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Comment

***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.***

**T. R. Marwick et al.**

trentrichard.marwick@ees.kuleuven.be

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General comments

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

- The section has been updated to include the range of  $\delta^{15}\text{N-NH}_4^+$  values expected

Full Screen / Esc

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Interactive Discussion

Discussion Paper



for ammonium sourced from sewage (from Sebilo et al., 2006).

(ii) 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.

- Data for mean monthly temperature was gathered from the World Meteorological Organization, available at <http://www.worldweather.org/071/m071.htm> - Data for potential evapotranspiration (PET) was gathered from: IAEA (2001), GNIP Maps and Animations, International Atomic Energy Agency, Vienna. Accessible at <http://isohis.iaea.org> Mean monthly PET was calculated at the basin scale in ArcGIS 10.1, as the mean cell value of all cells within the catchment boundary. - Both parameters (along with discharge and precipitation) have been included as a new figure following Fig. 1.

(iii) 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.

- Due to a lack of discharge data for the Athi catchment spanning the period we have sampled, we are unable to offer any quantitative data on water residence time, and take the obvious assumption that water residence time is decreased during the wet seasons due to significantly elevated discharge. The manuscript will be adjusted to more clearly reflect this assumption. A hydrograph for the Sabaki is presented in Figure 1, and although it is based on historical discharge data (1959-1977) we believe it is representative of the conditions observed on-site.

(iv) 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 be 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.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



- See response (iii): we do not have access to recent discharge data, hence we cannot convert our measured concentrations into actual fluxes. However, since this section is based on a comparison of concentrations between subsequent sampling stations, we assume a similar discharge for the stations which are directly compared, given the relatively short distance between them and since there are no major tributaries between comparative sites during the dry season.

(v) 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.

- We have re-written this section to more accurately reflect the different mechanisms involved in the different processes, and refer to Sebilo et al. (2006). - Adjusted to read: 'Particulate N in the Athi River at S1 has a  $\delta^{15}\text{N}_{\text{PN}}$  value of +3.1‰. The ammonification of the PN to  $\text{NH}_4^+$  between S1 and S3, with a bias towards the lighter  $^{14}\text{N}$  isotope being incorporated into the product, leads to the observed enrichment of the residual PN pool at S3 (+19.3‰. Although we did not measure  $\delta^{15}\text{N}$  of either the  $\text{NH}_4^+$  or  $\text{NO}_3^-$  pools, we may expect the process of volatilisation to lead to enrichment of the residual  $\text{NH}_4^+$  pool, where for example, Sebilo et al. (2006) measured a mean  $\delta^{15}\text{N}-\text{NH}_4^+$  value of  $9.5 \pm 1.7\text{‰}$  in raw and treated wastewater of the Seine River, attributed to the volatilization of  $^{15}\text{N}$ -depleted  $\text{NH}_4^+$ . Isotopic enrichment factors for nitrification, -20‰ in the Seine River for example (Sebilo et al, 2006), suggest the  $\delta^{15}\text{N}-\text{NH}_4^+$  pool will become increasingly enriched in  $^{15}\text{N}$  through the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . As such, following ammonification of PN, volatilization, and nitrification of  $\text{NH}_4^+$ , we can expect the residual DIN pools to be heavily enriched in  $^{15}\text{N}$ , and although we have no

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direct measurements, Kreitler (1979) suggest the conversion of animal waste (with a  $\delta^{15}\text{N}$  value of about +5‰ to  $\text{NO}_3^-$  results in  $\delta^{15}\text{N}$  values generally between +10‰ to +20‰<sup>3</sup>

(vi) One of the key shortcomings of the paper is that the authors did not measure the  $^{15}\text{N}$  values of the predominant pollution source (sewage) nor the  $^{15}\text{N}$  values of riverine ammonium or nitrate. Instead they report the  $^{15}\text{N}$  values of particulate organic matter, but do not always explain how the  $^{15}\text{N}$  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.

- This is a very good point, and we acknowledge that these data would have ideally complemented our dataset. However, the data presented in the manuscript is a component of a broader study, in which the idea was to focus on organic carbon cycling within different African river basins. When setting up the sampling in the AGS catchment, we did not design our sampling to focus on N cycling in depth, hence we did not envisage the necessity of  $\delta^{15}\text{N}$  measurements of riverine DIN species or predominant pollution sources.

