table with studies that have shown daily variations of pCO₂ with other variables such as average Chlorophyll-a content or POC, daily changes in temperature, . . .

Thank you very much for the suggestion. We revised the text for discussing the temperature influence on pCO₂ and fCO₂ of the Red River in page 9, section “4.1 Temporal variations of pCO₂ and CO₂ fluxes of the lower Red River” as suggested.

For example, we revise the text in page 9:

“Concerning the lower Red River, water temperature did not show clear variation between the day and the night. In addition, low Chl-a concentrations were measured, from 0.5 to 3.1 µg L⁻¹, probably as a result of the high turbidity limiting light penetration in the water column. Thus, phytoplankton activity had a low influence on C dynamic in the lower Red River system. Consequently, there are no clear variations of pCO₂ and CO₂ fluxes between the day and the night time at the different stations along the lower Red River”

- Overall the spatial gradients (differences among sites) are very low, except for Hoa Binh. Probably that all sites are located very close and correspond to similar sized rivers with similar catchment characteristics (land cover + lithology) so that the spatial differences are low. An explanation for the higher values of Hoa Binh is needed. Is it because it's downstream of a dam? This would make sense based on existing literature (Sinnamary river, cf paper by Guérin et al.). Maybe it's mentioned somewhere in the text, but I missed the information being distracted by all of the other marginal bits and pieces of discussion.

Thank you for the suggestion. We revised the discussion about the influence of the dam in page 10 and 11, section "Influence of dams on pCO₂ and CO₂ emission"

"4.2.4 Influence of dams on pCO₂ and CO₂ emission

Previously, reservoirs were suggested to decrease riverine pCO₂ due to increased residence times and autotrophic production (Wang et al., 2007). However, Lauerward et al., (2015) found a low negative correlation between them. Abril et al., (2005) noted that intense mineralization of organic matter (OM) originating from the reservoir was possibly a significant source for pCO₂ value in downstream river. In addition, the influence of the dam on the gas transfer velocity and then CO₂ outgassing flux in the river downstream of the dam was also demonstrated in the study of the Sinnamary River (Guérin et al., 2007). In the present study, in the upstream part, pCO₂ ranged from 964 ppm (at Yen Bai) to 3,830 ppm (at Hoa Binh), being highest at the Hoa Binh site where the lowest pH values were measured. Higher k₆₀₀ values (from 63 to 68 cm h⁻¹) were also observed at the Hoa Binh and Vu Quang sites. Noted that the Hoa Binh site is situated downstream a series of reservoirs, which have been constructed in both Chinese and Vietnamese parts including two large dams Hoa Binh (in 1989) and Son La (in 2010). The Vu Quang site is located in the downstream of a series of reservoirs, including two important Thac Ba (in 1970) and Tuyen Quang (in 2010). Previous studies emphasized that these dams have impacted water and sediment discharges downstream (Ha and Vu 2012; Ngo et al. 2014; Lu et al. 2015) with significant sediment deposition being observed in the reservoirs (Dang et al. 2010; Vinh et al. 2014; Lu et al. 2015). Thus, the higher pCO₂ measured at these sites (average value of 3129 ± 32 ppm) may reflect the increased decomposition of OM and/or the water perturbation due to dam construction, especially for the Da River. The impact of dams on downstream pCO₂ may be less for the Lo and the Thao Rivers (average values of 1395 ± 63 ppm and 993 ± 14 ppm, respectively), where less numbers and less size (only small and medium) of dams/reservoirs were built up in their upstream parts. Thus, the high pCO₂ measured at these stations may reflect the increased decomposition of OM and/or the water perturbation due to the large dam construction."

- The seasonal variations are comparatively very small (except for Hoa Binh). This is an intriguing result that deserves being explored. The authors should compile in a table studies that report seasonal cycles of pCO₂ (report the min-max of pCO₂) and other relevant variables such as ratio of max/min of discharge, seasonal changes (minC₂ max) of POC and DOC. It might be useful to show a plot with the full seasonal cycle of

freshwater discharge and indicate the two sampling periods. This would allow readers to situate the samplings on the hydrograph.

