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Interactive comment on “Spatial variability and temporal dynamics of greenhouse gas (CO₂, CH₄, N₂O) concentrations and fluxes along the Zambezi River mainstem and major tributaries” by C. R. Teodoru et al.

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Response to Referee #3

We thank referee#3 for his/her thoughtful and constructive comments, and provide a detailed point-by-point reply below.

This study assesses the spatial and temporal variability of various greenhouse gas concentrations and fluxes in the Zambezi River basin. Recent work has revealed the important role that inland waters play as processors of carbon in the global carbon cycle

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and that inland outgassing fluxes often exceed fluxes to the ocean. In this context, the work done by the authors is very important, as they have taken high-precision measurements in a relatively understudied region. This manuscript is also potentially important as the authors find gas concentrations below the assumed value for tropical rivers, which could have implications for future assumptions about tropical rivers.

However, the study is extremely descriptive and there is little clear interpretation of what is driving these fluxes or why they are lower than typical values. The Discussion section in particular has a heavy focus on descriptive statistics, has long dense paragraphs, and will need to be re-focused on interpretation. That said, I'm excited by the work, and strongly encourage the authors to present as clear and concise as possible.

REPLY: We thank the reviewer for the positive notes on the importance of the data. The (too) descriptive nature of the manuscript was also commented on by other reviewers, and the revised manuscript has been restructured and re-focused to the extent possible (keeping in mind there is a very large amount of data presented, which should in one way or another first be described).

Specific comments below:

REF: 2.1 Overly long and descriptive, details do not add to the reader's understanding of the study or the stated goals of the manuscript. For example, why is there so much background on land-cover if it is never mentioned again in the paper?

REPLY: We understand the concern of the referee about the descriptive nature of the manuscript. Yet, the manuscript presents a large dataset of GHG measurements along the Zambezi mainstem and various tributaries and during different years and seasons, of which clear understanding, to our opinion, requires detailed description. The info on the land cover has been partially removed (the last 7 lines) keeping only the first two lines.

REF: Fig. 3a,b Horizontal axis is slightly confusing. There are multiple rivers but differ-

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ent sources. Maybe rephrase to “Distance from mouth”?

REPLY: As the river mouth is not the same for all rivers (i.e. Indian Ocean only for the Zambezi, Zambezi river below Kariba dam for Kafue River, Zambezi 200 km below the confluence with Kafue for Luangwa, etc), “Distance from mouth” on the X axes would require recompiling all plots which would add, if any, the exact same ‘confusion’. So we considered more appropriate keeping it as it is.

REF: Fig 3c. Would be most helpful to see this as mol vs mol, not % sat O₂. Also interesting to see if the slope is 1.3 as that is the value used to convert O to C values.

REPLY: This comment is in line with a similar comment from Referee#1. We followed these suggestions and modified Figure 3c, now presenting the plot as $\mu\text{mol L}^{-1}$ CO₂ versus $\mu\text{mol L}^{-1}$ O₂. The paragraph in the revised version was modified accordingly: “Overall, there was a relatively good ($r^2=0.78$), negative correlation between CO₂ ($\mu\text{mol L}^{-1}$) and DO concentration ($\mu\text{mol L}^{-1}$) for all sampled rivers, tributaries and reservoirs, and during all campaigns (Fig. 3c) with mostly reservoir samples characterized by high DO and low CO₂ content while hypoxic conditions associated with high CO₂ values were characteristic for the Shire River, and several stations on the Zambezi and the Kafue Rivers (mostly downstream of floodplains). The slope of this relationship of 0.79 ± 0.04 , could provide an estimate of the respiratory quotient (RQ) defined as the molar ratio of O₂ consumed to CO₂ produced by respiration. The RQ value is in theory equal to 1 for the oxidation of glucose, but higher than 1 for more complex and reduced organic molecules containing nitrogen and phosphorous, such as lipids and proteins, or lower than 1 for highly oxidized and oxygen-rich molecules (e.g. pyruvic, citric, tartaric, and oxalic acids) (Berggren et al., 2012). The value we computed is lower than the RQ value of 1.3 established in a temperate stream with a catchment dominated by pastures (Richardson et al., 2013), but close to the one recently proposed for bacterial respiration in boreal lakes of 0.83 (Berggren et al., 2012). Berggren et al. (2012) attribute this low RQ to the bacterial degradation of highly oxidized molecules such as organic acids, likely to be also abundant at our sampling sites (Lambert et al., 2015).”

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The three mentioned references were added in the Reference list of the revised manuscript:

Richardson, D. C., Newbold, J. D., Aufdenkampe, A. K., Taylor, P. G. and L. A. Kaplan, L. A.: Measuring heterotrophic respiration rates of suspended particulate organic carbon from stream ecosystems. *Limnol. Oceanogr. Meth.*, 11:247-261, doi: 10.4319/lom, 2013.

Berggren, M., Lapierre, J-F, del Giorgio, P. A.: Magnitude and regulation of bacterioplankton respiratory quotient across freshwater environmental gradients, *The ISME Journal* 6, 984-993, doi:10.1038/ismej.2011.157, 2012.

Lambert, T., Darchambeau, F., Bouillon, S., Alhou, B., Mbega, J - D, Teodoru, C. R., Nyoni, F. C., and A V Borges, A. V.: The effect of vegetation cover on the spatial and temporal variability of dissolved organic carbon and chromophoric dissolved organic matter in large African rivers, submitted, 2015.

