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Interactive comment on "Dynamics of dissolved inorganic carbon and aquatic metabolism in the Tana River Basin, Kenya" *by* F. Tamooh et al.

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Anonymous Referee #2

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 REF: 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. Reply: The spellings for respective geologic terms have also been corrected (capitalized).

REF: 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. Reply: The inaccuracies in the description of the geology was an oversight on our part but has been appropriately rectified in the main manuscript.

REF: 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 d13C 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. 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. Reply: We thank the reviewer for the valuable suggestions that prompted us to further elaborate the issue of carbonate and silicate weathering. Based on the dissolved silicate (DSi), Ca2+ and Mg2+ we computed the theoretical total alkalinity (TA) due to weathering using the simple stoichiometric model of Garrels and Mackenzie (1971). The modeled TA is in fair agreement observations (fig. 5a) with the exception of 3 rivers in the Nyambene Hills. The computations using the simple stoichiometric model of Garrels and Mackenzie (1971) show that the relative contribution of silicate weathering to total rock weathering ranges between 7 and 78 % and averages 28 %, close the overall average of 24% for African rivers computed by Garrels and Mackenzie (1971). We also included a short description of possible origins of carbonate rocks in Kenya. Finally, we briefly discuss the possible reasons for the deviation of modeled and observed TA in the 3 rivers located in Nyambene Hills.

REF: 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 O2 and CO2? 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, espe-

cially for clear, shallow streams and rivers.

Reply: We have clarified that the method used to estimate the in-stream respiration is depth integrated and hence represent the whole water column but does not account for the sediment benthic respiration. Primary production estimates are based on the surface water column only (euphotic zone which is $\sim$0.5 m deep for lower Tana River mainstream). However, most of the headwater streams are shallow and clear and therefore the estimated primary production rates should be valid for the entire water column. However, we have further clarified this in the discussion section (Page- 5196-line 9-29) where we have estimated the CO2 evasion accounted by aquatic respiration.

REF: 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 pCO2 (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? Reply: We have clarified in the main manuscript that Masinga discharges from the bottom of the lake. In addition, we also wish to mention that during high discharge the reservoir also releases water from the spillway outlet which is generally vertically mixed. For examples during the end of wet season campaign, water from Masinga reservoir was flowing via the spillways as well through the bottom of the reservoir. We have also clarified in the method section and in the supplementary tables that water samples in reservoirs were taken from a depth profile within the dam. REF: 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. Reply: The diurnal cycle was carried out on the reservoir itself, not in the river below the dam. This is now specified explicitly. It is true that no diurnal pattern were observed at the Masinga reservoir, and this was in contrast to our expectations but can likely be ascribed to the timing of sampling which took place during a the period when the reservoir was completely full and turbid, and therefore most water was released from the spillway outlet. The depth profile shows the water at the sampling site was generally well mixed vertically, at least up to 20 m depth and thus the residence time was greatly reduced.

REF: 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., pCO2 vs. distance. If not, then that is good to know, and should be stated in the discussion. Reply: From a catchment perspective, the diurnal fluctuations did not significantly affect the outcome of the biogeochemical processes directly particularly along the main Tana River. In the discussion section we have categorically stated that the diurnal fluctuation we observe in the headwater stream are largely driven by periphyton community rather than phytoplankton community but the range of change in most biogeochemical parameters is within a considerable range. In addition, we have further discussed that while ideally we expected to observe pronounced diurnal fluctuations at the reservoir site, the timing of the sampling was rather unusual considering it coincided with high discharge, when the reservoir was completely full and relatively turbid. Water was released via the spillway and the low residence time of the water was likely unfavourable for phytoplankton production.

REF: Side Comment: There should probably be more attention paid in the Introduction to the phenomenon of diurnal cycling of DIC, DO, d18ODO, and d13CDIC, 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. Reply: The concern regarding lack of attention on diurnal fluctuation patterns of different biogeochemical parameters relevant for this study has been noted and some addition citations to relevant literature has been added accordingly in the introduction section of the manuscript.