A table with the values of pCO₂, POC, DOC, Chl a, SS and water discharge in dry and wet season was added in the in the Supplementary Material.

A figure of daily river discharges at the outlets of the Thao, Da and Lo tributaries and the main axe of the Red River at Hanoi and SonTay was added in the Supplementary Material.

- The fact that the city of Hanoi does not seem to influence markedly the O₂ and pCO₂ levels is also intriguing and deserves some discussion. Was the station located within the city itself or slightly downstream ? Could this be due to the fact that freshwater discharge is relatively important (2000-3000 m³/s ?). A tabular comparison of studies that have shown the influence of cities on river CO₂ might be useful. In rivers, the main driver of the gas transfer velocity is turbulence generated by flow. I suggest that the authors use flow velocity data (that are available at gauging stations) and use the equations of Raymond et al. (2012) to compute the gas transfer velocity and fluxes (equation N 5 of Table 2 of Raymond et al. (2012) is recommended).

Thank you very much for the suggestion. We now calculate the k₆₀₀ by using the equation of (Raymond et al 2012) as suggested.

Hanoi station locates within the city itself and at this site, the river has not received yet the wastewater discharge of the whole city. This may explain that the city of Hanoi does not seem to influence markedly the O₂ and pCO₂ levels. We revised the section “Influence of population density on pCO₂ and CO₂ emission” in page 12 as followings:

“4.2.5 Influence of population density on pCO₂ and CO₂ emission

Previous studies demonstrated very high value of pCO₂ in river estuaries as a result of different human activities. For instance, pCO₂ up to ~25,000 ppm was measured in the Rhine estuary (Kempe, 1982) or up to ~15,200 ppm in the Scheldt estuaries due to high discharge of pollutants (Borges and Frankignoulle, 2002).

Concerning the Red River, from the upstream to the downstream part of the main axe, pCO₂ together with CO₂ outgassing flux slightly increased from Yen Bai (993 ± 14 ppm and 364.9 ± 10.3 mmol m⁻² d⁻¹ respectively) to Hanoi (1,275 ± 17 ppm and 304 ± 7.3 mmol m⁻² d⁻¹), whatever the season. However, it is worth to note that the Hanoi station was located within the city itself and at this station, the river has not yet received the wastewater discharge of the whole city. Consequently, the Hanoi

station in this study may not reflect the influence of whole city, with probably lower O₂ and higher pCO₂ levels as observed for other urban rivers in the Red River Delta (Trinh et al., 2007; 2009; 2012)”

For all of the spatial and seasonal comparisons, some firm statistical testing is required (t-test, ANOVA, . . .).

We now checked all of the spatial and seasonal comparisons by statistical testing from t-test and ANOVA, in page 6 for the method and throughout the ms.

“Student t-test was used to test the difference of variables values between the two different times (the wet and the dry) and (the day and the night), whereas ANOVA was used to test the difference of variables within stations on the measured mean variables. Probabilities (p) were determined and a p value of < 0.05 was considered to be significant“

SPECIFIC COMMENTS

L29-30: could also be due direct inputs of CO₂ from soils or wetlands.

Yes, it is a possibility, and it was added

L48-51: this is a very complicated way to state that C fluxes from rivers depend on lithology and land cover.

This sentence was revised “Riverine carbon concentrations and CO₂ outgassing from rivers are impacted by both natural and human factors (Liu et al., 2016; Liu et al., 2017).”

L59: improve instead of “precise”

It was changed

L75: Please justify the choice of the 5 stations. Also, it needs to be clearly explained that one of the stations is influenced by seawater intrusion. Are the other stations affected by tidal wave propagation ?

