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Interactive comment on "The role of hydrodynamic and biogeochemistry on CO_2 flux and pCO_2 at the Amazon River mouth" *by* Diani F. S. Less et al.

Anonymous Referee #1

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The figures, writing and the scientific content of this manuscript are poor. It's extremely regretful that the more experienced (numerous) co-authors did not spend the time necessary to help improve the quality of the presentation and the content of the manuscript. It's certainly not the job of the reviewers to give such guidance.

I have the impression that at least a sub-set of the data reported in this paper was already published by Sawakuchi et al. (2017). I'm not perfectly sure since the material and methods of both papers are extremely vague regarding the timing of sampling, and the original data-sets are not publically available, so a direct comparison of data is not possible. But the average values of pCO2 and FCO2 in both studies are extremely close (by comparing tables in respective papers), suggesting that this ms uses part of the data-set reported by Sawakuchi et al. (2017). Anyway, the fact that I have

this impression is itself worrying, because in the case that both data-sets were totally independent, this should have been transparently explained in the text (since both papers report identical data-sets in the same place and time).

It's not a major problem to publish several times the same data-set on the conditions: 1) that it's clearly stated in the ms; 2) that a new analysis is made. Neither of these two conditions is met. In terms of analysis, this ms follows the same lines as the Sawakuchi et al. (2017), concluding (predictably) that CO2 concentrations follow the river stage, and exploring variations of pCO2, FCO2 and K600 with a correlation analysis.

The discussion of the results is superficial and slim. The only solid results are the seasonal cycle of pCO2 that follows nicely the hydrological cycle. However, this was also reported by Sawakuchi et al. (2017) at the same site, and is anyway a well established pattern initially reported by Richey et al. (2002). There are some unexpected results such as the correlation between K600 and temperature, for which the authors do not give a convincing explanation, and that in my opinion corresponds to a spurious correlation. There are some unexpected lack of correlations, such as lack of correlation between K600 and wind speed and some that are actually expected such as the lack of correlation between pCO2 and respiration. The discussion is again unconvincing and the lack of correlation is attributed to either a methodological flaw (respiration measurements flawed by lack of rotation during incubations) or to inadequate data (wind speed data obtained too far away from the study site). This makes the discussion not very interesting and not very useful. If there were strong doubts on the adequacy or the accuracy of these variables they should have been excluded from the analysis from the start.

Regarding statement (L 2 P 7): "Wind on the CO2 transfer rate in estuarine environments (Broecker and Siems, 1984; Wanninkhof 1992, Wanninkhof and McGillis 1999). However, we could not find a significant correlation between FCO2 and wind speed (p > 0.05) (Table 3)".

1) None of the cited references deal with estuarine environments. The paper of Broecker and Siems in fact deals with wind tunnel experiments. 2) Looking at the correlation between FCO2 and wind is on itself quite odd, since FCO2 depends on both K600 and pCO2 which can (and usually do) vary independently, so it's preferable to look into K600 vs wind (or other driver of turbulence such as water current) and independently look into correlations of pCO2 with DO, etc . . .

Regarding statement (L 4 P 7): "Water temperature (Fig. 7) indicated a significant influence on K600 (Spearman R = 0.66, p <0.01) and was more relevant than kinetic variables (Spearman R = 0.35, p >0.05), therefore being a suitable predictor variable for estimating K600."

K600 exclusively depends on water turbulence that is generated by wind speeds and/or water flow. Since the gas transfer velocity is normalized to constant Schmidt number (600) it is expected to be totally independent from temperature(effect on diffusion). It's worth recalling that correlation never implies causation. There are many examples of correlations for which causal interpretations do not make sense, and are simply spurious. So, it's not correct to state that temperature is "a suitable predictor variable", you only can state that there is a correlation statistically significant, but this does not automatically imply causality relation.

Regarding statement (L 6 P 7): "A negative correlation between FCO2, conductivity, DIN and NO3 was observed (R = -0.43, -0.31 and -0.30 respectively, Table 3). pCO2 presented a significant correlation with NO3-, DOC and Al+ (R = -0.4, 0.41 and -0.42, respectively, Table 3)."

I do not see the point of reporting these correlations that are spurious. In rivers all variables vary with water level stage, so it's not surprising to find co-variations among variables because they are driven by dilution by surface runoff.

Regarding statement (L 19 P 7): "The Amazon River pCO2 is characterize by a dynamic balance between inputs from respiration of organic matter in the mainstem and

floodplains and outputs from outgassing due to in situ primary production."

This sentence is unclear. In the main river channel of the Amazon, I would expect phytoplankton primary production to be extremely low, and to have no effect at all on carbon fluxes, hence, on CO2 levels.

Regarding statement (L 23 P 7): "Rainfall is the main factor that controls the inputs of allochthonous organic matter during rising and high waters to the mainstem, (. . .)"