Less important comments REF: 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? Reply: The downstream increase in DIC concentration along the lower Tana river mainstream is particularly evident during wet season which we largely attribute to DIC build up from organic matter respiration. However, we do not have data on Cl- ion to to confirm or refute the hypothesis on contribution of evaporation on DIC concentration.

REF: p.5192, line 5. The text states: “(equilibrium with atmospheric CO2 yields ?13CDIC values of about 1‰”. But this is highly dependent on pH and the speciation of DIC between dissolved CO2 and bicarbonate ion. A water with pH 8 in equilibrium with atm. CO2 will have total DIC dominated by HCO3-, and d13CDIC of around +2.5‰Ȧ water with pH 6.5 in equilibrium with atm will have nearly equal quantities of both HCO3- and CO2, and d13CDIC of around -3‰Ṙeply: DIC speciation calculated from our whole dataset shows that ~92% of DIC is dominated by HCO3- despite high longitudinal variability in pH. REF: 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 pCO2 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, CO2 can build up in the deep lake waters and pass through the dam, only to evade in the downstream tail water. 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. Reply: The stratification of the Masinga reservoir is highly dependent on the stage flow rate. During high flow rate, the reservoir is vertically mixed considering most water flows via spillway characterized by shorter residence time while during low flow rate the water flow rate is highly regulated and exits via reservoir's bottom outlet only thus enhancing stratification.

REF: 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 d13C-DIC. The authors should explain this better. I.e., there is a large isotopic fractionation between dissolved CO2 and HCO3-. As CO2 evades to the atmosphere, the d13C of total DIC is shifted to the value for HCO3?, which is isotopically heavier than CO2. Reply: The gradual increase in d13CDIC is due to the fact that CO2 is more 13C-depleted than bicarbonate and carbonate ions, by ~8-10‰ (temperature dependent). Hence, assuming rapid isotopic re-equilibration between different DIC species, CO2 evasion leads to a 13C-enrichment in the remaining DIC pool (as described also in the studies referred to in the relevant section).

REF: 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? Reply: Basically, almost all biogeochemical parameters discussed in the main manuscript were also collected along a depth profile. These data were presented in the supplementary tables, but indeed received little attention in the manuscript text. We have now explicitly described this in the method section as suggested.

REF: p. 5198, l. 26 the text states: "...with a record fluctuation of 1.133 mmolL-1 re-

ported 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 instream, biological processes. Reply: In the statement; "with a record fluctuation of 1.133 mmol-1 reported by Parker et al. (2010)" the authors were basically trying to underscore the significance of calcite precipitation over other in-stream processes (primary production and respiration) in regulating the DIC diurnal fluctuations which generally is in contrast to our present study whose DIC diurnal fluctuations are generally driven by primary production and respiration process.

REF: 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). Reply: The figure is not a modification of one particular citation but is loosely based on a number of citations.

REF: 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 cross plots. Reply: The data points do not show systematic ellipse pattern

Editorial Comments REF: Abstract, |11: "higher" should be "more positive" Reply: This has been corrected REF: Abstract, |17: "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. Reply: This has been corrected in the whole manuscript REF: Abstract, |23-25. 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. Reply: This has been corrected in the whole manuscript REF: Abstract, |19-23 is a run?on sentence. Should be split up. Reply: This sentence has been split up REF: Abstract, |22 “than respiration” should be “other than respiration” Reply: This has been corrected REF: P5178, |9: delete “both” (since there are 3 objects). Reply: this has been deleted REF: P5179: |22-27 is a run?on sentence. Split this into 2 or 3 sentences. Delete the parentheses and fix grammar. Reply: This sentence has been split up and grammar fixed. REF:P5180, |6. The comma should be placed before “whereas”, not after. Reply: This has been corrected in the revised manuscript REF: P5180, |8. No comma after “(> 7th-order)” Reply: This has been corrected in the revised version of the manuscript REF:P5180, |29: “within Tana River basin” should be “within the Tana River basin” Reply: This has been corrected in the revised version of the manuscript REF:P5182: |19: “1.7 higher” should be “1.7 times higher” Reply: This has been corrected in the revised version of the manuscript REF:P5182, |24: did you sample the reservoirs at their outlets? Within the lake? Reply: The reservoirs were sampled within but close to the outlets. REF:P5182, |5: “with polarographic” should be “with a polarographic” Reply: This has been corrected in the revised version of the manuscript REF:P5182, |7: “during end of wet season” should be “during the end of wet season”. Reply: This has been corrected in the revised version of the manuscript REF:P5186, |9: “all the three” should be “all three”. Do a global find and replace, as this grammar mistake occurs throughout the paper. Reply: This has been corrected in the revised version of the manuscript REF:P5191, |2: the comma should be before “but”, not after Reply: This has been corrected in the revised version of the manuscript REF:P5191, |17: “strong a” should be “a strong” Reply: This has been corrected in the revised version of the manuscript REF:P5193, |7: “stream” should be “streams” Reply: This has been corrected in the revised version of the manuscript REF: P5193, |8: change the wording so it reads “. . .characterized by relatively low pCO2 compared to other . . .” Reply: This has been corrected in the revised version of the manuscript REF: p. 5194, l. |3-18. Another run?on sentence. Reply: This sentence has been