(vii) On page 8659 the authors explain the variation in  $^{18}\text{O}$  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  $^{18}\text{O}$  for seasonally varying rainfall. Also, is there an altitude effect in  $^{18}\text{O}$  of precipitation given the significant elevation change in the catchment? What is the  $^{18}\text{O}$  of groundwater? More background information would be desirable.

- Seasonal and elevational effects on, as well as estimated values of,  $\delta^{18}\text{O}$  of precipitation have now been included in the discussion section, please see comment (li). - We do not have measurements of groundwater  $\delta^{18}\text{O}$  values, but we have assumed groundwater to be more enriched in  $^{18}\text{O}$  than reported precipitation  $\delta^{18}\text{O}$  values, as a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



result of evaporative processes between rainout and groundwater recharge.

(viii) On page 8661, the authors suggest correctly that  $15\text{N}$  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  $15\text{N}$  values of the major N pollution source in the current study when the opportunity existed to do so in their study.

- See response (vi)

(ix) 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”  $15\text{N}$  values. If “enriched” is used, it must be added whether enriched in  $15\text{N}$  or  $14\text{N}$ ? 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”  $15\text{N}$  values is much clearer and hence recommended.

- Indeed - adjustments have been made accordingly.

Specific comments

Page Line Comment

(x) 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.

- Adjusted to read: “Riverine total dissolved inorganic nitrogen (DIN) at the most upstream site on the Athi River...”

(xi) 8638 20 if you use the term “enriched” you should add enriched in what,  $15\text{N}$  or  $14\text{N}$ ? Note that a  $15\text{N}$  value can not be enriched.

- Adjusted to read: “significantly enriched in  $15\text{N}$ ,...”

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10, C5438–C5451, 2013

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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

- Adjusted to read: “...(1) intense cycling and removal of DIN in the upper- to mid-catchment leads to significantly lower DIN concentrations at the river mouth (relative to upper-catchment conditions) during the dry season, and (2) as a result of the cycling and removal of DIN from the river system, dry season particulate N (PN) becomes significantly enriched in the heavy N stable isotope ( $^{15}\text{N}$ ), strongly reflecting the dominance of untreated waste water as the prevailing source of riverine DIN.”

(xiii) 8639 3 again: you cannot “enrich” a  $^{15}\text{N}$  value, but this value can increase;

- Adjusted to read: “leads to significant enrichment of  $^{15}\text{N}$  in the particulate nitrogen. . .”

(xiv) 8639 6 add: isotope ratios of river water

- Adjusted to read: “A strong correlation between the seasonal N stable isotope ratios of PN ( $\delta^{15}\text{N}_{\text{PN}}$ ) and oxygen stable isotope ratios of river water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ; as a proxy of freshwater discharge) presents. . .”

(xv) 8639 20 “industrial usage” of what?

- Adjusted to read: “...the development of the Haber-Bosch process (and increasing synthetic fertiliser application)...

(xvi) 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)?

- Adjusted to read: “Within agro-ecosystems, for example, of the approximately  $170 \text{ Tg N yr}^{-1}$  introduced to crops globally, over 70% of this N may be lost to the atmosphere and waters annually (Galloway et al., 2003). Upon entering riverine systems,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

either through point source (predominantly urban and industrial effluents) or diffusive source (such as leaching from agricultural land and atmospheric deposition) pathways (Bouwman et al., 2005), insufficient storage or removal of N may lead to..."

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

- This statement stems from the fact that nitrification is a process requiring O<sub>2</sub>. In restructuring the discussion, however, this sentence was omitted in the revised version.

(xviii) 8640 26 should this read: . . . due to the decreased production of NO<sub>3</sub>?

- See response (xvii).

(xix) 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.

- Adjusted to read: "Recent modelling of lentic systems has conservatively estimated their ability to remove 19.7 Tg N yr<sup>-1</sup> from watersheds globally (Harrison et al., 2009), with small lakes (<50 km<sup>2</sup>) accounting for almost half this estimate (9.3 Tg N yr<sup>-1</sup>), while reservoirs, accounting for only 6% of the global lentic surface area, are estimated to retain approximately 33% of the total N removed by lentic systems."

