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 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 pCO_2 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 µmol L^{-1} CO2 versus µmol 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 CO_2 (µmol L^{-1}) and DO concentration (µmol 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 CO_2 content while hypoxic conditions associated with high CO_2 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 O_2 consumed to CO_2 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)."*

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. 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 δ^{13}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 (δ^{13}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: 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 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 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.

Response to Referee #2

We thank referee#2 for his/her thoughtful and constructive comments, and provide a detailed point-by-point reply below.

REF: The study by Teodoru et al. presents an analysis of spatio-temporal variability in GHG concentrations and fluxes in the Zambezi river system based on field observations. The discussion of patterns and probable drivers is supported by dissolved oxygene and d13C observations. Measurements of alkalinity, Ca, Mg, and DSi are used to analyses and discuss weathering derived fluxes of DIC to the oceans. In combination with observations of organic C concentrations at the river delta and literature on burial of org. C in reservoirs, the authors present a C mass balance of the Zambezi river mainstem, which is further critically discussed by the authors.
Teodoru et al. present an interesting and quite comprehensive analysis of C and GHG dynamics in the Zambezi river system. While most of similar work on tropical rivers has so far been concentrated on the Amazon River system, there is still a need of studies of rivers in tropical Africa and Asia. This fact might have skewed the estimates for GHG fluxes from tropical river systems at global scale, as this study (and similar work on African rivers by the groups in Leuven and Liège) indicates.
The MS is well written. Methods are, with a few exceptions, appropriate and clearly described. Results are presented in a clear and comprehensive way. The discussion is mostly logical and comprehensive. I suggest publication after some minor revisions.

Specific comments:
REF: The results section focusses only on CO2, CH2, and N2O concentrations. The discussion section presents observation of fluxes, DO, d13C, alkalinity and some inorganic solutes not presented in the results. I would suggest combining the results and discussion section as 'results and discussion'. The general order and structure of the subsections could be retained.

REPLY: *This comment is in line with suggestions by other referees to restructure the manuscript. We have incorporated this and other related suggestions 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: I have some problems with the method used to distinguish carbonate and silicate weathering contributions to carbonate alkalinity based on Ca+Mg equivalents (as being an indicator for carbonate weathering) vs DSi concentrations (as being an indicator of silicate weathering). This refers to the two Equations R1 and R2 on Page 16415. Firstly, there might be a significant fraction of Mg originating from silicates, like Olivine. Olivine is an important mineral in basalts. Further, DSi is biogeochemically active and subject to cycling in terrestrial and aquatic ecosystems [Struyf and Conley, 2009; Struyf et al., 2010]. It was further shown that deforestation can increase DSi fluxes from amorphous silica stocks in soils [Conley et al., 2008; Clymans et al., 2011]. SO4 does not necessarily originate from Gypsum dissolution, but could also come from the oxidation of Pyrite or sulfur in organic sediments. Particularly for the shales this could be an issue. At least a short discussion on the uncertainties related to this method. Some information about soils in the study area would also be interesting. Are there deeply weathered soils like laterites covering the bedrock? Does this concern some specific

lithologies more than others? In case of deep laterites or other deeply weathered tropical soils, this could be an additional explanation of low DIC [see, e.g. Hartmann et al., 2014].

REPLY: *We agree with the referee over several relevant points (the weathering of Mg rich silicate rocks, the additional provenience of SO4 from the oxidation of Pyrite and sulfur, low DIC due to weathered laterites soils) but for most we do not have data to properly address them. We do not fully agree with the comment regarding Si, since all models rely on DSi concentrations and ignore whatever processes that can affect DSi in rivers. We acknowledge our limitation by adding in the revised manuscript the following paragraph:*
"We acknowledge that the approach used while very simple and straightforward could be prone to several caveats such as the occurrence of weathering of Mg rich silicate rocks such as Olivine or the non exclusive provenience of $SO4^{2-}$ *from gypsum but also from the oxidation of Pyrite or sulfur in organic sediments. However, it is difficult to fully address these issues given for instance the lack of information on the lithology of catchment, and a more in depth investigation of rock weathering is beyond the scope of the present study.".*

REF: The MS presents much more than an analysis of spatio-temporal patterns of GHG concentrations and fluxes. They also analyze DIC fluxes and try to give a C-budget for the Zambezi river system. Maybe the authors should make this clearer also in the title of the study.

