

Interactive comment on “Decadal trajectories of nitrate input and output in three nested catchments along a land use gradient” by Sophie Ehrhardt et al.

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General response: We thank the referee for the valuable inputs and remarks. We address all comments below and hope to clarify the questions raised.

1. How is error propagated? The authors often report four significant figures, but do not report standard deviation, confidence intervals, or some other estimate of uncertainty. Given the compound assumptions of the input chronicle models and the hydrological components, a sensitivity analysis or some kind of quantification of uncertainty seems warranted.

C1

R1: Right, an uncertainty analysis was missing so far and will for sure improve the analysis. We suggest to give the mean standard error of the WRTDS regression analysis (for the modelled concentration) to provide this information. For the input of nitrogen, we refer to the methodological error provided by Bach & Frede (1998). We, moreover, will perform an uncertainty analysis for estimating effective travel times of N using a Monte-Carlo approach assuming normal distributed errors.

2. The idea of comparing biogeochemical and hydrological legacies is very compelling but it remains unclear to me how these parameters were estimated and compared. Structuring the methods around the research questions or overarching hypotheses and carrying this through the manuscript would make this flow clearer would make the results/discussion more impactful.

R2: That is a very helpful comment. We will revisit the research questions and make them more clear especially on where we see the potential of using the C-Q relationships to better disentangle the biogeochemical and hydrological legacies. Moreover, we will write an overview section for the method part to better integrate research questions with the method steps. Finally we will make the discussion on this topic more explicit in the discussion part as well. Based on the results of our analyses, we will improve upon the discussion part raising new hypothesis on dominant legacy types. Since our study is based on a data-driven analysis, we can't test such new hypothesis – but certainly we feel it is worth raising them from the data evidence so that a future imitative could start looking into those new aspects.

3. I think the discussion would be more engaging if the authors focused on the applicability of this approach to catchments generally, rather than explaining specific observations from their study. They do this effectively several times (e.g. starting on page 22 starting around line 20), but there is also quite a bit of retreatment of the results, which are specific to these sites.

R3: We will carefully review and revise the sections that are specific to our catchments

C2

-potentially shorten them without losing the main message. Here we will more explicitly indicate where we discuss and draw conclusions for the studied catchment and where we can generalize our findings. We also see a greater potential of applying this local analysis to a wide range of catchments where we can more easily draw general conclusions (stated Page 28 Line 30-34).

4. The authors present an interesting puzzle of massive nitrogen retention/removal that cannot be attributed to typical pathways (e.g. denitrification, uptake, mineral association). The authors then conclude that N storage (the biogeochemical and hydrological legacies) account for the disconnect. However, the dismissal of denitrification seems to be based on a few studies from this area, which are not described in detail (e.g. Page 23, line 15). If these other studies are definitive and reliable, more description of their methods should be given. Another explanation is associated with point 1 - could the N removal be much lower when uncertainty in inputs and outputs are included?

R4: Yes – as given in R1 we will address the issue on uncertainty of the regression approach and the N input from agricultural areas. We would like to note here a recent paper published in November 2018 giving an overview on denitrification potential in the federal state this catchment is part of (Hannappel et al. 2018). It connects hydrochemical analysis of groundwater nitrate, oxygen and redox potential to the hydrogeological units in this region and states a general weak potential for denitrification for the study site. While revising our manuscript, we will include this study with methodological details to strengthen our argumentation on the denitrification part. It is however worth mentioning here that local groundwater information (which is also the base of this new paper by Hannappel et al. 2018) is hard to scale to the effective behavior at catchment scale. We have touched on this issue on Page 22, Lines 23-29. We already included the study by Müller et al. (2018) around the same study area that provided strong evidence on the lack of denitrification in their assessment based on isotopic signatures in the integrated nitrate signal in the surface water. We will put more emphasis on discussing this study as well to better argue our case in the revised manuscript.

C3

5. Line edits Page 2 Line 5: (Elser et al. 2007)

R5: We will add this reference here.

