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Interactive comment on "Dynamic seasonal nitrogen cycling in response to anthropogenic N-loading in a tropical catchment, Athi–Galana–Sabaki River, Kenya" *by* T. R. Marwick et al.

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General comments:

The authors have submitted an interesting manuscript describing the sources, transit and transformations of several N species in a river in a tropic catchment in Kenya, Africa. Since there is rather little published in the refereed literature about nitrogen cycling in rivers in Africa, this contribution should be in principle of significant interest for the readership of Biogesciences Discussions.

The authors present data from a well-designed sampling campaign conducted at different flow conditions with a rather comprehensive set of analytical parameters determined with state-of-the-art analytical approaches. The results are for the most part clearly presented and the majority of the conclusions are justified by the available data and statistical approaches. There are, however, also a number of key issues that remain unclear and require further clarification. These include:

- In the introduction (page 8642 lines 9-11), the authors report ranges of δ^{15}N values for nitrate in wastewaters, sewage and manure. In the context of this paper it would also be important to report ranges of δ^{15}N values of ammonium, since this compounds is often dominant in raw and poorly treated sewage.

- On page 8645, the authors report some hydrological and climatic parameters for the watershed. I suggest to add information on monthly temperatures and on evapotranspiration in the watershed, in case these data are available.

- Water residence times are cited as a key driver for N export with riverine flows on page 8652 and elsewhere. However, the paper does not report any quantitative data on what these water residence times are and by how much they change between dry and wet seasons. This should be addressed in a revised version of this manuscript.

- On pages 8653-8655, the authors discuss processes that remove ammonium and generate nitrate based on changes of riverine concentrations of these N species. It would to excellent to support this discussion by flux data (N concentrations times flow) to provide evidence that variations in concentrations are not mainly due to changes in water flows but rather due to N transformation

processes as suggested.

- The section on N isotope fractionation during conversion of raw sewage to riverine nitrate on page 8656 is incomplete and in part misleading and requires improvement (see also specific comments below). The authors may want to consult SEBILO ET AL. (2006): Assessing nitrification and denitrification in the Seine River and estuary using chemical and isotopic techniques. – Ecosystems, 9(4): 564-577. DOI:10.1007/s10021-006-0151-9. This paper describes the chain of events and associated isotope effects between release of ammonium-dominated waste water and export of riverine nitrate into the ocean for a case study in France.

- One of the key shortcomings of the paper is that the authors did not measure the δ^{15}N values of the predominant pollution source (sewage) nor the δ^{15}N values of riverine ammonium or nitrate. Instead they report the δ^{15}N values of particulate organic matter, but do not always explain how the δ^{15}N of particulate matter reflects the nitrogen isotopic composition of dissolved inorganic nitrogen compounds such as nitrate and/or ammonium. This is, in my view, one of the key deficits of this study that requires further explanation.

- On page 8659 the authors explain the variation in δ^{18}O values of water but do not supply enough information for the reader to follow or verify their arguments. They refer to seasonal variation in rainfall, but do not provide the range of δ^{18}O for seasonally varying rainfall. Also, is there an altitude effect in δ^{18}O of precipitation given the significant elevation change in the catchment? What is the δ^{18}O of groundwater? More background information would be desirable.

- On page 8661, the authors suggest correctly that δ^{15}N values may serve as a tracer for historical evolution of N sources as recorded in historical archives such as sediments, bivalves, or corals. While this is intriguing, it remains puzzling why the authors have not reported a measurement of δ^{15}N values of the major N pollution source in the current study when the opportunity existed to do so in their study.

- A more technical issue is that the language used to report isotope ratios should be cleaned up. It is not accurate to talk about "enriched" δ^{15}N values. If "enriched" is used, it must be added whether enriched in ^{15}N or ^{14}N? Also inspection of the definition of the delta notation reveals that it is not clear how it can be "enriched". Using the terms "increasing" or "decreasing" δ^{15}N values is much clearer and hence recommended.

From a technical viewpoint, the manuscript is well written and organized in a logical order. Previous literature is appropriately considered and the figures and tables are clear and informative. If the authors are able to address the major concerns summarized above, and a number of specific suggestions listed below, then this paper should be of considerable interest to Biogeosciences Discussion after moderate revisions.

Further **specific comments** are listed below:

Page Line Comment

8638 11 rephrase: it is not the concentrations that enter the river but water that has certain concentrations. Also, what do you mean with "study area" (line 12)? Does that refer to upstream portions of the river, or the tropical catchment, or what? Please clarify.

8638 20 if you use the term "enriched" you should add enriched in what, ^{15}N or ^{14}N? Note that a δ^{15}N value can not be enriched.

