

Response to Review

Reviewer #2:

Referee report on: Droughts can reduce the nitrogen retention capacity of catchments

By Carolin Winter, Tam V. Nguyen, Andreas Musolff, Stefanie R. Lutz, Michael Rode, Rohini Kumar, Jan H. Fleckenstein

I agree with the first referee that this is a nicely written manuscript with clear hypotheses and a good concept to analyse altered N dynamics under drought conditions within a mesoscale catchment. In particular, I like the strategy to combine a data-driven and model-based analysis. Although I am no native speaker, I think that language issues are largely settled, which is why a reviewer can concentrate on the most important issues: science and novelty behind the presented analysis. So I congratulate all authors for this work.

We would like to thank the reviewer for his/her very positive and encouraging feedback. This is very nice to hear. We would further like to thank the reviewer for the constructive remarks and suggestions, which we address point by point below.

This said, I still have some major points that I think should be addressed prior to publication in egushere.

1. Information about N-Inputs

You state that exported N loads have generally decreased (e.g. L 268). What about the input? I propose to present the entire N-balance for the different subcatchments instead of only four components in Table 2. Moreover, a diagram would be more intuitive than a table.

Thank you for this suggestion. We agree that it would be beneficial to the reader to have the entire N balance, including N input, presented as a figure. Therefore we will include N input and present all N fluxes in form of a stacked bar-plot. We will display N fluxes leaving the system (denitrification, plant uptake and leachates) as negative values and N fluxes entering the system, (N input, amt. deposition and mineralization) as positive values. Furthermore, we will add error bars to visualize the inter-annual variability in the long-term reference period (1997-2017). Regarding trends in N input: In the Selke catchment, N inputs have stabilized since around 1995 (Winter et al., 2021). Therefore long-term N input to mHM-SAS does not show any trend.

2. Stability of catchment properties

This is a general drawback: If you compare N-retention–discharge relations during the recent drought to longterm values, you assume that catchment properties stayed the same. Can you really do this? There might be landuse changes (forest diebacks after storm events, or due to preceding droughts, e.g. 2003) and there is for sure a rising trend in temperatures. This trend per se alters the N-cycle, prolongs vegetation periods and presumably intensifies processes. I would like to see this point in the discussion section.

We thank the reviewer for this important remark. We agree that catchment properties are not necessarily stable in time, especially not in the face of climate change. In the following we will discuss in more detail which characteristics might have changed, which characteristics are relatively stable and the potential implications for N retention:

Land cover change: We used the CORINE land cover map of the Copernicus Programme (<https://land.copernicus.eu/pan-european/corine-land-cover>) to check for land use changes from 1990 over 2000 until 2018. Overall, land use changes were minor. We detected a slight increase in urban areas (<1% of the catchment area), a slight decrease in agricultural areas (around 1.6%) and a slight increase in grasslands. An open mining pit in the downstream part of the catchment was closed down around 1996/1997 and was transformed into a lake (see Winter et al., 2021). On this basis, we expect no major trends in catchment functioning in terms of N cycling from land use changes, at least within our observation period.

Forest damage: The mortality rate of trees in the forests of Saxony Anhalt (the state where the Selke catchment is located) remained relatively stable below 1% in the years from 1991 until 2017 (State-of-the-forest Report Saxony Anhalt, 2020). Therefore we do assume forest dieback to be relatively stable across our long-term control period. Only with the beginning of the severe drought, mortality rates increased above 1% and even towards >4% in 2019, which we have discussed in our manuscript.

Temperature Increase: With global warming, also temperatures in the Selke catchment increased significantly on the long term. Increasing temperatures have been found to cause an increase in microbial N cycling, including increased rates of mineralization, nitrification and denitrification (Dai et al., 2020). During the severe summer drought, soils were too dry for denitrification and plant uptake, so that the temperature increase did not play an important role anymore. However, just as mentioned by the reviewer, given sufficient soil moisture, increasing temperatures can potentially intensify biogeochemical processes within a catchment. We will add this to our discussion section.