(xx) 8641 16 Removal of what? Nitrate?

- Adjusted to read: "Removal of NO<sub>3</sub><sup>-</sup> by fluvial systems may occur through denitrification..."

(xxi) 8641 20 could use "avoided" or "not occurring" instead of "bypassed"

- Adjusted to read: "The production of N<sub>2</sub>O is avoided..."

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

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- Adjusted to read: "...resulting in isotopic fractionation of the residual N pool, and the newly produced N compounds..."

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

- Adjusted to read: "...results in minimal N isotope fractionation..."

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

- Adjusted

(xxv) 8642 27 I am not clear what "total yield" refers to? Total DIN export? Total N export? Please clarify.

- Adjusted to read: "...with two thirds of DIN yield entering..."

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

- Adjusted to read: "...with seasonal variation measured between 0.5 m<sup>3</sup> s<sup>-1</sup> and 758 m<sup>3</sup> s<sup>-1</sup> (1957-1979 mean: 48.8 m<sup>3</sup> s<sup>-1</sup>) (Fleitmann et al., 2007) in the Sabaki River." - Note: These flow rates are valid for site S20 only.

(xxvii) 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.

- i.e. 80% of annual sediment yield may occur over as little as 36.5 days of discharge in a 365 day year. - Adjusted to read: "...as much as 80% of the annual mean sediment yield can be carried by the upper 10% of daily flows (ie. by discharge occurring over 36.5 days of a 365 day year)."

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

- Adjusted to read: "...the Tsavo (5 sites sampled each season), whereas during both

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the OND and MAM rains it was possible to sample within the Keite (4 and 3 sites sampled during the OND and MAM rain seasons, respectively) and Muoni (1 site sampled during both rain seasons) watersheds also.”

(xxix) 8647 18 Check whether the reported enrichment is really given as 13C or whether the enrichment refers to 13C (without delta).

- Delta removed.

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

- Adjusted to read: “Laboratory analysis of riverine NH<sub>4</sub><sup>+</sup> (based on the modified Berthelot reaction) and NO<sub>3</sub><sup>-</sup> (based on the hydrazanium sulfate reduction method) concentration was...”

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

- Adjusted to read: “Concentrations of CH<sub>4</sub> and N<sub>2</sub>O were determined by a head-space equilibration technique (20 ml N<sub>2</sub> headspace in 60 ml serum bottles). Samples were shaken vigorously after creating the headspace, equilibrated overnight (min. 12hrs) in a thermostated bath (constant temperature within 0.5°C of the average of all in-situ riverine water column temperature data), and again vigorously shaken prior to injection.”

(xxxiii) 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.

- pH range and mean ± SD values added for each season in the Results section. - pH discussion in results moved below dissolved oxygen in order to agree with Fig. 2 caption.

(xxxiiii) 8649 22 Dissolved oxygen is shown in Figure 2b. Also, data on electrical con-

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ductivity are shown (Fig. 2d) but not mentioned in the text. Are they not important?

- Dissolved oxygen and pH order arranged as above (xxxii) - The conductivity panel has been removed from Fig.2. The data remain included in the Supplementary Materials.

(xxxiv) 8650 23 Dissolved N<sub>2</sub>O is reported, but dissolved CH<sub>4</sub> data are not despite being shown in Figure 4b.

- The Results section has been updated to include dissolved CH<sub>4</sub> data.

(xxxv) 8650 25 Enriched in what? 14N or 15N?

- Adjusted to read: "...with elevated  $\delta^{15}\text{NPN}$  signatures at most sites during the dry season."

(xxxvi) 8651 1-3 What was the range in observed 18O values of water?

- The range of d18O-H<sub>2</sub>O values has been added to Results section.

(xxxvii) 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.

- Adjusted to read: "Riverine POC:PN ratios were significantly higher during..."

(xxxviii) 8651 23 Have you reported how CH<sub>4</sub> saturation levels were calculated?

- The relevant procedure has been added to the Methods section.

(xxxix) 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.