REPLY: *This is a good suggestion but we feel that title is already too long. However, we could mention DIC and C budget at the end of the title so it can read: "****Dynamics of greenhouse gases (*** CO_2, CH_4, N_2O***) along the Zambezi River and major tributaries, and their importance in the riverine carbon budget".***
The title has been modified in the revised version

Technical comments/corrections:
REF: Page 16393, L24-25: There might be a word missing before "groundwater"

REPLY: *"Groundwater" has been moved before inputs to read: "Resulting from groundwater inputs of dissolved inorganic C..."*

REF: Page 16395, L21: remove comma after "Middle Zambezi"

REPLY: *Done*

REF: Page 16397, L29: Maybe add a "by" after "dropped"

REPLY: *"by" was added after "dropped" to read: "...has dropped by 18%..."*

REF: Page 16398, L3: Add comma after "floodplains"

REPLY: *Done*

REF: Page 16399, L7: Replace "form" by "from"

REPLY: *Done*

REF: Page 16400, L25: Remove "concentration" after "pCO2"

REPLY: *Done*

REF: Page 16401, L24-26: By this, you correct for non-carbonate contribution to alkalinity? Please, clarify.

REPLY: *This approach does not correct for the contribution of non-carbonate alkalinity since the anions that contribute to non-carbonate alkalinity are titrated by HCl during analysis so this is inherently included in the alkalinity measurement.*

REF: Page 16404, L18-20: How was that average calculated? From all samples? Or did you first calculate one average for the wet season and one average for the dry season, and then the average from both averages?

REPLY: *The average values here refer to all samples average over both wet and dry sampling periods. " Both wet and dry" was added in parenthesis after the "entire sampled period" to clarify this.*

REF: Page 16404, L22: What would be the effect of turbidity on pCO2?

REPLY: *Based on the work of Abril et at. (2009) (Abril G., Commarieu M.V., Sottolichio A., Bretel P. and Guérin F. (2009) Turbidity limits gas exchange in a large macrotidal estuary. Estuarine Coastal and Shelf Science, 83: 342-348, http://www.epoc.u-bordeaux.fr/indiv/Abril/documents/publi/Abril_et_al_2009_ECSS.pdf), turbidity can reduce turbulence, the gas transfer velocity and emissions of CO_2 to the atmosphere. Highly turbid systems such as the Luangwa and Mazoe (with TSM between 300 and 1000 mg/L) are characterized by lower pCO2, but also lowest %POC and %PN. While these large inputs from soil erosion may on the one hand provide a large source of POC available for mineralization, it appears that the influence of wetlands along other tributaries and the mainstem have a much more pronounced effect of increasing pCO2. However, in the revised manuscript we deleted the part which linked high turbidity to low pCO2.*

REF: Page 16405, L10: Replace "and" by "but"

REPLY: *Done*

REF: Page 16405, L11: Replace "significantly" by "significant"

REPLY: *Done*

REF: Page 16405, L19-24: What about CH4 concentrations below the dams? Before it was written that water downstream of the dams was enriched in CO2 because the outlets release hypolimnetic water. It would be interesting for the reader if the same can be observed for CH4.

REPLY: *As for CO2, CH4 concentrations measured downstream of the different dams were consistently higher compared to concentrations in the surface water of reservoirs. To highlight this, we add "…and consistently below levels measured at the stations immediately downstream both dams". The paragraph at page 16405, L19 reads:*

"CH_4 concentrations in the surface water of the two reservoirs on the Zambezi were generally lower compared to the riverine values, and consistently below levels measured at the stations immediately downstream both dams (Fig. 4a)".
We further highlight the hypolimnetic origin of CH4 together with CO2 below both Kariba and Cahora Bassa dams at page 16409 and 16410

REF: Page 16406, L13: Replace "week" by "weak"

REPLY: *Done*

REF: Page 16406, L13-18: Is there a correlation between CH4 and dissolved oxygen?

REPLY: *There is a negative correlation, rather weak (r^2 = 0.3) between CH4 and %DO*

REF: Page 16406, L18-20: Was this average weighted by season (the one sample for dry period counts double, because there are two samples for the wet season)?