The paragraph was revised as followings:

“Five stations were studied in the lower Red River (Vietnam): Yen Bai station (at the outlet of the Thao river); Hoa Binh station (after Son La and Hoa Binh reservoirs, at the outlet of the Da River); Vu Quang (at the outlet of the Lo River); Hanoi and Ba Lat stations (in the main course of the Red River downstream). The three stations Yen Bai, Vu Quang and Hoa Binh are representative for three main tributaries (Thao, Da and Lo) of the upstream Red River whereas the Ha Noi station is representative for the main course Red River after confluence of three main tributaries. Within 5 stations observed, only the Ba Lat station which is located in the Red River mouth, about 13 km from the sea is influenced by seawater intrusion (Fig 1).”

L94: provide information on land cover, lithology, and other relevant catchment characteristics for the studied rivers.

Some information concerning geomorphology, lithology or other river characteristics of the studied rivers were added in the text (page 3) as suggested.

“The Delta is located in a very flat and low land, with an elevation ranging from 0.4 to 12 m above sea level (Nguyen Ngoc Sinh et al., 1995). Previous studies showed the difference of lithology in the three upstream tributaries: Paleozoic sedimentary rocks (55.5%), Mesozoic silicic rocks (18.0%) and Mesozoic carbonated rocks (16.7%) dominate in the Thao basin, whereas Paleozoic sedimentary rocks (85.3%) and Mesozoic carbonated rocks (14.7%) cover the Da river basin, and the Lo is composed of Mesozoic silicic rocks (21.5%) and Paleozoic sedimentary rocks (72.7%). The delta area is totally covered by alluvial deposits (100%) (Moon et al., 2007; Le et al., 2007). ”

L107: replace “sensor” by CTD

It is not a CTD. It is a YSI probe with different sensors. So we revised the sentence

“Physico-chemical parameters were automatically recorded every minute during 24h for each sampling campaign: pH, turbidity, salinity, chlorophyll a by a YSI6920 multiparameters probe (YSI, USA)”

L110: “all data must be entered on the documents” ? What does this mean ?

This sentence was deleted

L113: total “alkalinity”

It was corrected

L117-126: provide precision and accuracy of all the measured variables. Everywhere in the ms (text and tables) pCO₂ values should not be given at the tenth of ppm, given that with an equilibrator precision of pCO₂ measurements is typically of +/-1 ppm and accuracy of pCO₂ measurements is typically of +/- 3-5 ppm (at best).

Precision and accuracy of the measured variables were added in the section 2.2 Sampling procedures and analysis

L125: what was the volume of sample water? What acid and concentration was used ? How was the end-point determined? What titrator was used? The authors discuss the differences of pCO₂ measured directly and calculated from pH and total alkalinity (TA). However, for this discussion to be meaningful it is necessary to have an idea of the quality of the pH and TA measurements, and this is only possible if analytical techniques are described in detail. This is lacking for TA here, and elsewhere the authors need to provide information on the pH electrode calibration. Type of buffers, frequency of calibration, etc.

The method for alkalinity determination was added in page 4

“Total alkalinity of the hourly samples was immediately determined on non-filtered water samples (30ml water sample) in situ by titration method with 0.01M HCl (APHA, 1995). For each sample, triplicates were titrated and the analytical error was below 3 %.”

pH electrode was calibrated using standard solutions (pH = 4.01 and pH = 6.88, Merck) and the pH precision and accuracy was ± 0.01.

TA data need to be expressed in μmol/L (as by convention). This is the unit of the TA as input variable for the CO₂sys program. So why express the data in mg/L ? Further the data expressed per mass (mg/L) instead of per moles are extremely confusing. Is it mg of C ? Or mg of H⁺ ? (based on the conventional definition of TA as the quantity

(number of moles) of protons to titrate bases in one kilogram (or L) of water). Should it be mg of C, then the TA for the first line of Table 2 (105 mg/L) would be 8750 $\mu\text{mol/L}$. In this case the computation of pCO_2 gives 3670 ppm for a pH of 8.2 and 26.4 C (and not 270 ppm as stated). Should it be mg of CaCO_3 , then the TA for the first line of Table 2 (105 mg/L) would be 1050 $\mu\text{mol/L}$. In this case the computation of pCO_2 gives 440 ppm for a pH of 8.2 and 26.4 C (and not 270 ppm as stated). Should it be mg of CO_3 , then the TA for the first line of Table 2 (105 mg/L) would be 1750 $\mu\text{mol/L}$. In this case the computation of pCO_2 gives 733 ppm for a pH of 8.2 and 26.4 C (and not 270 ppm as stated).

