Review of BGD paper: bg-2013-101

Overall I feel this is a good paper with a large amount of seasonal and longitudinal data on DIC and DO chemistry, stable isotopes, and metabolism in a tropical river that transitions from high elevation to sea level. I have a large number of comments that I feel should improve the manuscript, and have grouped these into three categories: "More important", "less important", and "editorial".

More important comments

Comment 1: More information on the geology of the watershed is needed. Only one sentence covers this important topic (Lines 12-15 of p. 5191), and there appear to be several inaccuracies. The sentence reads: *"The Nyambene Hills sub-catchment is lithologically distinct from the rest of the Tana River basin, as it shows a dominance of quaternary sedimentary rocks, as opposed to the precambian or tertiary volcanic rocks dominant in the rest of the basin (King and Chapman, 1972)".* First of all, the geologic terms "Quaternary", "Tertiary" and "Precambrian" (note correct spelling) should be capitalized. Second: I was curious about this, so went on-line and found a geologic map of Kenya at http://library.wur.nl/WebQuery/isric/17894). In fact, the Nyambene Hills appear to be underlain by Quaternary volcanic rocks, not sedimentary rocks, whereas most of the lower 2/3rds of the watershed is underlain by Quaternary sediments. The rest of the paragraph reads: "*Overall, carbonate mineral weathering in the entire Tana River basin was reflected by strong a positive correlation between TA and sum of Ca2+ and Mg2+ solutes (Fig. 5a). Theoretically, carbonate weathering produce a ratio of 2 : 1 between TA and sum of Ca2+ and Mg2+ solutes (Barth et al., 2003). In contrast, the ratio in the present study deviated from this expected behavior with higher TA of approximately 5 : 1 (n =75) recorded among tributaries and 3 : 1 (n =41) along main Tana River (Fig. 5a; Supplement Table 1) indicating the additional contribution of TA from silicate weathering".* The authors should discuss whether or not there are any mapped carbonate rocks, such as limestone or dolomite, in their study area. If such rocks are absent, then what is the source of carbonate weathering? Could it be dissolution of calcite that forms in soils during the dry season, and is (partly) dissolved during the wet? For example, "biogenic calcite", or "caliche", can be abundant in semi-arid soils, and typically has d^{13}C values that are much lighter than marine limestone (-2 to -9 ‰, see Chapter 5 of Clark and Fritz, 1997, Environmental Isotope Hydrology). Also, a recent paper by Hughes et al. (2012) has noted high dissolved silica in streams draining the Nyambene Hills, which they attribute to rapid weathering of pyroclastic ash. Such rocks can be rich in volcanic glass (obsidian) that can weather very quickly. Might this be a "silicate weathering" source of TA?   I think there should be more integration of the results of the present study with the earlier study of Bouillon et al (2012, BGD 6, 5959-6023). Does the new paper shed light on questions that were raised in the earlier paper?

> Hughes et al. (2012) The effects of weathering variability and anthropogenic pressures upon silicon cycling in an intertropical watershed (Tana River, Kenya). Chemical Geology 308-309, 18-26.
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> You might also want to take a look at this paper:
> Mathu and Davies (1996) Geology and the environment in Kenya. J. African Earth Sciences. 23, 511-539.

Comment #2: Do the methods used to determine in-stream R and P rates (i.e., incubated chambers) take into account benthic production/consumption of O$_2$ and CO$_2$? I don't think they do. So, it needs to be clearer to the reader which methods of quantifying "R" and "P" are based solely on suspended

biomass in the water column, and which methods take into account inputs and sinks from the river bottom. Given the presence of rooted macrophytes and other forms of periphyton, it would seem that the calculated P and R rates from incubation chambers could be underestimated, especially for clear, shallow streams and rivers.