REPLY: *Those are normal average (all samples, all seasons – 769 and 381 nmol/L for the Zambezi and Kafue respectively). A weighted average would reach 640 and 391 nmol/L respectively. This is now clarified in the revised version.*

REF: Page 16407, L2-3: At the beginning of section 3.2, it was said that for CH4 concentrations, there was only a weak temporal variation. Here, it is written that temporal variation in N2O was high, and that would be in consistence with what was found for CH4. Please, clarify.

REPLY: *While N_2O concentrations along the Zambezi were also variable (although with a much lower max/min ratio than for pCO_2 and CH_4), there was little interannual variability but high seasonality. We clarify this by removing the reference to the temporal variability of pCO_2 and CH_4 stating:*
"N_2O in the Zambezi River was also characterized by high spatial variability".

Statements describing low interannual variability and high seasonality follow.

REF: Page 16407, L21-22: Please, give the values for these minima.

REPLY: *Values of 3.9 and 3.0 nmol L-1 for the 2012 and 2013 wet seasons, respectively, were added in the text to describe minimum CH4 records at KAF.8 in the Kafue Flats.*

REF: Page 16409, L9: Did you mean "high" instead of "height"?

REPLY: *We replaced "height" by "high".*

REF: Page 16409, L23-27: Can the authors argue why they are sure that 70 km downstream of the dam they still see the effect of the hypolimnetc water inputs? Can other sources be excluded? Would the degassing be slow enough that excess CO2 can be transported so far downstream? Can they recalculate, based on estimates of flowing velocity and gas exchange rates, how high the pCO2 would have been at the outlet of the reservoir?

REPLY: *We did not find an access point to the river immediately below the Kariba dam until the wet season 2013 campaign, when pCO2, %DO and water temperature measured 15 km below the dam (ZBZ.10) were 2600 ppm, 65% and 24.1°C, respectively, and 1600 ppm, 82% and 24.3°C further down at ZBZ.11 (70 km below the dam), while values in the epilimnion of the reservoir were 150 ppm, 105% and 27.4°C, respectively. During the previous two wet season campaigns, pCO2, %DO and water temperature measured only at ZBZ.11 were 2008 ppm, 78% and 27°C in 2012 and 2260 ppm, 76% and 26.6°C in 2013, respectively, compared to values in the surface water of the Kariba reservoir of 370 ppm, 105% and 29.9°C in 2012 and 180 ppm, 101% and 28.1°C in 2013, respectively.*

While this consistently higher riverine pCO2 (and lower %DO and temperature) downstream the dam compared to surface water of the reservoir, and the steady CO2 decrease (and slowly increased %DO and temperature) downriver reflected by 2013 dry campaign data may suggest the release at the dam of highly CO2-loaded, hypolimnetic water and the exchange with atmosphere of the CO2 load, the presence of additional lateral sources cannot be ruled out. However, no important diffusive or point sources (major tributaries or wetlands) exist along this stretch of the river, the area being mostly dominated by the narrow and steep valley of the Kariba Gorge. Low re-aeration rates with hypoxic conditions caused by periodically hypolimnetic water discharge have been previously described to last for more than 100 km downstream the Itezhi Tezhi dam dam:

- ***Kunz M.J., Senn D.B., Wehrli B., Mwelwa E. M., Wüest A.*** *2013 Optimizing turbine withdrawal from a tropical reservoir for improved water quality in downstream wetlands. WRR, 49, 1-15. doi:10.1002/wrcr.20358.*
- ***Zurbrügg, R., Wamulume, J., Kamanga, R., Wehrli, B., Senn, D.*** *2012 River-floodplain exchange and its effects on the fluvial oxygen regime in a large tropical river system (Kafue Flat, Zambia) J. Geophys. Res.* ***117****, G03008, doi:10.1029/2011JG001853.*
- ***Wamulume J., Landert J., Zurbrügg R., Nyambe I., Wehrli B., Senn D.B.*** *2011 Exploring the hydrology and biogeochemistry of the dam-impacted Kafue River and Kafue Flats (Zambia). J. Phys. Chem. Earth.* ***36,*** *(14-15) 775-788 doi:10.1016/j.pce.2011.07.049.*

Using a mass balance approach which assumes no additional lateral CO2 source along this 70 km stretch, and considering the CO2 emission at ZBZ.11 as representative for the entire stretch, pCO2 at the outlet of the reservoir would vary between only 3500 and 4600 ppm. These estimated values could be slightly however higher, since the (low) flux measured at ZBZ.11 may not be representative for the entire 70 km stretch, as the turbulent flow through the Kariba Gorge should result in higher CO2 exchange with the atmosphere.