The result from TA analysis is in mg/l CaCO_3 as units. During calculating pCO_2 by CO2-SYS, when needed, it was converted into $\mu\text{mol/l}$ or mol/l .

In the revised version we re-calculated pCO_2 values

L140: Abbreviation IRGA not defined.

It was added in the text “a portable InfraRed Gas Analyser (IRGA) (Licor 820, Licor®, USA)”

L144: replace “balanced” by equilibrated.

It was replaced

L156: This equation was established in the 1970’s well before the paper of Raymond and Cole.

This sentence was deleted for the revised version

L160: replace “function” by parameterization.

This sentence was deleted for the revised version.

L167: *solubility changes with temperature, why did you state a constant value ?*

We calculated the $f\text{CO}_2$ at 5 sites of the Red River with different α values : $\alpha = 3.941 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ at 24 °C for dry season and $\alpha = 3.138 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ at 27 °C for rainy season. The average flux of CO_2 outgassing was $525.7 \text{ mmol.m}^{-2}.\text{d}^{-1}$. Then, this value was very closed with the one calculated from the constant $\alpha = 3.4 \cdot 10^{-2} \text{ mol.L}^{-1}.\text{atm}^{-1}$ we used for both rainy and dry seasons of the Red River in this study, which resulted in the $f\text{CO}_2$ average of the whole Red River $530 \text{ mmol.m}^{-2}.\text{d}^{-1}$.

An explanation was added in page 6

“ α is the solubility coefficient of CO_2 for given temperature and salinity (Weiss, 1974) ($\text{mol L}^{-1} \text{ atm}^{-1}$). In this case, $\alpha = 0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$. In this study, salinity variations were low, except for the Ba Lat station. Temperature did not change a lot. We checked the influence of different α values in the dry ($\alpha = 3.941 \cdot 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 24 °C) and the wet season ($\alpha = 3.138 \cdot 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 27 °C) at the 5 sites and compared with the constant α value of $0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$ ”

L174-190: I suggest that this section is removed, as this topic has been discussed at length in several dedicated papers.

This section was deleted as suggested

L195: The speciation of DIC was established decades before the papers of Cai et al. 2008 and Sun et al. 2010). The paper of Park (1969) formalised the equations to compute the speciation from all of the possible combinations.

The reference Park (1969) was added

L203: The calculated $p\text{CO}_2$ is about 5 times lower than the $p\text{CO}_2$ measured directly, this can hardly be considered as ‘similar results’ as stated.

We apologize for the error of values $p\text{CO}_2$ calculated in the table 2. The text was also revised for discussion about the difference between $p\text{CO}_2$ measured and calculated in page 7-8, as followings:

“3.3. Comparisons of the $p\text{CO}_2$ results obtained by the two methods

$p\text{CO}_2$ along the lower Red River (Vietnam) in the dry and the wet seasons were determined by two methods: i) direct measurements using an equilibrator connected to an IRGA, ii) calculated from pH and alkalinity using the $\text{CO}_2\text{-SYS}^{\text{®}}$ software. The direct $p\text{CO}_2$ measurements gave slightly higher values than the calculated ones (Table 2), but the values of two methods were similar and presented the same

trend of spatial and seasonal variations ($R^2 = 0.77$, Fig. 2; Table 2). Lower values of the calculated $p\text{CO}_2$ in this study may be caused by the analytical errors in pH or under-estimation of total alkalinity. Similarly, the CO_2 outgassing rates which were calculated from measured $p\text{CO}_2$ from equilibrator were higher than the ones derived from the calculated $p\text{CO}_2$ from CO_2 -SYS, however they are in the same orders and have similar variation trends (Table 3, Fig 2).

”

L230-235: Present and discuss either salinity or conductivity but not both as they provide the same information.