Extension of vegetation period: With climate change, also the length of the vegetation period increases. Menzel et al. (2001) reported an increase of up to 0.2 d yr^{-1} across Germany, but with high inter-annual variability. However, over the 23 years of data used for our study, this corresponds to <5 days, which does likely not have a stronger impact than the overall hydro-meteorological variability. Furthermore, over the period from 1997-2018, no clear trend in the overall length of the vegetation period could be observed from the Germany-wide averages (Figure 1 below). We, therefore, conclude that the extension of the vegetation period very likely impacts N cycling but not in a way that it has fundamentally changed catchment functioning in terms of N retention within the observation period of our study.

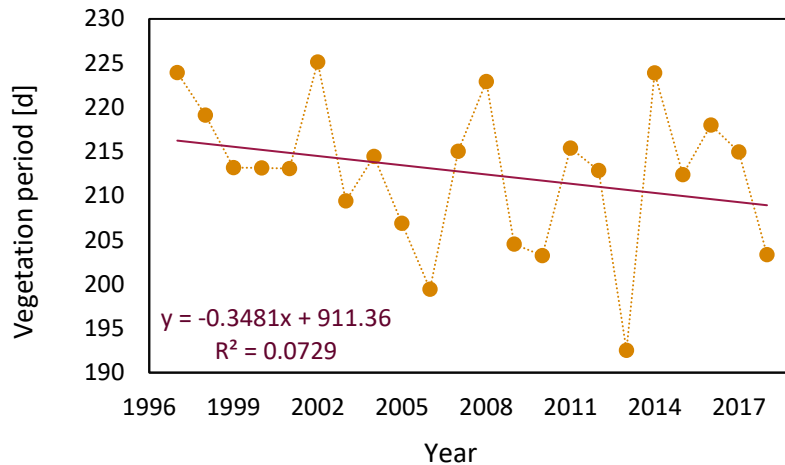


Figure 1. Annual averages of the vegetation period in Germany. Data source: Umweltbundesamt (<https://www.umweltbundesamt.de/daten/klima/veraenderung-der-jahreszeitlichen#weiterfuehrende-informationen>, retrieved 7/25/2022)

Nevertheless, the long-term L-Q relationship as well as the N_{ret} -Q relationship across all years previous to the drought could be very well fitted (R^2 0.91 – 0.96; Figure 2 d-f and Figure 4). This indicates that despite changing temperatures, nitrate load export and retention have been dominantly controlled by discharge. Temperature increase and variability, along with other extreme events, such as floods, are likely to explain a part of the residuals in the L-Q and the N_{ret} -Q relationships, however, none of these years stood out to the same degree as 2018 and 2019 in the upper Selke. Consequently, we argue that the unprecedented 2018-2019 drought also caused unprecedented changes in N export and retention that are not only controlled by low discharge but also by changes in catchment functioning. This can explain the deviation between 2018 and 2019 from the long-term L-Q and N_{ret} -Q relationships.

We will add a paragraph on the long-term stability with a focus on rising temperatures to our discussion around Line 435 (chapter 4.3 Exported nitrate loads and catchment retention capacity).

3. Scenario of forest dieback

This point was already raised by referee #1: Omit the simplistic scenario of forest dieback. You only simulate reduce N uptakes but there are surely more effects on the N cycle here: e.g. mineralisation of dead organic material, altered soil characteristics, etc.

We fully agree and will remove the part of the forest dieback scenarios and only leave a short part on forest dieback (also regarding catchment stability) in the discussion.

4. Increased N-mineralization during droughts

You speculate that mineralization during droughts might increase, based on a single study that found increased rates of depolymerisation during droughts in a montane grassland in Austria. I

would be more careful when transferring these findings to the forested Selke catchment. E.g. depolymerisation in montane grasslands might principally be temperature dependent. In forest soils, I would rather argue that mineralization is hampered by soil moisture deficits during droughts and subsequently reduced microbial activity. Your data only shows increased mineralization during the entire dry-wet cycle which could be due to onset of strong mineralization during re-wetting. Then mineralization could be more intense, because you have an organic N-pool accumulated during the drought.

Thank you for this comment. We understand the point that evidence from a single case study in a different ecosystem is a little weak for the base of our argumentation and will therefore remove the sentence about depolymerization. Overall, our line of argumentation is very much in line with what the reviewer suggests here: “the rewetting of dry soils in autumn can cause a peak in Mineralization that transforms accumulated organic material into mobile inorganic N” (Line 371-372). We will further add the reviewer’s argument that mineralization is likely more intense, due to the accumulated pool of organic N under very dry summer conditions.

