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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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Received and published: 12 March 2015

Response to Referee #1

We thank referee#1 for his/her thoughtful and constructive comments, and provide a detailed point-by-point reply below.

This study assesses the spatial and temporal variability in the concentrations and fluxes of the three main GHG found in the Zambezi river. Based on state of the art techniques and measurements, the authors calculate mass-balance for CO₂, CH₄ and N₂O across

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the Zambezi river, which drains 1.4 millions km² of African territory. Global estimates of GHG emissions from aquatic ecosystems in last 5-10 years have been constantly going up, either due to different methodology or due to the inclusion of systems or regions that had traditionally been underestimated. Yet the estimated aquatic emissions cannot constantly increase if the global C budget is to be resolved. In this context, the results of this study have important implications for global extrapolation exercise because 1) they report high-quality data on aquatic biogeochemistry for an under-studied region of the globe and 2) concentrations and fluxes of GHG are typically lower than what has been reported in other tropical regions.

This study, however, is very highly descriptive. While overall I believe that its descriptive nature fits rather well this data-intensive manuscript, I think the main claims tend to be buried among masses of secondary details, and that readability and potential impact suffer from it, especially in the “Discussion”. Below I provide suggestions that mainly aim at improving readability and better emphasizing what I consider to be the main novel aspects of the manuscript.

REF: Specific comments: Figure 1: It would be helpful to show the previously studied African areas (in terms of GHG dynamics), perhaps on the inset (could be bigger). Right now a number of studies are cited in the intro, but without reading all of them it is hard to quickly judge how the current ms represents a significant advancement over the study referred to (in terms of the magnitude of the spatial extent and the distribution of the areas covered).

REPLY: The inset of Figure 1 is small enough to make the visual identification difficult, so instead, we add the name of those sited studied rivers (and their location) before the mentioned reference. The paragraph became: “While our understanding of C dynamics in tropical regions comes mostly from studies of the Amazon River Basin, up to date only a handful of studies explored the biogeochemical functioning of equally important African rivers such as the Bia, Tanoé and Tanoé rivers in Ivory Coast (Koné et al., 2009, 2010), the Tana (Kanya) and the Oubangui rivers (Congo River basin) (Bouillon et al.,

2009, 2012, 2014; Tamooh et al., 2012, 2013), the Congo River (Wang et al., 2013; Mann et al., 2014), and the Athi-Galana-Sabaki River (Kenya) (Marwick et al., 2014)”.

REF: Section 2.1: Very long section, but I rather enjoyed reading it

REPLY: The section has been shorted as much as possible

REF: Figs. 3,4,5 and 9: Including a line that would represent the weighted average for all the sites included in this study would help placing those results in a larger context

REPLY: Figs 3d, 4d and 5d have been modified by introducing full lines to suggest median pCO₂, CH₄ and N₂O for all sites and all sampled periods. In Fig 9a and b, similar full lines represent median CO₂ and mean CH₄ flux. A short note was added in the caption of all these figures indicating the meaning of the line, i.e. “Full line represents median pCO₂ value (1753 ppm) of all sites during the entire sampling period”.

REF: Fig. 3c: It would be useful to present this graph in terms of mol for mol of CO₂ vs O₂

REPLY: This comment is in line with a similar comment from Referee#3. 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,

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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).”

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: p.16 409L1: “T” missing in “starting”

REPLY: ‘t’ was added to “starting”.

REF: Section 4.1: This section is very long and descriptive, and most of it is actually result. There is barely any interpretation in it. Parts of this section could be cleaned up by merging some results in the corresponding place in the “Results” section while focusing on interpretation here, and the implications for the main points of the study.

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Same applies to similar comments below.

REPLY: This comment is in line with suggestions by other referees to restructure the manuscript. We avoid presenting all data in the Results as the section would have been far too long compare to other sections. We have incorporated this and other related suggestions in the revised version by combining the two sections into a Results & Discussion section, and by doing so we could remove some repetitive elements, avoid long descriptive sections and have tried to make the overall text more concise.

REF: P16412L2: s missing to “alteration”

REPLY: ‘s’ was added to “alteration”.