We revised the sentence as followings:

“Conductivity followed the same trend of the salinity variation which were around $0.2 \pm 0.0 \text{ mS cm}^{-1}$ for 4 upstream sites and higher values were found for the Ba Lat site, especially in dry season (up to $6.6 \pm 3.4 \text{ mS cm}^{-1}$) ($p < 0.05$)” in page 7.

L233: Statistical test needed.

Statistical test was added throughout the revised ms as suggested

L245-251: Statistical test needed.

Statistical test was added throughout the revised ms as suggested

L260: The “good” correlation is of marginal interest what’s relevant is that the $p\text{CO}_2$ values from the two methods differ by a factor of 5

Again, the text was also revised for discussion about the difference between $p\text{CO}_2$ measured and calculated, as followings in page 7 -8

“3.3. Comparisons of the $p\text{CO}_2$ results obtained by the two methods

$p\text{CO}_2$ along the lower Red River (Vietnam) in the dry and the wet seasons were determined by two methods: i) direct measurements using an equilibrator connected to an IRGA, ii) calculated from pH and alkalinity using the CO_2 -SYS[®] software. The direct $p\text{CO}_2$ measurements gave slightly higher values than the calculated ones (Table 2), but the values of two methods were similar and presented the same trend of spatial and seasonal variations ($R^2 = 0.77$, Fig. 2; Table 2). Lower values of the calculated $p\text{CO}_2$ in this study may be caused by the analytical errors in pH or under-estimation of total alkalinity. Similarly, the CO_2 outgassing rates which were calculated from measured $p\text{CO}_2$ from equilibrator were higher than the ones derived from the calculated $p\text{CO}_2$ from CO_2 -SYS, however they are in the same orders and have similar variation trends (Table 3, Fig 2).

L261-269: This result is extremely intriguing because the sampled rivers are within the “acceptable” range of applicability of the computation of pCO₂ from pH and TA, with low DOC and high pH values. The under-estimation of the computed pCO₂ could be due to a bias in the measurements of pH and TA, which is not possible to evaluate given the lack of information in the material and methods. Anyway, the under-estimation of TA and/or over-estimation of pH could explain why the computed pCO₂ is very low compared to directly measured pCO₂.

The method for TA and pH determination was added in the revised manuscript in page 4. We may under-estimate TA resulting the lower computed pCO₂ compared to directly measured pCO₂. A paragraph was added to explain the difference of pCO₂ computed and pCO₂ measured in page 7 -8

“3.3. Comparisons of the pCO₂ results obtained by the two methods

pCO₂ along the lower Red River (Vietnam) in the dry and the wet seasons were determined by two methods: i) direct measurements using an equilibrator connected to an IRGA, ii) calculated from pH and alkalinity using the CO₂-SYS[®] software. The direct pCO₂ measurements gave slightly higher values than the calculated ones (Table 2), but the values of two methods were similar and presented the same trend of spatial and seasonal variations (R² = 0.77, Fig. 2; Table 2). Lower values of the calculated pCO₂ in this study may be caused by the analytical errors in pH or under-estimation of total alkalinity. Similarly, the CO₂ outgassing rates which were calculated from measured pCO₂ from equilibrator were higher than the ones derived from the calculated pCO₂ from CO₂-SYS, however they are in the same orders and have similar variation trends (Table 3, Fig 2).

L271-298: This discussion is of marginal interest because it depends on the way the gas transfer velocity was computed from a parameterisation as function of wind speed. pCO₂ did not change markedly from night to day, but wind speed was higher during the day than the night. This is somewhat trivial, and if the authors re-compute the fluxes with a parameterization as function of flow, this day-night difference will be erased.

Thank you for the comments. We remove this previous discussion since we recalculated the k₆₀₀ and flux of CO₂ outgassing.