5. Groundwater data to illustrate longer term N-effects

You hypothesize that in the upper Selke short TTs lead to visible effects of N-retention rather than in the low Selke, where longer TTs might cause longer term effects. This is a logic outcome of your transit time model. I think this could nicely be proved by groundwater data. Do you have well or spring data that could be used to support your hypothesis here? Recent papers have looked on groundwater nitrate responses after droughts and e.g. found instantaneous or delayed reactions depending on aquifer types.

This is an interesting point. We found one observation well in Wilsleben in the lower Selke catchment, maintained by the LHW, which supports our results:

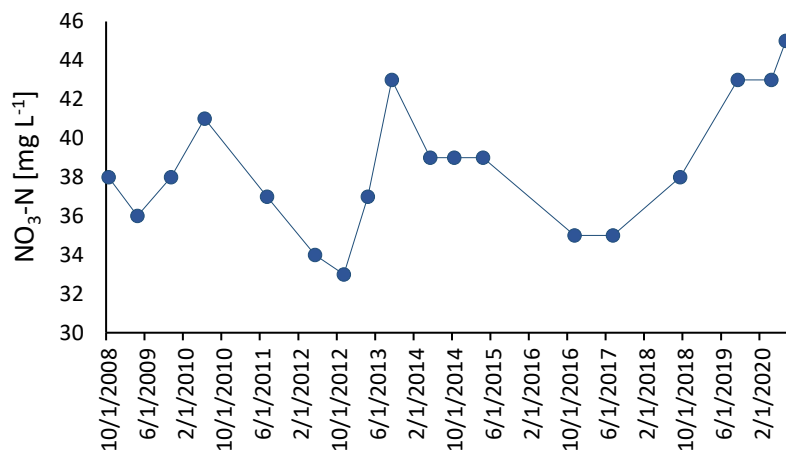


Figure 2. Groundwater observation well in Wilsleben (lower Selke catchment). Data provided by the LHW.

Nitrate-N concentrations in the groundwater from 2019 onwards were among the highest values of the time series (starting in 2008). So, while the decrease in nitrate retention (i.e., higher nitrate

concentrations) in the downstream part of the catchment have not (yet) reached the stream network, there is already some indication for higher nitrate concentrations in the groundwater. We will add this plot to the supplement and add the information to our discussion (around line 390). However, there is a high variability in nitrate concentrations, measured at this well and therefore we see it as an indication that supports our results rather than a real proof of concept, which would require data from more than just one well. Other studies, just as mentioned by the reviewer, found a similar increase in groundwater nitrate concentrations looking at a large number of wells (e.g., Jutglar et al., 2021), which we will therefore mention in our discussion as well.

6. Shape of the Retention-Discharge-Relationship

I disagree with the shape of the function between retention capacity and log-scaled discharge, as presented in Figure 4 and in the conceptual framework in Figure 5. A linear relationship is not meaningful here, maximum retention is 1 (at zero discharge), and your figure implies higher values. The data of HD shows this shape quite nicely. So put in the upper limit and an asymptotical approach of the function to this value when it comes to very low Q.

Thank you for this well thought out advice. To address this comment, we have put a lot of thoughts into the ideal N_{ret} -Q relationship and are now confident that we can present a solution that would certainly improve the quality of our manuscript. To assure that the retention capacity does not exceed 1, we will change to an asymptotical approach, just as suggested, using the following systematic derivation:

According to the general framework of the C-Q relationship, we assume that discharge (Q) is log-normally distributed and related to nitrate loads (L) as:

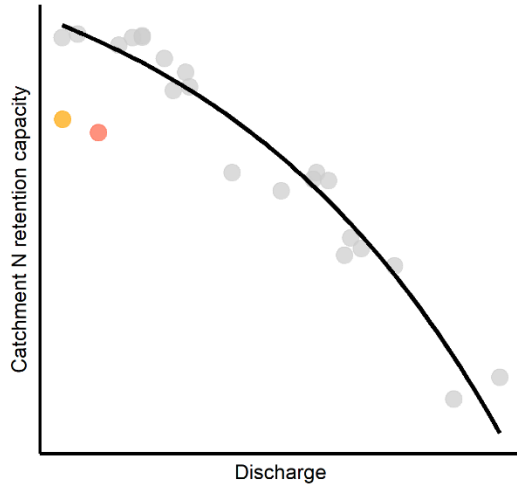
$$L = \alpha Q^{\beta+1}, \quad (1)$$

with $\beta+1$ being the L-Q slope. With $N_{ret} = 1 - N_{out}/N_{in}$ and assuming N input (N_{in}) to be constant, N retention (N_{ret}) can be calculated as:

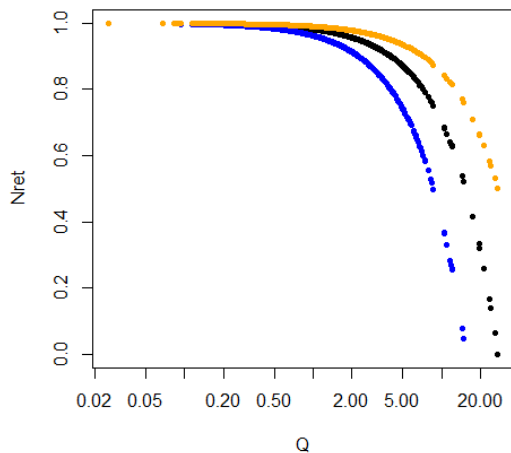
$$N_{ret} = 1 - \frac{\alpha Q^{\beta+1}}{N_{in}} \quad (2)$$

Therefore, $N_{ret} \sim Q^{\beta+1}$ can be described as a non-linear relationship and $N_{ret} \sim Q$ is linear if $\beta=0$ or in other words if the L-Q slope equals 1. The result is an N_{ret} -Q relationship that asymptotically approaches 1 and that is zero if $L = N_{in}$.

We will use the fitted L-Q slopes for the Selke sub-catchments (1.14, 1.21 and 1.01 for SH, MD and HD, respectively) to fit individual N_{ret} - $Q^{L-Q \text{ slope}}$ relationships, as can be seen here in the example of the discussion plot:



Just as foreseen by the reviewer, the new shape matches better N retention at low discharge, especially in the lower Selke. Even more so for the soil leachates, where even under the 2018-2019 drought, values are relatively close to the new long-term N_{ret} - Q relationship. On the other hand, the sensitivity of N retention towards changes in load export strongly decreases towards low Q , as can be derived from eq. 1. Considering the low sensitivity at low discharge, the decreased N retention at the upper Selke is even more remarkable. However, at the lower Selke, any drought-induced reduction in N retention is now largely covered by the low sensitivity, especially given the relatively high N input. The following graph shows a theoretical example of N retention given the same Q and the same N input but one scenario with doubled nitrate loads (blue) and one time with halved nitrate load export (orange):



In this case, drought-induced increases in nitrate leaching from the soils (relative to Q) are more telling if depicted as a simple L - Q plot, which we will therefore add to the supplement. Hence, we decided to make all suggested corrections, but we will additionally move the $N_{soi-ret}$ - Q panels of Figure 4 (a-c) to the supplement. We will base our discussion more on the catchment N retention (in line with the comment of reviewer #1) and on the decreased rates of denitrification and plant uptake.

Coming back to the main comment of reviewer 2: We will change the shape of the N_{ret} -Q relationship throughout our manuscript and will adapt our Method and Results section accordingly.

Minor issues (line by line):

L99: Check throughout the manuscript if you introduce abbreviations, I did not find this for TTs

We will add the abbreviation for TTs in line 99 and check the entire manuscript, if this is missing for any other abbreviation.

L103 (Fig. 1): Colourscale for discharge anomaly could be clearer

We will add a grey color for values around average discharge and change the color for low discharge from orange to red to highlight anomalies and to make their difference clearer.

L128: you speak about multi-year drought, although you only analysed the first two years of this event. I agree that the drought lasted longer, in some areas this event is somehow present up to now. But in your analysis this is a two-year event..

We will change our wording to two-year drought throughout our manuscript.

L204: these numbers refer to the subcatchments? This is not clear..

That is right and we also agree that it was not clear to the reader. We will add that these numbers refer to the sub-catchments SH, MD and HD, respectively.

L292: I understand that more details of the mHM-SAS-model are given in the supporting material. But still I would like to have a couple of sentences also in the main document that explain what a/b ratios and SAS functions are and why they are indicative of water age.