A similar explanation was introduced in the revised version of the manuscript:
"In contrast to the CO_2 undersaturated (and warmer, DO saturated) epilimnetic conditions of the Kariba Reservoir, much higher pCO_2 (>2000 ppm), accompanied by colder water and undersaturated DO conditions measured 70 km downstream of the Kariba Dam (at ZBZ. 11) suggest the discharge at the dam of hypolimnetic, low DO and CO_2-loaded waters, formed as a result of thermal stratification of the water column of the reservoir (Kunz et al., 2011a). Even no major tributaries or other point sources (i.e. wetlands) exist along this 70-km stretch, the potential contribution of lateral sources to the CO_2 level measured at ZBZ.11 cannot be totally ruled out. However, measurements during 2013 dry campaign showed a constant decrease in pCO_2 (and an increase in %DO and water temperature) between the intermediate point ZBZ.10 (located 17 km downstream the dam) and ZBZ.11 from 2600 ppm (65% DO and 24.1°C) to 1600 ppm (82% DO and 24.3°C), respectively. This higher upstream pCO_2 level at ZBZ.10 and the steady downstream decrease (accompanied by increase in %DO and water temperature) support idea of hypolimnetic water discharge with high pCO_2 content which,

even partially exchanged with the atmosphere along this stretch, it is still reflected in the level measured 70 km downstream at ZBZ.11. Low reaeration rates with hypoxic conditions caused by periodically hypolimnetic water discharge have been previously describe to last for more than 100 km downstream the Itezhi Tezhi dam (Kunz et al., 2013). A simple back calculation based on mass balance approach which assumes no additional lateral CO_2 source along this 70 km stretch, and uses the CO_2 concentrations and fluxes measured at ZBZ.11 during all three sampling campaigns and the corresponding daily discharge rates at Kariba dam suggest that pCO_2 at the outlet of the reservoir would vary between only 3500 and 4600 ppm. Even these estimated outflow figures are expected to be in fact slightly higher since the (low) fluxes measured at ZBZ.11 may not be representative for the entire 70 km stretch (especially for the narrow and steep Kariba Gorge section), they are still substantially lower compared to pCO_2 ranges measured in the hypolimnion of several tropical reservoirs (Guérin et al., 2006)".

The two references were also added in the References of the revised version:
Guérin, F., Abril, G., Richard, S., Burban, B., Reynouard, C., Seyler, P., and Delmas, R.: Methane and carbon dioxide emissions from tropical reservoirs: significance of downstream rivers. Geophys. Res. Lett., 33, L21407, DOI: 10.1, 029/2006GL027929, 2006.

Kunz, M. J., Senn, D. B., Wehrli, B., Mwelwa, E. M., and Wüest, A.: *Optimizing turbine withdrawal from a tropical reservoir for improved water quality in downstream wetlands. Water Resour. Res, 49, 1-15. doi:10.1002/wrcr.20358), 2013.*

REF: Page 16411, L13-17: Why would an increased gas exchange velocity lead to oversaturation of dissolved oxygen?

REPLY: *We did not intend to suggest that increased gas exchange resulted in DO oversaturation but instead, a turbulent flow over this stretch associated with low water level which increases the gas exchange and therefore CO2 evasion, together with CO2 uptake during primary production may have been reduced there the pCO2 close to atmospheric levels and enhance the DO.*

REF: Page 16416, L14-22: Note that even for carbonate weathering half of the carbonate alkalinity (HCO3- and CO32-) would originate from soil respiration. If silicates are weathered (which can contribute substantially to carbonate alkalinity fluxes, see specific comment #2), the whole carbonate alkalinity would originate from soil respiration for which d13C is highly negative.