K₆₀₀ was calculated as presented in the section “2.5 CO₂ fluxes determination” , page 5-6: “In this study, k₆₀₀ was calculated using the equation from Raymond et al. (2012) based on stream velocity (V, in m s⁻¹), slope (S, unitless), depth (D, in meters) and discharge (Q, in m³ s⁻¹), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

L298: Regarding the Ho et al. (2016) study, a note of caution is needed. This study used wind speeds from a sonic anemometer above the mangrove forest (obviously higher wind speeds than the level of the river below the canopy) and located 4 km from the coastline while the tracer injection point was located 12 km away from the coastline. For both these reasons, wind speed data used to build the Ho et al. (2016) relationship is over-estimated, meaning that the relationship itself is not reliable, and the role of currents in generating turbulence (and driving the gas transfer velocity) probably underestimated.

Thank you for the comments. We remove this part of the discussion since we now recalculate the k_{600} and flux of CO_2 outgassing of the Red River using a different equation.

K_{600} was calculated as presented in the section “2.5 CO_2 fluxes determination”, page 5-6:

“In this study, k_{600} was calculated using the equation from Raymond et al. (2012) based on stream velocity (V , in m s^{-1}), slope (S , unitless), depth (D , in meters) and discharge (Q , in $\text{m}^3 \text{s}^{-1}$), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

L299-312: In this discussion there's a mix of studies in lakes and mangroves, which makes little sense when discussing CO_2 dynamics in rivers.

Thank you for the suggestion. We revised the paragraph and removed all reference studies unnecessary in lakes and mangroves throughout the revised ms.

L302: Roulet et al (1997) report on beaver ponds. This is a very specific environment that is not very relevant for comparison with Red river.

The reference Roulet et al (1997) was removed as suggested.

L321: references are needed to back this statement.

The reference (Richey et al 2002) was added in the revised ms.

L323: or (in addition) inputs of CO_2 from wetlands.

It was added as suggested

L335: Chanda study deals with mangroves and Takahashi with oceans. This is irrelevant (and out of scope) to discuss CO₂ dynamics in rivers.

The references were removed.

L338: Comparison with Southern Ocean is irrelevant (and out of scope).

The sentence was removed

L346: Why did you not include freshwater discharge in the PCA and the correlation matrix analysis ?

The PCA and the correlation matrix took into account river discharge.

L359: Statistical test needed.

Statistical test was added throughout the revised ms.

L397: The cited references deal with Artic Ocean and sea-ice, not with Pearl River.

This was removed from the revised ms.

L401: Statistical test needed.

Statistical test was added throughout the revised ms.

L407-408: The city of Ha Noi does seem to influence DOC and POC but there seems to be little effect on O₂ and pCO₂. This is intriguing.

We revised the discussion in page 12, in the section

“4.2.5 Influence of population density on pCO₂ and CO₂ emission

Previous studies demonstrated very high value of pCO₂ in river estuaries as a result of different human activities. For instance, pCO₂ up to ~25,000 ppm was measured in the Rhine estuary (Kempe, 1982) or

up to ~15,200 ppm in the Scheldt estuaries due to high discharge of pollutants (Borges and Frankignoulle, 2002).

Concerning the Red River, from the upstream to the downstream part of the main axe, $p\text{CO}_2$ together with CO_2 outgassing flux slightly increased from Yen Bai (993 ± 14 ppm and 364.9 ± 10.3 mmol $\text{m}^{-2} \text{d}^{-1}$ respectively) to Hanoi ($1,275 \pm 17$ ppm and 304 ± 7.3 mmol $\text{m}^{-2} \text{d}^{-1}$), whatever the season. However, it is worth to note that the Hanoi station was located within the city itself and at this station, the river has not yet received the wastewater discharge of the whole city. Consequently, the Hanoi station in this study may not reflect the influence of whole city, with probably lower O_2 and higher $p\text{CO}_2$ levels as observed for other urban rivers in the Red River Delta (Trinh et al., 2007; 2009; 2012). ”

L410: some of the cited “rivers” are in fact mangrove brackish systems (irrelevant and out of scope).

We checked the cited “rivers” in this paragraph

L426-429: the authors provide no evidence to back up this hypothesis that is mainly speculation.

The sentence was removed from the revised manuscript.