Comment #3. p. 5187, l. 10. The authors should point out here that the outlet to Masinga reservoir discharges water from the bottom of the lake, and so this explains the high pCO_2 (much higher than atmospheric equilibrium). The fact that Masinga lake outlet discharges bottom water was discussed in the previous paper by Bouillon et al (2012). Also, in the methods, more information is needed as to where exactly the samples were collected for the reservoirs. Was this done at the outlet only? Or were samples collected out on the lake? Were all samples collected from the surface, or were some collected at depth as well? Also: p. 5189, l. 24 and on p. 5197, line 12: No diurnal changes were noted at Masinga Dam. Were samples collected from the surface of the lake or from the lake outlet? Since the dam discharges water from the bottom of the lake, I would not expect to see diurnal variations in this water. Please clarify where exactly the reservoir samples were collected.

Comment 4: p. 5190, l. 5-8. It is good to see the ranges in different concentration and isotopic readings over the diurnal cycle. However, later in the paper, there should be some kind of discussion as to whether these short-term fluctuations are important or non-important to discussion of the overall trends that are seen for the entire watershed. In other words, in certain river stretches, you get a different [DIC] value depending on what time of day you sample. Were all samples in the study from headwaters to mouth of Tana River collected at the same time of day? Probably not. So, are the diurnal variations significant compared to the longitudinal variations? If so, then you have a potential problem with the data, and this might explain some of the scatter in your plots, e.g., pCO_2 vs. distance. If not, then that is good to know, and should be stated in the discussion. Side Comment: There should probably be more attention paid in the Introduction to the phenomenon of diurnal cycling of DIC, DO, $d^{18}O$-DO, and $d^{13}C$-DIC, and why this might be important to studies of large rivers. This is a big part of the results and discussion, but is only glossed over in the Introduction/literature review.

Less important comments

p. 5191, line 8. The text states: "*This is particularly evident along the main Tana River, where DIC strongly increased downstream during all seasons*". How much of this increase might be due to evaporation? Do you have a conservative solute (e.g., Cl- ion) that you can use to track evaporation?

p. 5192, line 5. The text states: " *(equilibrium with atmospheric CO2 yields d13CDIC values of about 1‰)*". But this is highly dependent on pH and the speciation of DIC between dissolved CO_2 and bicarbonate ion. A water with pH 8 in equilibrium with atm. CO_2 will have total DIC dominated by HCO_3^-, and $d^{13}C$-DIC of around +2.5‰. A water with pH 6.5 in equilibrium with atm will have nearly equal quantities of both HCO_3^- and CO_2, and $d^{13}C$-DIC of around -3‰.

p. 5192, line 13. The text states : "*The increase in water residence time at the reservoir also favours the CO2 exchange with the atmosphere*". But this is not necessarily true if the reservoir is vertically stratified most of the year. Earlier the authors show very high pCO_2 in the outlet to Masinga Reservoir, which is due to the discharge of deep lake water. Clearly, the reservoir was not vertically mixed during this time period. So, CO_2 can build up in the deep lake waters and pass through the dam, only to evade in the downstream tailwater. More discussion should be given earlier in the

paper as to whether or not this reservoir is meromictic (permanently stratified), holomictic (stratified for the majority of the year but with at least one top to bottom turnover annually), or continually mixed.

p. 5193, l. 24. It is easy to understand why degassing below the springs causes a rapid decrease in DIC concentration. However, it is less obvious why this causes an increase in $d^{13}C$-DIC. The authors should explain this better. I.e., there is a large isotopic fractionation between dissolved CO_2 and HCO_3^-. As CO_2 evades to the atmosphere, the $d^{13}C$ of total DIC is shifted to the value for HCO_3^-, which is isotopically heavier than CO_2.

p. 5194, l. 13-18. Reference is made to "depth-profile data" collected from the reservoir. This was not explained in the methods nor anywhere else in the paper. What kind of information was collected with depth and on what dates? Has this information been published somewhere?

p. 5198, l. 26 the text states: *"…with a record fluctuation of 1.133 mmolL₋₁ reported by Parker et al. (2010). However, this large diurnal change in DIC concentration is reported to have been driven by unique calcite precipitation and not in-stream P or R (Gammons et al., 2007; Nimick et al., 2011)".* The authors should probably re-read the pertinent sections in Nimick et al. (2011) and Parker et al. (2010). Whereas daytime precipitation of calcite was suggested to be important by Gammons et al. (2007) for lower Silver Bow Creek, most of the examples of diurnal DIC variations in the Parker and Nimick papers were driven by in-stream, biological processes.