split up REF: P5195, |3-8: this is another run-on sentence. Reply: This sentence has been split up REF: P5195, |9: needs a period after “(Fig. 6a)” Reply: This has been corrected in the revised version of the manuscript REF: P5196, |16: “the that” should be “that the” Reply: This has been corrected in the revised version of the manuscript REF: Table 1 caption should be: “Summary of the ranges in physico?chemical parameters for diurnal sampling sites” Reply: This has been corrected in the revised version of the manuscript REF: Table 2 caption: “flux evasion” should be “evasion flux” Reply: This has been corrected in the revised version of the manuscript REF: 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? Reply: We mean within the dam but we have further clarified this in the method section of the revised version of the manuscript. REF: 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. Reply: Yes, we have corrected caption in Fig. 3 in the revised version of the manuscript by indicating that dry season sampling in 2008 has already been presented in Bouillon et al. (2009). REF: Fig. 4. If dry season data are from Bouillion et al. (2012), then this should be stated in the caption. Reply: Yes, we have corrected caption in Fig. 3 in the revised version of the manuscript by indicating that dry season sampling in 2008 has already been presented in Bouillon et al. (2009) and not Bouillon et al. (2012). REF: Fig. 5. Caption: Spell out “TA”. Also, instead of “&” or “and”, I would use a “+” symbol, as in “sum of Ca2+ + Mg2+” Reply: This has been corrected in the revised version of the manuscript REF: 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? Reply: Yes, we have but we did not include the figure in the manuscript. Overall, we have indicated in the result section of the manuscript that d13CDIC showed a negative correlation with DIC concentrations (Pearson correlation, $p < 0.01$, $r2 = 0.49$, $n = 122$) during all three campaigns REF: 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). Reply: “P” is based on in-situ bottle incubation technique. The headwater streams were generally shallow characterized by periphyton but the water was generally clear thus measurements represented the whole water column. REF: Fig. 8 and 9. What does a cross?plot of P vs. R for all data points look like? Reply: Considering primary production (P) measurements particularly for lower Tana River were not depth integrated (primary production was limited to euphotic zone) while the respiration (R) measurements were depth integrated, a cross-plot of P vs. R would overestimate the P:R ratios and hence such a cross-plot would be inappropriate. REF: Fig. 10. Maybe add another diagram at the bottom, which would show 24-h changes in [DIC], pCO2, d13C?DIC. Reply: The proposed diagrams have already been presented in Fig 12. REF: Fig. 11a: "O2" should be "O2" 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. Reply: The anomalies have been noted and duly rectified in the revised version of the manuscript. REF: Figure 14 caption. This isn't really a "crossplot". Also, you are plotting CO2 concentration, not pCO2 flux. Note that the phrase "pCO2 concentration" is redundant, since the "p" denotes partial pressure. Check the rest of the paper for other places where this mistake is made Reply: The anomalies have been noted and duly rectified in the revised version of the manuscript.

Interactive comment on Biogeosciences Discuss., 10, 5175, 2013.