L427: Elsewhere in the discussion the authors say that the Hoa Binh site has high $p\text{CO}_2$ because downstream of a dam, and here the authors say the low $p\text{CO}_2$ values in the Red River is also due dams. This cannot work both ways. Should the authors want to explore why $p\text{CO}_2$ values are lower in the Red River than other rivers worldwide comparing levels of DOC and POC with other rivers might be useful. Also, some studies have provided hypothesis to explain large-scale variations of $p\text{CO}_2$ across river catchments such as productivity, population density, temperature, . . . e.g. the Lauerwald study that is cited by the authors.

The sentence was removed from the revised manuscript. The discussion about different factors that impacted on $p\text{CO}_2$ and $f\text{CO}_2$ of the Red River was re-written and re-organized through the revised manuscript.

L434-451: This section provides a summary of the paper (and duplicates the abstract) and does not provide a real conclusion.

The conclusion was revised

L565: typo in “Costs”

The reference was removed from the revised manuscript

L598: Nathalie is the first name not the family name.

The first name and family name of the authors in this reference were corrected

L616: Patricia is the first name not the family name.

The reference was removed from the revised manuscript.

L618 and L650: This reference appears twice.

The reference was removed from the revised manuscript.

Table 3: There's no need to provide the air-water CO₂ fluxes derived from the pCO₂ calculated from pH and TA. Since calculated pCO₂ is under-estimated compared to directly measured pCO₂, this is also the case for the fluxes, in a very predictable and trivial way.

The flux of CO₂ outgassing derived from the pCO₂ calculated from pH and TA was removed from the table 3.

In tables and figures is given in the turbidity of the probe in NTU, when in fact authors measured TSM. Why not show also (or instead) the TSM data ?

Also, it might be useful to show the %POC data instead (or in addition to) POC, since POC follows closely TSM, but %POC gives some info on the origin of POC.

The data on TSM and % POC were added in the table SMI

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This paper documents the chemical conditions and concentrations of dissolved carbon dioxide in the Red River system of Vietnam. The data contribute to the "database" of concentration values for the globe, with one goal of further constraining the CO₂ source strength of inland waters. Therefore, the data are valuable on their own, especially given that they fill in geographic gaps for SE Asia. The main criticism of this paper is the use of a wind-driven gas exchange model. While criticism of gas exchange models are prevalent within the community of researchers, this example is especially problematic as it relies on unlikely drivers of turbulence (and thus gas exchange) in riverine systems. There is some evidence that gas exchange is enhanced by some wind patterns in very large rivers, however, gas exchange in rivers is not considered to be a major driver. Rather, it is turbulence generated by water flow that drives gas exchange rates in these systems. Therefore, the CO₂ emission estimates are not only biased, as recognized by the authors, but are likely to be highly inaccurate due to the model selected. It is hard to believe the results without some other line of confirmation. In addition to the criticism of the estimates of gas exchange, I did not find the discussion points to be well supported by the data especially given the limited time and geographic scope of the measurements. There is simply not enough evidence to support any of the inferred drivers of CO₂ variability in this river system.

Thank you for the comments. We revised the manuscript in taking into account all comments from reviewers.

Specific Comments:

48: what references support plate tectonics as major drivers of carbon fluxes in this system?

We added the information in page 3

“The Delta is located in a very flat and low land, with an elevation ranging from 0.4 to 12 m above sea level (Nguyen Ngoc Sinh et al., 1995). Previous studies showed the difference of lithology in the three upstream tributaries: Paleozoic sedimentary rocks (55.5%), Mesozoic silicic rocks (18.0%) and Mesozoic carbonated rocks (16.7%) dominate in the Thao basin, whereas Paleozoic sedimentary rocks (85.3%) and Mesozoic carbonated rocks (14.7%) cover the Da river basin, and the Lo is composed of Mesozoic silicic rocks (21.5%) and Paleozoic sedimentary rocks (72.7%). The delta area is totally covered by alluvial deposits (100%) (Moon et al., 2007; Le et al., 2007). ”

53: are changes in sediments the hypothesized drivers of changing carbon fluxes in this study?