- See other replies above: while we do not have actual daily discharge data, the sampling periods corresponded to clearly different hydrological conditions, consistent with the average annual hydrograph based on historical discharge data (as presented in Figure 1). Hence, while we cannot calculate actual nutrient/material fluxes, we can be confident on the patterns observed and their link with discharge. However, we agree

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10, C5438–C5451, 2013

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Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



with the general comment and have re-written our statements to explicitly mention the absence of discharge data.

(xl) 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.

- See reply to comment above.

(xli) 8653 16-17 Have you reported how N<sub>2</sub>O saturations were calculated?

- This information was indeed missing but has been added to the Methods section in the revised version.

(xlii) 8656 3-4 I thought N<sub>2</sub>O is a product of denitrification but you write “removal of N<sub>2</sub>O by denitrification”? Please add clarity.

- Denitrification can indeed be a source of N<sub>2</sub>O, but can also be responsible for the removal of N<sub>2</sub>O produced e.g. by nitrification – depending on the oxic/anoxic conditions prevailing. Appropriate references are available in the relevant section. - Adjusted to read: “...N<sub>2</sub>O is removed through the denitrification pathway...”.

(xliii) 8656 22 “DIN derived from N<sub>2</sub> fixation”? Isn't it organic N that is formed by N<sub>2</sub> fixation which may subsequently be converted to DIN?

- Indeed, this is a clearer way of stating what we were attempting. This section has been adjusted accordingly, please see comment (v).

(xliv) 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 15N values from sewage and waste water is. These lower 15N values are often associated with release of raw sewage, which is relevant here. Also: 15N-depleted compared to what?

- This section has been adjusted accordingly, please see comment (v).

(xlv) 8656 25 . . . remaining NH<sub>4</sub><sup>+</sup> “becomes progressively enriched in 15N”, and may

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



be subsequently oxidized . . . . Question: Is there further N isotope fractionation during this oxidation = nitrification?

- Correct, further N isotope fractionation does occur through the nitrification process, and we have included the isotope enrichment factor (from Sebilo et al., 2006) for nitrification in the discussion.

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

- We should have noted volatilization also, thank you. This section has been adjusted accordingly, please see comment (v).

(xlvii) 8657 7 water column d15N values

- Adjusted.

(xlviii) 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 15N values. Please explain. Also is there N isotope fractionation associated with primary production?

- The benthic denitrification comment related to the lowering of riverine DIN concentrations between S3 and S6, poor wording resulted in implying it also influenced  $\delta^{15}\text{N}$ -PN values, contrary to previous statements. See below for adjustment. - Adjusted to read: "By S13 a combination of intense denitrification (between S3 and S6) and high pelagic primary production (between S6 and S13) lower DIN to levels equivalent to observations in other African river catchments (see Fig. 8), whilst the latter process simultaneously leads to elevated  $\delta^{15}\text{N}$  values not previously recorded in African river catchments (Fig. 9)."

(xlix) 8659 5 replace "under" with "in"

- Adjusted.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



(I) 8659 8 depleted in what? 15N or 14N?

- Adjusted.

(li) 8659 15 How large is the seasonal variation 18O of rainfall?

- We gathered  $\delta^{18}\text{O}$  of precipitation data for the headwaters of the A-G-S system (Muguga, station #6374101) from the IAEA website: (<http://www-naweb.iaea.org/naweb/ih/documents/userupdate/Waterloo/index.html#Africa>). - The mean seasonal  $\delta^{18}\text{O}$  of precipitation was calculated from the mean monthly values (dry season = Jun-Jul-Aug-Sep). Precipitation indeed becomes considerably enriched in 18O during the drier months ( $-2.1 \pm 0.9\%$  compared to the wet seasons (MAM =  $-5.1 \pm 1.4\%$ .  $OND = -5.1 \pm 1.2\%$ , agreeing with our suggestions regarding seasonal river water sources.

(lii) 8659 17 What is the 18O value of old groundwater?

- To the best of our knowledge, no data from this catchment exist on groundwater  $\delta^{18}\text{O}$ ; see comment (vii).

(liii) 8659 23 relative “to” 15N . . .

- Adjusted.

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

- Adjusted.

(lv) Figure 1 Is missing a North arrow.

- Adjusted.

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

- Adjusted.

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

Full Screen / Esc

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Discussion Paper



- Adjusted.

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10, C5438–C5451, 2013

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Interactive Discussion

Discussion Paper

C5451