REF: P16412 L16 : P16413 L7: This is what I consider as the most novel aspect of the work, but it is completely lost among a nearly 6 pages long section

REPLY: The section has been shorted.

REF: Section 4.2: I am not sure what this brings to the rest of the ms. I understand that the authors aim at describing the different sources of carbon for the Zambezi river, but DIC stable isotopes come out of nowhere that far in the manuscript. There is nothing in the introduction that sets up why we should care about DIC stable isotopes, and, again, most of this section is actually results. The authors should consider removing this section, or better placing it in the overall context of the paper. If the latter is done, I believe that this section should be condensed.

REPLY: A short discussion around the use of $\delta^{13}\text{C}$ -DIC has been added in the introduction: “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”.

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REF: Section 4.3: Again, this is mostly results, and new figures keep being introduced that far in the ms. Why did the authors present these numbers in the discussion?

REPLY: As mentioned above, we avoid presenting all data in the Results as the section would have been far too long compare to others. In the revised version, we merge the two distinct sections into “Results and Discussion”.

REF: Section 4.4: I believe that readability suffers from having the discussion of the concentrations and fluxes of GHG so far apart form each other, with so much new content (i-e results) in between

REPLY: We understand the concern of the referee but we consider preferable presenting and discussing first GHG concentrations, identifying sources and factors affecting their variability while dealing latter with fluxes as their application is more closely related to the mass balance calculation.

REF: p.16421 L 16-23: This is a rather critical claim, which would actually help explaining why this study measured typically lower fluxes than other tropical regions. It would further suggest that riverine fluxes estimated from chamber measurements around other rivers of the world may have been systematically over-estimated. I would expect to see the data here as this directly contributes to one of the main conclusions of the paper.

REPLY: This technical/methodological issue related to flux chamber measurements suggests that, for a correct determination of GHG emission rates in rivers and streams, measurements must be performed on drift, with the chamber flowing alongside the current. We would not go as far as using this argument to explain why our fluxes were overall lower compared to other tropical regions, since most CO₂ exchange rates from other rivers were derived from pCO₂ data and estimated k values, not from floating chambers which are more commonly in use in lakes and reservoirs.. Moreover, we did not intend to focus the paper around the comparison between drift and static mode fluxes. We did not present such data here (drift versus static determination) because

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this comparative dataset is mostly based on 2 field campaigns on the Congo River and contain only a limited number of measurements on the Zambezi.

We clarify this in the revised manuscript by modifying the paragraph as follow: “In situ experiments, mostly on the Congo River, designed to explore the effect of additionally induced turbulence by the chamber walls on the flux chamber determination in rivers, and performed both on static mode at various water velocities as well as drift mode, suggest a clear, linear dependency of k on the velocity of water relative to the floating chamber (Cristian R. Teodoru, unpublished data)”.

REF: p.16423 L10-13: I have some difficulties with this equation. Conceptually, is not that an empirical way to estimate an average regional “ k ” for all the systems studied here? (i-e flux = concentration * “something”). I did not do the math but I suspect that the product of the different parameters, with proper transformation, would yield close to the average k for the studied sites. I am not sure why someone would want to use this equation when you can simply multiply measured (excess) CO₂ by a realistic estimate of k for a given type of systems. It may be more useful to simply report the average k measured here if this is to be used for extrapolation purposes.

REPLY: We removed the section describing the relation between measured flux and pCO₂ from the revised manuscript .

REF: Section 4.5: Again, very long and descriptive, and mostly results, and nearly 4 pages of text without a paragraph. I got completely lost in reading this section and I could not identify the main points. What are the implications of those results, and why are they included in the discussion?

REPLY: In the revised version, this section was shorted as much as possible and belongs now to Results and Discussion. The sections represent an important component of the paper and relates back to the original goal of the study to construct a mass budget for the Zambezi Basin. While acknowledging limitations in the estimation of balance components, the section highlights the importance of C emissions to the atmosphere

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relative to transport, suggest the need of further incorporation of seasonally or permanently flooded wetlands and floodplains in C budgets and stresses out overall role of aquatic systems in C cycles.

Interactive comment on Biogeosciences Discuss., 11, 16391, 2014.

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