6. Line 6: It seems odd to say these changes were strictly terrestrial. It seems they influenced both.

R6: We would drop the word “terrestrial” at the specified location.

7. Line 10: Do the authors mean the natural rate of reactive N fixation has been doubled (e.g. (Vitousek et al. 1997))?

R7: Yes, Vitousek et al. (1997) and Smil (1999) refer to the same: Human activities are mainly responsible for doubling the amount of reactive/ biological active N that enters the element's cycle from the unreactive atmospheric pool of N₂. We will add these references and adjust the sentence, accordingly.

8. Page 3 Line 2: management interventions (instead of “measures”)?

R8: Thanks – we will change that.

9. Line 2: Recent study from similar agricultural and climatic context that found decadal hydrologic (Kolbe et al. 2016; Marçais et al. 2018)

R9: We will consider these new studies.

10. Line 16: I actually think there are quite a few studies, especially recently (Dupas et al. n.d.; Howden et al. 2010; Burt et al. 2011; Minaudo et al. 2015; Meter & Basu 2017; Abbott et al. 2018; Coble et al. 2018; Garnier et al. 2018; Marcé et al. 2018; Pinay et al. 2018; Fanelli et al. 2019)

R10: Thanks for the input. We will check and consider these new studies.

11. Line 20: How do these analyses compare with soil-surface N balance approaches that include a crop and livestock removal component (Poisvert et al. 2017; Abbott et al. 2018)?

C4

R11: Both, Jawitz and Mitchell (2011) as well as Musolff et al. (2015) are not based on N balances but on an interpretation of the temporal dynamic (or lack of temporal dynamic) in the observed nitrate concentrations. We will add that to this sentence. Our paper aims at a combination of both approaches – N balancing (since the N-input takes crops and livestock into account) and C-Q assessment.

12. Line 30: Recent paper on concentration-discharge responses to catchment saturation (Moatar et al. 2017)

R12: Thanks, we will refer to the suggested reference.

13. Page 5 Line 18: In what dimensions is this catchment especially vulnerable to climate change?

R13: A recent study by Wollschläger et al (2017) states a high vulnerability due to low water availability and a pronounced risk of summer droughts that is likely to be exacerbated by decreasing summer precipitation and increasing temperature/ potential evapotranspiration. Two new references can be included here as well (Marx et al. 2018, Samaniego et al. 2018). We will add this information in the revised manuscript.

14. Page 8 Line 13-20: Interesting that the primary datasets do not include non-agricultural land for N deposition. Why did the authors not use one of the products that provided a consistent N deposition rate across land-use types? Perhaps this is a small portion of the overall N budget, but it would be worthwhile to specify.

R14: We combine two products for N input to agricultural and non-agricultural land as there is no consistent product available in Germany, covering both with the required spatial and temporal precision. We will add this information to the text.

15. Page 9 Figure 2: The dissimilarity in the NO₃ concentration time series is striking as are the drops to zero mg/L even at the lowest site. Consider combining Figures 2 and 3 to allow visual comparison of discharge and concentration.

R15: The “drops to zero” are actually the no-data-values that are erroneously displayed

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as zero (but not considered in the WRTDS regressions). We will adjust the figure and also consider a combination with the discharge in Fig. 3.

16. Page 10 Line 9: the discharge time series were used. . . R16: Thanks – we will change this in the revised manuscript.

17. Page 11 Line 8: allows increasing . . . R17: Thanks – we will change this in the revised manuscript.

18. Page 12 Line 10: Because our purpose was to balance and compare . . . R18: Thanks – we will change this in the revised manuscript.

19. Line 12: This justification seems unclear. Is it simply claiming that the longer-term trends are accurate, though the daily values are not?

R19: No, the daily values are accurate but just that they not available at a daily time scale. We thus refer to the robust aggregated annual wastewater flux that much better fits to the flow normalized fluxes provided by the WRTDS regression analysis (see statement P12L10-14). Daily values are used to estimate an average fraction of NO₃-N in the wastewater N flux.

