

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.

Anonymous Referee #2

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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 oxygen and d13C 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 riverdelta 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.

C7408

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:

#1 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.

#2 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

C7409

would be necessary.

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].

#3 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.

Technical comments/corrections:

Page 16393, L24-25: There might be a word missing before “groundwater”

Page 16395, L21: remove comma after “Middle Zambezi”

Page 16397, L29: Maybe add a “by” after “dropped”

Page 16398, L3: Add comma after “floodplains”

Page 16399, L7: Replace “form” by “from”

Page 16400, L25: Remove “concentration” after “pCO₂”

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

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?

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

Page 16405, L10: Replace “and” by “but”

C7410

Page 16405, L11: Replace “significantly” by “significant”

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.

Page 16406, L13: Replace “week” by “weak”

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

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)?

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.

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

Page 16409, L9: Did you mean “high” instead of “height”?

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?

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

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

C7411

weathered (which can contribute substantially to carbonate alkalinity fluxes, see specific comment #2), the whole carbonate alkalinity would originate from soil respiration for which $\delta^{13}\text{C}$ is highly negative.

Page 16416, L25-28: Is part of the increase in POC due to phytoplankton? Page 16417, L18: Maybe, use “half” instead of “twice as low”

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

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

Page 16419, L7-12: If the pCO_2 is higher at midnight, wouldn't daytime sampling lead to overestimation of pCO_2 and CO_2 evasion?

Page 16419, L17: Is the data used by Aufdenkampe et al. mainly from the Amazon Basin? That could mean that pCO_2 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.

Page 16422, L20: Maybe add “reported” or “estimated” before “global range”

Page 16422, L25: Replace “in term” by “in terms of”

Page 16424, L2: “longitudinal” instead of “longitudinag”

References

Clymans, W., E. Struyf, G. Govers, F. Vandevenne, and D. J. Conley (2011), Anthropogenic impact on amorphous silica pools in temperate soils, *Biogeosciences*, 8(8), 2281–2293, doi:10.5194/bg-8-2281-2011.

Conley, D. J., G. E. Likens, D. C. Buso, L. Saccone, S. W. Bailey, and C. E. Johnson (2008), Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest, *Global Change Biology*, 14(11), 2548–2554, doi:10.1111/j.1365-

C7412

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Hartmann, J., N. Moosdorf, R. Lauerwald, M. Hinderer, and A. J. West (2014), Global chemical weathering and associated p-release - the role of lithology, temperature and soil properties, *Chemical Geology*, 363, 145–163.

Struyf, E., and D. J. Conley (2009), Silica: an essential nutrient in wetland biogeochemistry, *Frontiers in Ecology and the Environment*, 7(2), 88–94, doi:10.1890/070126.

Struyf, E. et al. (2010), Historical land use change has lowered terrestrial silica mobilization, *Nat Commun*, 1(8), 129, doi:10.1038/ncomms1128.

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C7413