

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 #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

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oxygen and $\delta^{13}\text{C}$ observations. Measurements of alkalinity, Ca, Mg, and DSi are used to analyse 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, $\delta^{13}\text{C}$, 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.

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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—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-

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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 (CO₂, CH₄, N₂O) 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.

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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 al. (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 CO₂ 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

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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: "CH₄ 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.

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REPLY: While N₂O concentrations along the Zambezi were also variable (although with a much lower max/min ratio than for pCO₂ and CH₄), there was little interannual variability but high seasonality. We clarify this by removing the reference to the temporal variability of pCO₂ and CH₄ stating: “N₂O 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 hypolimnetic 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

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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 con-

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trast to the CO₂ undersaturated (and warmer, DO saturated) epilimnetic conditions of the Kariba Reservoir, much higher pCO₂ (>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 CO₂-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 CO₂ level measured at ZBZ.11 cannot be totally ruled out. However, measurements during 2013 dry campaign showed a constant decrease in pCO₂ (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 pCO₂ 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 pCO₂ 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 CO₂ source along this 70 km stretch, and uses the CO₂ concentrations and fluxes measured at ZBZ.11 during all three sampling campaigns and the corresponding daily discharge rates at Kariba dam suggest that pCO₂ at the outlet of the reservoir would vary between only 3500 and 4600 ppm. Even these estimated out-flow 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 pCO₂ 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, C9116

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 δ¹³C is highly negative.

REPLY: Yes, this is precisely the point of Figure 7c, which shows the relationship between δ¹³CDIC 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 HCO₃⁻ which originates from silicate rock weathering comes exclusively from CO₂, 1/2 of the C in HCO₃⁻ derived from carbonate rock comes from CaCO₃ and the other 1/2 from CO₂. If the CO₂ involved in the weathering comes from organic C degradation, δ¹³CDIC should have a negative signature, while marine CaCO₃ has a δ¹³C

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%,

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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

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

REPLY: Done

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

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