REPLY*: Yes, this is precisely the point of Figure 7c, which shows the relationship between $\delta^{13}C_{DIC}$ and DSi:Ca ratios as a relative proxy for silicate versus carbonate weathering. However, in the initial version this was likely not well explained (line 24 of P 16416 "suggest the relative importance of carbonate to silicate mineral weathering"), an additional sentence explaining this relationship has been added:*
"While carbon in HCO_3^- which originates from silicate rock weathering comes exclusively from CO_2, 1/2 of the C in HCO_3^- derived from carbonate rock comes from $CaCO_3$ and the other 1/2 from CO_2. If the CO_2 involved in the weathering comes from organic C degradation, $\delta^{13}C_{DIC}$ should have a negative signature, while marine $CaCO_3$ has a $\delta^{13}C$ signature close to 0% (Mook and Tan, 1991)".

The following reference was also added in the in the References of the revised version:

Mook, W. G. and Tan, F. C.: Stable carbon isotopes in rivers and estuaries, in: Biogeochemistry of Major World Rivers*, edited by: Degens, E. T., Kempe, S., and Richey, J. E. John Wiley, Hoboken, N. J., 245–264, 1991.*

REF: Page 16416, L25-28: Is part of the increase in POC due to phytoplankton?

REPLY: *We did not measure phytoplankton biomass. While in other similar studies we typically aim at measuring chlorophyll a concentrations, logistical constraints did not allow for adequate sample preservation for phytoplankton pigments. However, there is a relative increase in primary production rates in the lower Zambezi, especially in the delta, and therefore, it can be assumed that the increased POC there can be partially due to phytoplankton. We specify this in the text:*
"…alongside with an increase in POC in the lower Zambezi (data not shown), mostly laterally derived but also partially in-river produced as suggested by increased primary production rates, points out to the interplay…".

REF: Page 16417, L18: Maybe, use "half" instead of "twice as low"

REPLY: *Done*

REF: Page 16418, L16-17: Does this refer to water temperature?

REPLY: *Yes, we refer here to water temperature. We specify this in the text of the revised version.*

REF: Page 16418, L16 and following: Why is the temperature and DO increasing from midday to midnight? This makes me curious.

REPLY: *A close examination of the T and DO graphs (Fig. 8b, c) show a stabilization or a small decrease of both parameters between 4 pm and 7 pm. The small observed increase in T (of 0.1 °C, e.i. the resolution of measurements) and DO (from 91 to 92%, e.i. close to typical error of O2 probe) between ~7 pm and midnight is sufficient to be considered as a further increase.*

REF: Page 16419, L7-12: If the pCO2 is higher at midnight, wouldn't daytime sampling lead to overestimation of pCO2 and CO2 evasion?

REPLY: *This was indeed an error on our side - we replaced 'underestimated' with 'overestimated'.*

REF: Page 16419, L17: Is the data used by Aufdenkampe et al. mainly from the Amazon Basin? That could mean that pCO2 and evasion rates are higher in the Amazon Basin and upscaling from that region to the whole tropical zone could probably lead to an overestimation. That could be an important point and should be shortly discussed.

REPLY: *This is a good point. However it is unclear how the CO2 median values given by Aufdenkampe et al. were calculated (data source are not provided in detail), but we agree with the reviewer that they most probably reflect data from the Amazon. We stressed this in the Concluding remarks section by the addition of the following two lines:*

"While comparable with other studied river systems in Africa, the range in GHG concentrations and fluxes in the Zambezi River Basin were generally below the reported global median for tropical rivers, streams and lakes/reservoirs, for which the current empirical dataset is strongly biased towards studies of the Amazon River Basin. While GHG concentrations and evasion rates may generally be higher in the Amazon Basin, upscaling from that region to the whole tropical zone is prone to high uncertainties".

REF: Page 16422, L20: Maybe add "reported" or "estimated" before "global range"

REPLY: *We added 'reported' before 'global range'.*

REF: Page 16422, L25: Replace "in term" by "in terms of"

REPLY: *Done*

REF: Page 16424, L2: "longitudinal" instead of "longitudinag"

REPLY: *Done*

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 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 different 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 µmol L^{-1} CO2 versus µmol 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 CO_2 (µmol L^{-1}) and DO concentration (µmol 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 CO_2 content while hypoxic conditions associated with high CO_2 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 O_2 consumed to CO_2 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)."

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 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 CO_2 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.

REPLY: *The section has been reduced and condensed. References to the importance of δ^{13}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 (δ^{13}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 pCO2, CH4 and N2O 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 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”.*