I assume that authors refer to surface runoff rather than "Rainfall"

Regarding statement (L 2 P 8): "This can be related to the bacterial growth rates, which were higher during highrising and high-falling water than during low-rising water. Patterns of community respiration were the opposite, with respiration rates highest during low-rising water. The combination of high rates of bacterial production and low rates of respiration during high water suggests that bacterial growth efficiencies were maximal during high water (Benner et al., 1995). It is important to consider, however, possible methodology inconsistences. Ward et al., (2018) showed that the titration method may lead to an underestimation of the respiration rates in the lower Amazon River, which could be the cause of the lack of correlation between these parameters. For example, it was observed that respiration rates were tightly linked to how rapidly they were mixed in carefully controlled incubation chambers and the authors further concluded that river flow 10 rates may control microbial respiration rates by controlling the suspension of sediments and particle-bound microbes (Ward et al., 2018)."

So which of the two possible explanations is more likely ? This is not a very interesting way to discuss results. Make a list of possible explanations, and let the reader decide which one is could be correct. A paper needs a solid story line.

Regarding statement (L 15 P 8): "These elevated DOC levels, and previously measured lignin phenols, indicate more abundant substrates for microbial decomposition, which is coincides with high pCO2 and FCO2."

This cannot work both ways. In section (L 2 P 8) you state that bacterial respiration rates are low during high water, and here you say that microbial decomposition should high because there are abundant substrates. There are clear contradictions in the discussion which makes it very confusing. A paper needs a consistent story line.

Regarding statement (L 16 P 9): "NO3- concentrations showed the same pattern, considering that increasing nitrogen could elevate aquatic photosynthesis and reduce pCO2, limitation of bacterial growth by nitrogen and organic carbon was also observed in some freshwater ecosystems (Wang et al., 1992; Benner et al., 1995; Elser et al., 1995; Li et al., 2012)."

There are several problems in this statement. In the main river channel of the Amazon, I would expect phytoplankton primary production to be extremely low (close to inexistent), and to have no effect at all on carbon fluxes, hence, on CO2 levels. Phytoplankton in the Amazon only occur in floodplain lakes and are dominated in biomass by cyanobacteria that in some cases over-come N limitation with N2 fixation. Simple dilution will also lead to a parallel decrease of both NO3- and CO2 concentrations independently from biological activity.

Regarding statement (L 25 P 9): "In addition, the combination of hydrodynamic and meteorological parameters, such as water velocity, water temperature and wind speed determine the air-water turbulence which controls the CO2 outgassing (Barth and Veizer, 1999; Alin et al., 2011)."

None of the cited references show an effect of water temperature on "air-water turbulence"

Regarding statement (L 3 P 10): "Our results showed that water and air temperature presented a strong influence on FCO2 (Table 3) and K600 (Fig. 8). As observed in other tropical rivers (Li et al., 2012, Liu et al., 2017) the mean water temperature is considered relatively high at the Amazon River (Moreira-Turcq, 2013). Thus, water temperature and turbulence, both factors can reduce the gases solubility in the water

leading to a higher exchange ratio (for instance, CO2 and DO) and in addition accelerating the decomposition of organic matter (Alin et al., 2011, Li et al., 2012, Ward et al., 2018)."

There are several problems in these statements. The results did not show "a strong influence" only a surprising (and probably spurious) correlation that emerged between temperature and K600. Turbulence does not reduce the gas solubility (Henry's constant only depends on temperature and ionic strength). It's unclear what is meant by "exchange ratio"; if it refers to the gas transfer velocity, then the statement does not make sense since the gas solubility does not affect the gas transfer velocity. "accelerating the decomposition of organic matter" does not affect the gas transfer velocity, it might affect CO2 levels, but these are different quantities that vary to a large extent independently.

Regarding statement (L 11 P 10): "However, the absence of correlation with U10 and FCO2 in our investigation may be explained by the use of wind velocity data, obtained from weather stations located on land relatively far from sampling points, leading to the use of possible non-representative data."

This is a somewhat depressing conclusion, and shows a poor design of the experiment. It's fairly easy and relatively inexpensive to make wind speed measurements in the field. It's incomprehensible that wind speed measurements where not carried out in parallel with the FCO2 measurements, and instead the authors preferred to rely on a faraway meteorological station.

Regarding statement (L 24 P 10): "Our results can support the development, adjustment and parameterization of regional models of CO2 emissions in the study area, providing a significant contribution for the understanding of carbon cycle of the Amazon River mouth, reducing the FCO2 estimates errors for different temporal scales in large tropical rivers."

It's totally unclear how a handful of spurious correlations (such as K600 vs temperature) and lack of correlations (CO2 vs respiration) can help in “the development, adjustment and parameterization of regional models”. The only sound relations in this work are between CO2 levels and water stage but this was been established since the work of Richey et al. (2002).

Regarding figures, I’ll only elaborate on the last (and worse) one. This plot would have looked much better if its shape was square, or wide rectangle, but a tall rectangle is a very poor choice for a correlation plot. The plot is of poor resolution (highly pixelized), and the top brown band awkward. The legend on this brown band seems to have been added on top of the original plot as the shade of brown is different and the font of text different from the rest of the plot. Finally, the legend mentions a r2 of a linear correlation, although the line itself of the correlation is not shown on the plot. The figure legends are too short and do not informative enough.

The quality of text is very poor, with numerous syntax problems, and poor terminology. This is very regretful considering that a few of the co-authors are native English speaking.

Refs

Richey et al. (2002) Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO2, Nature, 416, 617-620

Sawakuchi et al. (2017) Carbon emissions along the lower Amazon, Froniter in Marine Science, 4:76

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