REF: 4.1 This section is very long and much of it could be slimmed down and moved to the results section. The interpretations of the pCO₂ levels should be condensed and related back to the main goals of the study. There are several interesting interpretations here (outgassing due to large waterfalls) + the importance of floodplain input of CO₂, but they are lightly buried in the descriptive nature of this section.

REPLY: The section has been reduced.

REF: The primary production rates are measured several times in this section, but are not included in the results or a table. The same goes with the respiration rates mentioned in the methods section.

REPLY: All primary production and respiration rates are indeed not presented in the Results section (this would increase the length of data description) but are mentioned when needed in the Discussion to explain variability in CO₂. The full data are, however, presented in the Supplementary material. We leave it up to the handling editor to

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decide if we should include a description of these data.

REF: P16512L2-4 The mechanism behind the high pCO₂ isn't really described here. Could link this "false" floodplain created by the damming back to the elevated CO₂ levels seen in the natural floodplains.

REPLY: Indeed, the main message here is that, similar to elevated pCO₂ in the Kafue Flats during wet campaigns, the observed high pCO₂ there also during the dry season may be explained by the water exchange between river and the artificially created permanent flooded area as a result of river damming. This is highlighted in the revised version of the manuscript by the following improved sentence: "This hydrological alteration due to river damming responsible for the creation of a permanent flooded area within the Kafue Flats which constantly exchanges water with the Kafue River mainstem could explain the observed high riverine pCO₂ levels there encountered also during the dry season 2013 (Fig. 3b)".

REF: P16412L23 – P16413L7 This seems to be the most interesting finding of the paper, and needs to be expanded upon. As it stands, it is nearly buried by descriptive statistics.

REPLY: We reduced the section to the extend permitted and introduce a short paragraph to better explain why our CO₂ values may be lower compare to global CO₂ average: "This may be explained by the fact that global CO₂ levels for tropical aquatic systems originates mostly from studies on the Amazon River basin where highly acidic and CO₂ loaded "black water" rivers prevails".

REF: 4.2 The purpose of this section seems to be to determine whether the DIC levels in this river can be explained by weathering. However, it is difficult to follow as written and does not add much to the overall manuscript. As before, this section is mainly results. There are some interesting findings, but the interpretations must again be condensed and tied back to the original goal of the study. The isotope values do not add to the study as it stands.

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REPLY: The section has been reduced and condensed. References to the importance of $\delta^{13}\text{C}$ -DIC in determining the source of riverine DIC was added in the introduction section: “Controlled by several biogeochemical processes (i.e. organic matter oxidation, photosynthesis and respiration, and exchange with atmosphere) and characterized by distinct isotopic signature, DIC stable isotopes ($\delta^{13}\text{C}$ -DIC) is a powerful tool which can be used to distinguish between different riverine DIC sources (i. e. atmospheric/soil CO_2 or carbonate dissolution), to trace the DIC transport to the ocean and to assess the carbon transformation in the river itself”.

REF: 4.3 This section is mostly results and seems unnecessary. The authors state that the overall effect of the diel variation on riverine variability seems small. The data can be included in the supplement if the authors are concerned w/ diel variability.

REPLY: Due to the restructuring work of the revised manuscript, this sections belong now to Result and Discussions. We believe that even diel variation in our dataset is small, that this is still an important finding since it suggest that timing of in situ measurements has little influence of the on the overall results. We leave it up to the handling editor to decide if we should move this section to the Supplementary material.

REF: 4.5 This section gets at the stated goal of the paper(calculated fluxes). This section actually contains a lot of information, but I think that again, most of it could be moved to the results.

REPLY: We understand the reviewer concern but as previously stated, we could not present everything in the Results section (which is already very long as it is) and we chose to focus there on the temporal and spatial variability of pCO_2 , CH_4 and N_2O along the Zambezi mainstem and all sampled main tributaries. Fluxes and several other data were therefore shown and discussed in the Discussion section. To solve this issue, in the revised version of the manuscript, we merged and condensed the two distinct sections into a single section: Results and Discussion.

REF: P16423E3: I do not see the need to include this exponential fit. It is unlikely to

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hold true in any different system and would likely be specific to this unique sample site (and at the times sampled).

REPLY: The section describing the correlation between pCO₂ and CO₂ flux has been removed from the revised manuscript.

REF: 4.5 This section could be very interesting, but the errors associated with some of these values might be too high to accurately calculate a mass-balance. The authors mention that when they include floodplain fluxes, their values are more consistent with global estimates of riverine export. Could these values have been included in the mass balance in the beginning? This section has the potential to be interesting and important, despite the large error in several measurements. However, the authors need to relate this to the overall goals of the project and tie their interpretations in with the rest of the results.

REPLY: We agree that the uncertainties are large, and acknowledged this, but we feel that these initial calculations are still valuable as long as the caveats are explicitly mentioned. We expect that the largest errors may have occurred due to the lack of real sedimentation rates in river and the missing detailed discharge data for the study period at the Zambezi mouth. Similar results however, compared to the C budget of the Kafue River for which we used daily discharge data and where the largest error is associated with the sedimentation component, give us a certain degree of confidence. While recognizing the influence of wetlands on river biogeochemistry and especially GHGs, we did not sample inside wetlands/floodplains. Given their large areal extend and potentially large misrepresentation of fluxes, we did not feel confident to incorporate wetlands/floodplains in the main budget but instead we use a simple extrapolation to suggest their potential importance in C budgets.

REF: Fig. 10: Caption should read “diel variation” not “dial”

REPLY: “Dial” was replaced with “diel”.

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