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Discussions

Interactive comment on “CO_2 partial pressure and CO_2 emissions from the lower Red River (Vietnam)” *by* Thi Phuong Quynh Le et al.

Anonymous Referee #4

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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.

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, . . .

- 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.

- 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 (min-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.

- 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).

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

SPECIFIC COMMENTS

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

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

L59: improve instead of “precise”

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 ?

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

L107: replace “sensor” by CTD

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

L113: total “alkalinity”

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).

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. . .

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 μmol/L. In this case the computation of pCO2 gives 3670 ppm for a pH of 8.2 and 26.4°C (and not 270 ppm as stated). Should it be mg of CaCO3, then the TA for the first line of Table 2 (105 mg/L) would be 1050 μmol/L. In this case the computation of pCO2 gives 440 ppm for a pH of 8.2 and 26.4°C (and not 270 ppm as stated). Should it be mg of CO3, then the TA for the first line of Table 2 (105 mg/L) would be 1750 μmol/L. In this case the computation of pCO2 gives 733 ppm for a pH of 8.2 and 26.4°C (and not 270 ppm as stated).

L140: Abbreviation IRGA not defined.

L144: replace “balanced” by equilibrated.

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

L160: replace “function” by parameterization.

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

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

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.

L203: The calculated pCO2 is about 5 times lower than the pCO2 measured directly, this can hardly be considered as ‘similar results’ as stated.

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

L233: Statistical test needed.

L245-251: Statistical test needed.

L260: The “good” correlation is of marginal interest what’s relevant is that the pCO2 values from the two methods differ by a factor of 5

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.

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.

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 that 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.

L299-312: In this discussion there’s a mix of studies in lakes and mangroves, which makes little sense when discussing CO2 dynamics in rivers.

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.

L321: references are needed to back this statement.

L323: or (in addition) inputs of CO2 from wetlands.

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

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

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

L359: Statistical test needed.

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

L401: Statistical test needed.

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.

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

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

L427: Elsewhere in the discussion the authors say that the Hoa Binh site has high pCO2 because downstream of a dam, and here the authors say the low pCO2 values in the Red River is also due dams. This cannot work both ways.

Should the authors want to explore why pCO2 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 pCO2 across river catchments such as productivity, population density, temperature, . . . e.g. the Lauerwald study that is cited by the authors.

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

L565: typo in "Costs"

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

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

L618 and L650: This reference appears twice.

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.

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.

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