Yes. The information concerning changing of suspended solids of the Red River was added in page 12, in the section “Influence of dams on pCO₂ and CO₂ emission

” Noted that the Hoa Binh site is situated downstream a series of reservoirs, which have been constructed in both Chinese and Vietnamese parts including two large dams Hoa Binh (in 1989) and Son La (in 2010). The Vu Quang site is located in the downstream of a series of reservoirs, including two important Thac Ba (in 1970) and Tuyen Quang (in 2010). Previous studies emphasized that these dams have impacted water and sediment discharges downstream (Ha and Vu 2012; Ngo et al. 2014; Lu et al. 2015) with significant sediment deposition being observed in the reservoirs (Dang et al. 2010; Vinh et al. 2014; Lu et al. 2015).

184: if exchange is less related to wind, then what is the justification for using this model in the present study?

Thank you for the suggestion. But we now revise the ms by recalculating k₆₀₀ proposed by Raymond et al 2012

K₆₀₀ was calculated as presented in the section “2.5 CO₂ fluxes determination” , page 5-6:

“In this study, k₆₀₀ was calculated using the equation from Raymond et al. (2012) based on stream velocity (V, in m s⁻¹), slope (S, unitless), depth (D, in meters) and discharge (Q, in m³ s⁻¹), as follow:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029} \quad \text{Eq. (2)}$$

214: such low temperature variability leads to skepticism of this environmental parameter being a significant driver of CO₂ variability. In addition, the broad conclusion here is that water chemistry seems to be quite stable over time.

Thank you for the suggestion. The test by ANOVA and t-test results showed that no clear day-night variation but clear seasonal (dry-wet) variation of temperature was found at 5 sites. Other variables including pCO₂, organic matters ... showed seasonal variation.

So, we revised the section of temporal variation of pCO₂ and CO₂ flux in page 9 -10

273: a lack of CO₂ diel variability, but a finding of diel exchange variability, is a direct function of the model. This diel variability in fluxes then, is simply due to changes in wind which I do not believe are likely drivers of gas exchange in most river systems.

Again, we recalculated the k₆₀₀ by Raymond et al (2012), that lead to the change in CO₂ flux. We re-write the discussion.

276: this section reads more like discussion than results

We removed this section in the revised ms.

346: in contrast, this opening paragraph of the discussion most likely belongs in the results section of the manuscript

Thank you for the suggestion. In the revised ms, this paragraph is in the section Results/ 3.4. Relations between pCO₂ and water chemistry variables in page 8 -9.

359: what part of the study design allows for a significant investigation on the role of dams and gas exchange?

We added the paragraph for describing the 5 sites observed in page 3

“Five stations were studied along the lower Red River (Vietnam): Yen Bai station (at the outlet of the Thao River); Hoa Binh station (after Son La and Hoa Binh reservoirs, at the outlet of the Da River); Vu Quang (at the outlet of the Lo River); Hanoi and Ba Lat stations (in the main course of the Red River downstream). The three stations Yen Bai, Vu Quang and Hoa Binh are representative for water quality of the three main tributaries (Thao, Da and Lo) of the upstream Red River, whereas the Hanoi station is representative for the main course Red River after confluence of three main tributaries. Only the Ba Lat station, which is located at the Red River mouth (about 13 km from the sea) is influenced by seawater intrusion (Fig 1). A more detailed description of the river characteristics of the Thao, Da, Lo and the main branch of the Red River can be found in (Le et al., 2007)”

401: paragraph is too speculative

The paragraph was revised in page 13 (line 451)

449: but the temperature variation was very small. How much could this have possibly contributed to the variation in CO₂ exchange?

Thank you for the suggestion. As we mention above, we recalculate the k_{600} and fCO_2 . So the results now were represented and synthesized.

The discussion concerning day-night variations was rewritten. pCO_2 differences between night and day were really low, most probably because of low temperature difference and low photosynthetic activity due to the turbidity of the Red River.

The conclusion was also revised.