

Interactive comment on “Dynamics of dissolved inorganic carbon and aquatic metabolism in the Tana River Basin, Kenya” by F. Tamooch et al.

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fredrick.tamooch@ees.kuleuven.be

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Anonymous Referee #1

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Comments to bg-2013-101: REF: I think these are important data from a poorly represented landscape that will be a valuable addition to the literature. The use of mass balance, isotopes and attention to seasonality make this a high quality piece of work. The basin scale patterns shown by the authors that differ from the temperate zone are especially intriguing and highlight major differences in the tropics. I do however have a few suggestions that will need to be addressed in order to answer remaining questions regarding metabolism and dynamics, and gas transfer physics. These

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issues can be addressed with the available data and should not require major reformulations of the manuscript. General Comments: The attempt to balance gas emissions from metabolism is noteworthy here, but I found the discussion and interpretation to be somewhat problematic. Since CO₂ emissions were measured during the day, P and R should contribute to the drawdown and simultaneous production of pCO₂. However, the authors attempt to balance the CO₂ flux estimates using R alone. I'd really like to see CO₂ emissions compared with net production, and some reference as to the bias in daytime flux estimates could be noted or cited. The discussion of source strength and metabolism (i.e., page 5199) should be framed in terms of net ecosystem production, not just P or R. There is emerging evidence that lakes can be both net autotrophic and significant sources of CO₂ to the atmosphere, pointing to the large role of groundwater, which is probably important for streams too (see McDonald et al., 2013; Global Biogeochemical Cycles). CO₂ flux to the atmosphere does not necessarily equate to net heterotrophy. Reply: We fully understand the reviewer's concern regarding comparison of CO₂ emissions with net production. However, while our respiration estimates were depth-integrated, our primary production measurements were based on water samples taken in surface water representing the euphotic zone (~0.5 m depth) only considering that Tana River mainstream is quite turbid, and due to time and logistical constraints in performing more elaborate measurements to provide depth-integrated measurements. Therefore, we do not feel we have adequate data to reliably estimate P:R ratios (or net community production) based on our current dataset. REF: The second main criticism I have concerns the lack of observed diurnal patterns in the lower reaches of the basin. Given that P and R increase downstream, I might expect that diurnal patterns would become more pronounced, not disappear. More discussion and exploration of this phenomenon is needed. Reply: We agree with the reviewer that we would expect the amplitude diurnal cycle to increase with an increase of P and R at community level. However, we report P and R solely in the planktonic compartment and not in the benthic compartment. In the present version of the manuscript we included the computation of GPP and R at community level at Chania. This shows that the pe-

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riphyton (benthic) GPP and R are overwhelmingly higher than planktonic GPP and R. Hence, we concluded that the diurnal signal at Chania is driven by periphyton. In other two sites benthic primary production is probably inexistent because of light limitation due to the turbidity (for Tana) and due to depth (for Masinga dam). REF: If possible, I also suggest that the diurnal dissolved oxygen data from the 24 hour samplings be used to calculate whole ecosystem metabolism to supplement the incubation values for P and R. Reply: We computed whole community metabolic rates from the 24h cycle of O₂ at Chania, and the comparison with the pelagic incubations confirms our initial hypothesis that there is large contribution to P and R of periphyton. REF: There is currently no discussion of physical gas exchange. Like pCO₂, there are emerging basin scale patterns such as decreasing gas transfer velocity with increasing stream order (or in this case elevation as a proxy). Given that the authors have CO₂ concentrations and fluxes, the gas transfer velocity can be calculated with little extra effort. A presentation and discussion of the gas transfer velocity will help readers determine the potential bias of the chamber technique (which is not yet well understood) and the broad scale patterns of flux in this basin. Where are the physical hotspots? The headwaters as CO₂ emission hotspots might be driven by a combination of high transfer rates and/or high pCO₂, but here, the headwaters seemed to have much lower pCO₂ relative to the main river. A comparison of gas exchange potential from the different systems would add important detail to this variability. If the authors attempt to calculate whole ecosystem metabolism using diurnal dissolved oxygen data (or even better, both DO and CO₂) these gas transfer values can be used to constrain the atmospheric flux in the model structure. Reply: We agree with the reviewer that gas transfer velocity (k) is an important uncertainty in the evaluation of CO₂ fluxes. A recent literature review based on direct tracer estimates of k in rivers has shown that this variable can be parameterized as a function of slope and current velocity (Raymond et al. 2012). Since slope and current velocity vary along the stream order, there is an overall relation between k and stream order, with headwaters generally characterized by higher k values as also shown by Billett and Harvey (2012). However, since the primary aim of our