8638 21 you claim here that organic matter is the “source” of riverine N; however the increasing δ^{15}N values seem to indicate that this organic N was formed via reaction with ^{15}N-enriched DIN compounds. If so, this particulate matter is a product on in-river N cycling, not a source. Please clarify.

8639 3 again: you cannot “enrich” a δ^{15}N value, but this value can increase;

8639 6 add: isotope ratios of river water

8639 20 “industrial usage” of what?

8639 22 Can you quantify what you mean with “much”? More than 50%? Also, you may want to make a comment on which time frames this happens (months, years, decades)?

8640 23-25 Can you add a reference here that describes these observations in more detail?

8640 26 should this read: . . . due to the decreased production of NO_3^- ?

8641 6 specify more clearly what you mean with “total global removal”. Removal of what? Total anthropogenic N inputs to watersheds? Also, “and reservoirs” seems not properly connected in this sentence.

8641 16 Removal of what? Nitrate?

8641 20 could use “avoided” or “not occurring” instead of “bypassed”

8642 4 Not only on the residual N pool but also on the newly produced N compounds.

8642 8 . . . results in minimal N isotope fractionation (note: you can not fractionation only one isotope in isolation)

8642 9 replace “enriched” with “elevated” (also throughout rest of the text); see bullet point above.

8642 27 I am not clear what “total yield” refers to? Total DIN export? Total N export?

Please clarify.

8645 8-9 For which station are these flow rates valid?

8645 24 I am confused by the statement “upper 10% of daily flows”? Is it the 10% of highest flows you refer to here (not on a daily basis)? Please add some explanation on what exactly you refer to here.

8646 6-8 At how many sites did you sample these sub-catchments?

8647 18 Check whether the reported enrichment is really given as δ^{13}C or whether the enrichment refers to ^{13}C (without delta)

8648 8 State clearly that this refers to concentration measurements (as opposed to N isotope ratio measurements on these compounds).

8648 23 What was the equilibration time prior to headspace analysis?

8649 15-18 Report in the text what the pH values were rather than leaving it to the reader to find this information in Fig. 2c. Also the text refers to Fig. 2b, which shows dissolved oxygen rather than pH.

8649 22 Dissolved oxygen is shown in Figure 2b. Also, data on electrical conductivity are shown (Fig. 2d) but not mentioned in the text. Are they not important?

8650 23 Dissolved N_2O is reported, but dissolved CH_4 data are not despite being shown in Figure 4b.

8650 25 Enriched in what? ^{14}N or ^{15}N?

8651 1-3 What was the range in observed δ^{18}O values of water?

8651 8-9 I suspect it was the river water during the rainy season that has these ratios and not the rains as indicated in your sentence.

8651 23 Have you reported how CH_4 saturation levels were calculated?

8652 18 So far you discussed only concentration data, but here you make inferences about DIN export. This seems not justified unless you multiply concentration data by flow rates and show the data.

8652 20-23 While this may be true for transport of suspended matter, you have not provided any quantifiable data which justify to extend this argument to DIN.

8653 16-17 Have you reported how N_2O saturations were calculated?

8656 3-4 I thought N_2O is a product of denitrification but you write "removal of N_2O by denitrification"? Please add clarity.

8656 22 "DIN derived from N_2 fixation"? Isn't it organic N that is formed by N_2 fixation which may subsequently be converted to DIN?

8656 24 "values towards $+22$" indicates what the higher limit of a range of values is; however in your case you should also state what the lower limit of δ^{15}N values from sewage and waste water is. These lower δ^{15}N values are often associated with release of raw sewage, which is relevant here. Also: ^{15}N-depleted compared to what?

8656 25 . . . remaining NH_4^+ "becomes progressively enriched in ^{15}N", and may be subsequently oxidized . . . . Question: Is there further N isotope fractionation during this oxidation $=$ nitrification?

8656 26 Didn't you just say ammonia volatilization is the key process for N isotope fractionation? So why is it not listed here?

8657 7 water column δ^{15}N values

8657 26 Before you claimed that benthic denitrification causes little nitrogen isotope fractionation on the remaining nitrate in the water column, but here you use the same process as cause for increasing δ^{15}N values. Please explain. Also is there N isotope fractionation associated with primary production?

8659 5 replace "under" with "in"

8659 8 depleted in what? ^{15}N or ^{14}N?

8659 15 How large is the seasonal variation δ^{18}O of rainfall?

8659 17 What is the δ^{18}O value of old groundwater?

8659 23 relative "to" δ^{15}N . . .

8660 20-21 Why are there 4 numbers for 2 parameters?

Figure 1 Is missing a North arrow.

Figure 2 pH has no unit; I suggest to remove (NBS)

Figure 10 Units [] are missing on y-axes labels

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