Figure 1. I like this figure. Is it modified from a similar figure in another paper? (If so, you should probably say this in the caption and cite the source).

Figure 11. If you connect the data points to show changes from one hour to the next, do the data form an ellipse, or are they just scattered? Parker et al. (2010) showed some interesting elliptical trends (sometimes clockwise, sometimes counterclockwise) for similar diurnal crossplots.

Editorial Comments

Abstract, l11: "higher" should be "more positive"

Abstract, l17: "during 2009 wet season" should be "during the 2009 wet season". Do a search for the word "during" in the paper. In most cases (not all) there should be the word "the" after "during". Overall. the authors should have their paper proof-read by someone proficient in English to catch these errors.

Abstract, l23-25. In the same sentence, you use present tense "increase" and past tense "increased". Be consistent. Suggest to use past tense when discussing phenomena that happened in the past.

Abstract, l19-23 is a run-on sentence. Should be split up.
Abstract, l22 "than respiration" should be "other than respiration"
P5178, l9: delete "both" (since there are 3 objects)
P5179: l22-27 is a run-on sentence. Split this into 2 or 3 sentences. Delete the parentheses and fix grammar.
P5180, l6. The comma should be placed before "whereas", not after.
P5180, l8. No comma after "(> 7th-order)"
P5180, l29: "within Tana River basin" should be "within the Tana River basin"

P5182: l19: "1.7 higher" should be "1.7 times higher"

P5182, l24: did you sample the reservoirs at their outlets? Within the lake?

P5182, l5: "with polarographic" should be "with a polarographic"

P5182, l7: "during end of wet season" should be "during the end of wet season".

P5186, l9: "all the three" should be "all three". Do a global find and replace, as this grammar mistake occurs throughout the paper.

P5191, l2: the comma should be before "but", not after

P5191, l17: "strong a" should be "a strong"

P5193, l7: "stream" should be "streams"

P5193, l8: change the wording so it reads "…characterized by relatively low pCO2 compared to other …"

p. 5194, l. 13-18. Another run-on sentence.

P5195, l3-8: this is another run-on sentence.

P5195, l9: needs a period after "(Fig. 6a)"

P5196, l16: "the that" should be "that the"

Table 1 caption should be: "Summary of the ranges in physico-chemical parameters for diurnal sampling sites"

Table 2 caption: "flux evasion" should be "evasion flux"

Fig. 2 caption: When you say that "Masinga Dam is a 24-h sampling site", do you mean the outlet to the dam? How far below the outlet of the dam did you collect samples?

Fig. 3. Was the dry season sampling in 2008 part of the Bouillion et al. (2012) study? If so, then this should be stated in the caption.

Fig. 4. If dry season data are from Bouillion et al. (2012), then this should be stated in the caption.

Fig. 5. Caption: Spell out "TA". Also, instead of "&" or "and", I would use a "+" symbol, as in "sum of $Ca^{2+} + Mg^{2+}$"

Fig. 6A. Have you tried a plot (similar to Fig. 6A) of d13C-DIC vs. total DIC, or d13C-DIC vs. TA for all of your data? How do those graphs look?

Fig. 8A. Is "P" based on incubation chambers, and if so, is this a big underestimate if there are macrophytes and biofilms present? (Probably important for headwater streams).

Fig. 8 and 9. What does a cross-plot of P vs. R for all data points look like?

Fig. 10. Maybe add another diagram at the bottom, which would show 24-h changes in [DIC], pCO2, d13C-DIC.

Fig. 11a: "O2" should be "O_2" in x-axis caption. Also, why is the vertical dashed line corresponding to 100% saturation not crossing exactly at 100%? Same problem with D and E.

Figure 14 caption. This isn't really a "crossplot". Also, you are plotting CO_2 concentration, not pCO_2 flux. Note that the phrase "pCO_2 concentration" is redundant, since the "p" denotes partial pressure. Check the rest of the paper for other places where this mistake is made.