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study was not focused on the determination of k, we did not acquire the relevant data needed to study this variable, in particular and importantly current velocity. Hence, we could compute the k values (actually anyone can from the data given in the supplementary table) but we would not be able to compare them with those derived from the parameterizations given for instance by Raymond et al. (2012). Finally, we agree that there are potential biases associated with floating domes, but we feel a discussion on the topic is outside the scope and aims of the paper. This has been debated in other papers, for instance Kremer et al. (2002) and Borges et al. (2004). Also, we do not have the adequate data to address this, since in addition to the floating dome data, an independent measurement of turbulence or k is required, as for instance done by Vachon et al. (2010).

Billett, M. F. and Harvey, F. H.: Measurements of CO₂ and CH₄ evasion from UK peatland headwater streams, *Biogeochemistry*, doi:10.1007/s10533-012-9798-9, 2012. Borges A.V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., & Frankignoulle, M.: Gas transfer velocities of CO₂ in three European estuaries (Randers Fjord, Scheldt and Thames), *Limnology and Oceanography*, 49(5): 1630-1641, 2004. Kremer, J. N., Reischauer, A. D'Avanzo, S. C., Nixon, W., Buckley, B., and Roques, P.: Technical note: Conditions for using the floating chamber method to estimate air-water gas exchange, *Estuaries*, 26, 985-990, 2003. Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E., McDowell, W. H., and Newbold, D.: Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers, *Limnology and Oceanography—Fluids and Environment*, 2, doi:10.1215/21573689-1597669, 41–53, 2012. Vachon D, YT Prairie, and JJ Cole (2010) The relationship between near-surface turbulence and gas transfer velocity in freshwater systems and its implications for floating chamber measurements of gas exchange, *Limnol. Oceanogr.*, 55(4), 1723–1732.

REF: Finally, while the units are generally properly presented, the attention to metabolic mass balance requires compatible units for oxygen and CO₂. I generally think pCO₂

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should be presented in micro-atmospheres (or the SI units of pascals which aren't widely used) instead of parts per million by volume (as gases move across pressure gradients), but when comparing with oxygen, the best units would be moles of oxygen and CO₂ corrected for saturation. This would allow for easy comparison of the two gases, and would clearly show the dynamics due to metabolism. If you fit a line to this relationship (i.e., Fig 11) you could possibly calculate the respiratory quotient and determine if it truly is unity. This simple comparison is essentially absent in the aquatic literature and could be very useful for analyzing sources and dynamics of CO₂. Reply: We thank the reviewer for the suggestions. We do not have atmospheric pressure measurements to convert the pCO₂ from ppm to μatm . However, this would introduce relatively small variations of values, hence, not affecting the temporal and spatial patterns of the data, and hence not affecting our interpretations and conclusions. We feel that our data-set is inappropriate to derive respiratory quotient (RQ) for several reasons. Since the CO₂ is partly driven by equilibrium reactions with HCO₃⁻, to compute RQ we need to compare DIC and O₂ (and not CO₂ and O₂). However DIC variations in river networks are largely driven by those of HCO₃⁻ and to some extent independent of processes also affecting O₂. We could have done this exercise for the 24h cycle in Chania as suggested by the reviewer, but other processes affected CO₂ and DIC during the 24 h cycle as illustrated by Figure 13B (BGD version). While we do not fully understand what was going on, this seems to be a hydrological rather than a biological change of TA and hence also of DIC. We did attempt to account for TA changes on DIC, by using DIC* computed as DIC-TA/2 (eg Suykens et al. 2010). The slope of the linear regression of O₂ concentration versus DIC* during night-time during the Chania 24h cycle is 1.11 ± 0.48 ($r^2 = 0.37$, $n=11$), providing an RQ estimate above 1 but marred by a very large error. In conclusion, our data-set is inadequate for deriving RQ estimates, and we think that carefully executed incubations are more adequate to achieve this. Yet, we decided to convert the R values into carbon units using the RQ value of 1.3 as suggested by Richardson et al. (2013).