20. Page 14 Table 2: These differences in specific discharge are remarkable. Is this typical for this area or is the three-fold difference due to a known environmental or anthropogenic variable?

R20: Yes this is remarkable but typical, and one of the reasons behind the establishment of the TERENO observatory system (Wollschläger et al. 2017). Wollschläger et al. (2017) state the strong precipitation gradient from 1700 mm/a down to less than 500 mm/a within a range of 50 km due to the rain shadow of the Harz mountains. We will make a note on this in the revised manuscript.

21. Page 15 Line 11: Revise sentence for grammar and clarity (with implications for instead of with discussion on?)

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R21: Thanks - we will revise the sentence.

22. Page 16 Line 14: It is striking that the retention capacity increases 5-fold with landscape position. Is this because of shifts in soil and subsurface properties or because the retention or removal rates are dependent on substrate concentration?

R22: Yes, this is quite a strong difference that is stated here as an observed result. Discussion on the reasoning can be found later on in Section 4.1.

23. Page 22 Line 20: Nitrification also results in gaseous N loss via the “leaky pipe” pathway (Hart et al. 1994).

R23: Right – there can be losses of N₂O leaving the system at the nitrification step. However, in comparison to denitrification it does not appear to be a dominant loss term in N-budgets compared to denitrification (Rivett et al. 2008, Galloway et al. 2004). See also comment R4 – the paper by Müller et al. (2018) on the isotope evidence for the lack of N removal in our catchment.

24. Line 29: Is this referring to denitrification in the near-surface zone or throughout the whole catchment? With pyrite, sulfur, and other iron ubiquitous in the weathered and fractured zones, aquifer denitrification is likely occurring

R24: We refer to denitrification in general, taking both autotrophic and heterotrophic denitrification into account. Both need the absence of oxygen independent of whether electron donors are available or not. Also both affect the finally measured isotope signature in the remaining nitrate in the stream. See also our comment R4 with the new study (Hannappel et al. 2018) stating the lack of denitrification evidence that we will include in the manuscript.

25. Page 23 Line 18: New methods for constraining aquifer travel time to constrain removal rates using numerical or empirical methods (Kolbe et al. 2016; Marçais et al. 2018).

R25: Right. Enhanced knowledge on water travel time will improve the estimation of

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reaction rates. We will consider the suggested studies.

26. Page 25 Line 1: Similar to these observations, though they are on a much smaller scale (Thomas & Abbott 2018)

R26: Thanks – we will consider this in the revised manuscript.

27. Page 28 Line 9: were explained R27: Thanks – we will make change as suggested.

28. Line 14: catchment reaction seems like an odd description for transit time.

R28: That is right. We will change that phrase as suggested.

References (that are not in the main manuscript): *â* Hannappel, S., Kopp, C. and Bach, T. (2018) Characterization of the denitrification potential of aquifers in Saxony-Anhalt. *Grundwasser* 23(4), 311-321. *â* Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R. and Vorosmarty, C.J. (2004) Nitrogen cycles: past, present, and future. *Biogeochemistry* 70(2), 153-226. *â* Marx, A., Kumar, R., Thober, S., Rakovec, O., Wanders, N., Zink, M., Wood, E.F., Pan, M., Sheffield, J. and Samaniego, L. (2018) Climate change alters low flows in Europe under global warming of 1.5, 2, and 3 degrees C. *Hydrology and Earth System Sciences* 22(2), 1017-1032. *â* Samaniego, L., Thober, S., Kumar, R., Wanders, N., Rakovec, O., Pan, M., Zink, M., Sheffield, J., Wood, E.F. and Marx, A. (2018) Anthropogenic warming exacerbates European soil moisture droughts. *Nature Climate Change* 8(5), 421. *â* Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H. and Tilman, D. (1997) Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7(3), 737-750.

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