We fully agree. We will add an additional explanation on SAS functions, the a/b ratio and their relation to nitrate transport in the Method section from line 195 onwards. For more details, on what exactly we plan to write, we refer to our response to reviewer #1.

L297: a median of a median, really?

We agree with the reviewer that this sounds quite clunky. It is not, as one might assume, a typo. Instead, our rationale behind this is that we show median TTs for the separate drought years and compare it with the median TTs of previous years (Figure 3). In that sense we found the median of median TTs from previous years the most meaningful number to compare with the median of drought years. The mean would not be appropriate, due to the non-normal distribution of median TTs.

L303: you present a conceptual drawback of the model: it cannot handle TTs that are larger than the simulation period. Nevertheless your model fits are quite nice on the entire time series from

the very begin of grab sampling. Does this mean that your model is right for the wrong reasons and that you overcome structural deficiencies by calibration? I think this should be a point for discussion.

Thank you for this important remark. The maximum TT is restricted by the time frame of the simulation rather than the actual age of the oldest water, which is unknown (Nguyen et al., 2022). In order to have sufficient long age, to create an initial age distribution in storage, and to minimize the effect of initial conditions, we replicated model input data from the 1993-1996 period ten times and run the model with these data for warming up. In other words, the model states obtained from this model run were used as initial conditions for the actual model run from 1997-2020. We will add this point to the Method section around line 204.

L339: I think the post-drought nitrate pulses in soils do not only propagate through catchments and find their way to rivers, but that runoff generation processes are altered, too. This has been documented before, i.e. a change of HOF/SOF to more SSF in a forest catchment after drought (<https://doi.org/10.1016/j.jhydrol.2012.07.010>).

Thank you for this interesting point. We will add a discussion of results from the suggested study to our manuscript. Specifically we will add that droughts can also alter runoff generation processes during rewetting. In a forested headwater catchment, Lange and Haensler (2012) could show that immediately after a drought event, surface runoff with low nitrate concentrations prevailed, whereas subsurface runoff with elevated nitrate concentrations reach the river network somewhat delayed.

L351, L398: You claim that upper Selke is “very low in nitrate” during droughts. What is “very low”? I think in forest catchments a value of 1 mg/l Nitrate-N is not exceptional. Also here you should compare with other studies in forest streams.

We fully agree that 1 mg L⁻¹ is not exceptionally low. Please note that median nitrate concentrations during the drought were 0.2 and 0.4 mg L⁻¹ in SH and MD, respectively (line 165). Nevertheless, we agree that the term “very low” is not the best choice here and we will therefore reframe the sentence to “relatively low”, to point out the fact that concentrations are lower than during previous years.

L467: N uptake by denitrification?

Thank you for this remark. We will specify that we mean N uptake by plants and removal via denitrification.

References

- Dai, Z., Yu, M., Chen, H., Zhao, H., Huang, Y., Su, W., Xia, F., Chang, S. X., Brookes, P. C., Dahlgren, R. A., and Xu, J.: Elevated temperature shifts soil N cycling from microbial immobilization to enhanced mineralization, nitrification and denitrification across global terrestrial ecosystems, *Glob. Change Biol.*, 26, 5267–5276, <https://doi.org/10.1111/gcb.15211>, 2020.
- Jutglar, K., Hellwig, J., Stoelzle, M., and Lange, J.: Post-drought increase in regional-scale groundwater nitrate in southwest Germany, *Hydrol. Process.*, 35, e14307, <https://doi.org/10.1002/hyp.14307>, 2021.
- Menzel, A., Estrella, N., and Fabian, P.: Spatial and temporal variability of the phenological seasons in Germany from 1951 to 1996, *Glob. Change Biol.*, 7, 657–666, <https://doi.org/10.1111/j.1365-2486.2001.00430.x>, 2001.
- Nguyen, T. V., Kumar, R., Musolff, A., Lutz, S. R., Sarrazin, F., Attinger, S., and Fleckenstein, J. H.: Disparate Seasonal Nitrate Export From Nested Heterogeneous Subcatchments Revealed With StorAge Selection Functions, *Water Resour. Res.*, 58, e2021WR030797, <https://doi.org/10.1029/2021WR030797>, 2022.
- Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., and Fleckenstein, J. H.: Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales, *Water Resour. Res.*, 57, e2020WR027992, <https://doi.org/10.1029/2020WR027992>, 2021.