Richardson, D. C., Newbold, J. D., Aufdenkampe, A. K., Taylor, P. G., and Kaplan, L.
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A.: Measuring heterotrophic respiration rates of suspended particulate organic carbon from stream ecosystems, *Limnol. Oceanogr.: Methods* 11, , 247–261, 2013. Suykens K., Delille, B., Chou, L., De Bodt, C., Harlay, J., & Borges, A. V.: Dissolved inorganic carbon dynamics and air-sea carbon dioxide fluxes during coccolithophore blooms in the Northwest European continental margin (northern Bay of Biscay), *Global Biogeochemical Cycles*, 24, GB3022, doi:10.1029/2009GB003730, 2010.

Specific Comments REF:: 5183-28: what bias does the calculation of pCO₂ from TA have? The errors are reported, but I thought pH measurements caused a directional bias (see Butman and Raymond, 2011; *Nature Geoscience*). Reply: Based on the analytical errors or uncertainty in pH measurements and TA measurements, the theoretical uncertainty in pCO₂ is minimal (estimated here at ± 5 ppm). However, this assumes that the speciation of DIC follows the theory and it has been pointed out that these calculations can be biased, in particular in systems with extremely low TA and/or very high DOC concentrations. While we have not carried out direct measurements of pCO₂ (by equilibration) during this study, we have done so in a variety of African rivers (Congo, Zambeze, Betsiboka) in parallel with pCO₂ computed with pH and TA (Teodoru, Bouillon, Borges, unpublished). This analysis shows that both methods are in fair agreement in range of DOC values encountered in the Tana river. The significant discrepancies occur for for DOC > 7.0 mg/L, typically in “black waters”.

REF: 5184-10: present the equation used for flux measurements Reply: The equation for flux calculation has been presented as follows: $\text{FCO}_2 = (\text{dpCO}_2/\text{dt})(V/RTS)$, where dpCO_2/dt is the slope of the CO₂ accumulation in the chamber (atm s^{-1}), V is the chamber volume (L), T is air temperature (K), S is the surface area of the chamber at the water surface (m^2), and R is the gas constant ($\text{L atm K}^{-1} \text{mol}^{-1}$).

REF: 5188-17: are the rates μmol of oxygen? Reply: We converted the R values into carbon units using the RQ value of 1.3 as suggested by Richardson et al. (2013).

REF: 5193-24: What is the authors position on the hypothesis that pCO₂ is derived

from “production of carbon dioxide from soils?” Since none of the sites’ CO₂ fluxes can be balanced fully by respiration, is this the missing source? 5194-3: a whole ecosystem metabolism estimate might show a contribution from benthic sources (which in the headwaters might constitute the majority of respiration). Reply: We hypothesize that the excess CO₂ evasion may be explained by other watershed and in-stream processes including soil respiration (and hence, CO₂ inputs through groundwater) and/or benthic respiration. We propose that future studies should prioritize to constrain and quantify the role of groundwater input as well as examine the sediment benthic respiration to CO₂ evasion to better constrain the missing source. We agree that with perfect measurements of whole ecosystem metabolism, we could have disentangled origin of the missing CO₂. This approach will be in reality limited by the error propagation on the computation of whole ecosystem metabolism.

REF: 5194-19: Is there data to indicate physical stratification? Reply: The depth profile data (e.g. pCO₂ and O₂) at Kamburu dam shows clear stratification as shown in the supplementary tables during both the wet and end of the wet season campaigns. This will be mentioned in the text of the revised version of the manuscript.

REF: 5194-25: Is the dam designed to release hypolimnetic waters? Or do the turbines draw from multiple or variable depths? Reply: Masinga dam is designed to release hypolimnetic waters during low to intermediate discharge. However, during extreme high flows e.g during the end of wet season campaign, the dam releases water from both the spillway as well as hypolimnetic water through reservoir bottom exit. REF: 5196-5: use consistent units throughout Reply: The quantity referred here is based on depth integrated measurements of primary production but our primary production measurements are based on surface water measurements (euphotic zone - ~0.5 m). REF: 5196-16: the respiratory quotient is still unresolved, but recent work suggests that it may be closer to 1.2 for freshwaters (see Berggren et al. 2011; The ISME Journal). How would this influence your interpretation of metabolic contribution? Reply : We converted the R values into carbon units using the RQ value of 1.3 as suggested by

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Richardson et al. (2013).

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

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