

Supporting Information for

## **Droughts can reduce the nitrogen retention capacity of catchments**

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## Text S1

### Mechanistic process-based modeling with Storage Selection Functions

In the following, we provide a more detailed description of the soil and belowground processes implemented into mHM-SAS (Nguyen et al., 2022):

Within the soil compartment, different N pools (dissolved inorganic nitrogen - DIN, dissolved organic nitrogen - DON, active organic nitrogen -  $SON_A$ , and inactive organic nitrogen -  $SON_I$ ) and N transformation between these pools (mineralization, dissolution, and degradation) are considered. N in the DIN pool (Nitrate) can be removed by plant uptake, denitrification, and leaching to the subsurface. Transport of N in the subsurface is described by the water balance and the master equation (Benettin & Bertuzzo, 2018; Botter et al., 2011; Nguyen et al., 2022; Van Der Velde et al., 2012):

$$\frac{dS(t)}{dt} = J(t) - Q(t) \quad (3)$$

$$\frac{\partial S_T(T,t)}{\partial t} = J(t) - Q(t) \cdot P_Q(T,t) - \frac{\partial S_T(T,t)}{\partial T} \quad (4)$$

where  $S(t)$  [ $L^3$ ] is the subsurface storage at time  $t$ ,  $J(t)$  [ $L^3$ ] and  $Q(t)$  [ $L^3$ ] are inflow to and outflow from the subsurface, respectively,  $S_T(T,t)$  [ $L^3$ ] is the age-ranked subsurface storage,  $P_Q(T,t)$  or  $p_Q(T,t)$  are the transit time distribution of outflow,  $P_Q(T,t) = \int_0^\infty p_Q(T,t) \cdot dT$ . The transit time distribution relates to the residence time distribution,  $P_S$  [-], via a StorAge Selection (SAS) function,  $\omega_Q(P_S, t)$  [-], as follows:

$$p_Q(T,t) = \omega_Q(P_S, t) \cdot \frac{\partial P_S}{\partial T} \quad (5)$$

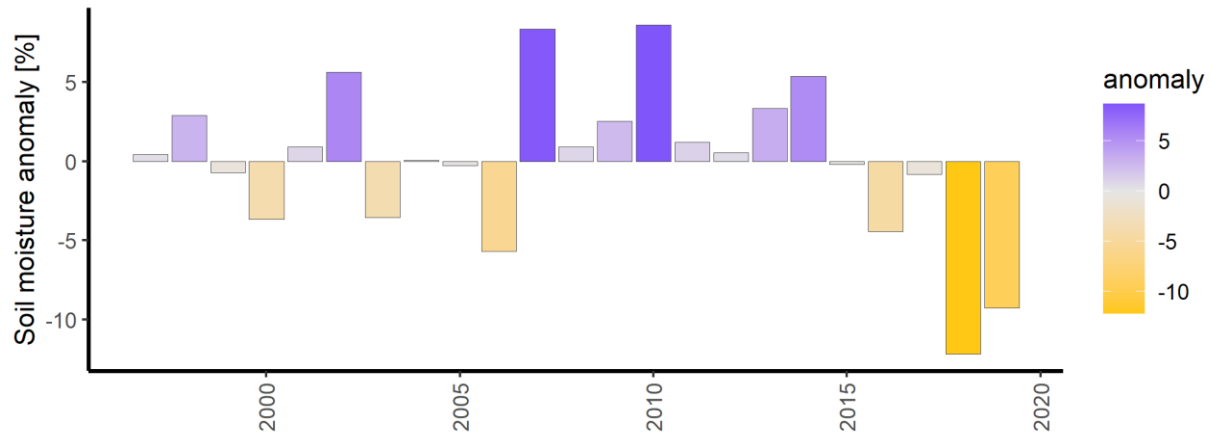
where  $\omega_Q(P_S, t)$  is approximated by the two-parameter beta function (Nguyen et al., 2022):

$$\omega(P_S, t) = \text{beta}(P_S, a, b) \quad (6)$$

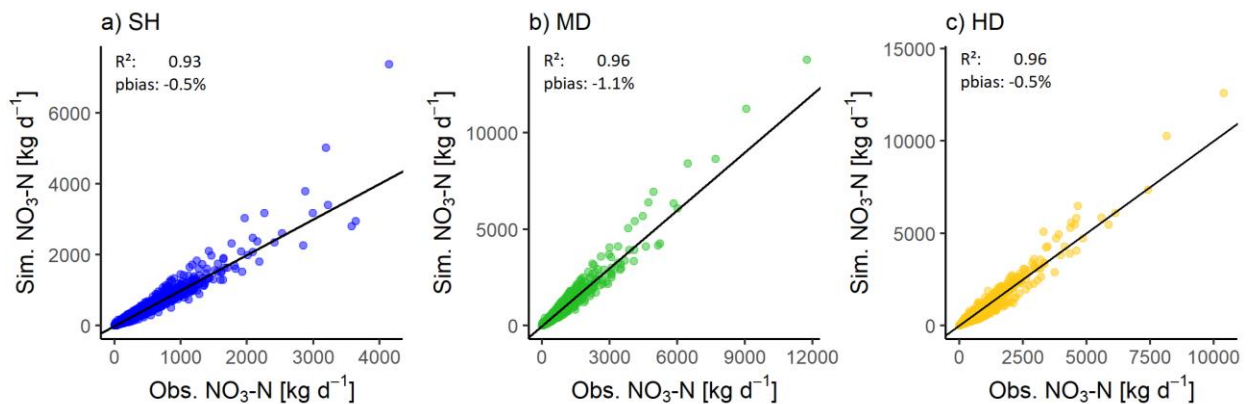
where  $a$  and  $b$  are the two parameters of the beta function ( $a/b > 1$ : preference for young water;  $a/b < 1$ : preference for old water). Parameters  $a$  and  $b$  vary in time, depending on the antecedent inflow  $J$  and outflow  $Q$  (Nguyen et al. 2022). Assuming denitrification in the subsurface is a first-order process with a rate constant  $k$  [T], nitrate concentration in the outflow from the subsurface is (Nguyen et al., 2022; Queloz et al., 2015):

$$C_Q(t) = \int_0^\infty C_J(t-T, t) \cdot p_Q(T, t) \cdot \exp(-k \cdot T) \cdot dT \quad (6)$$

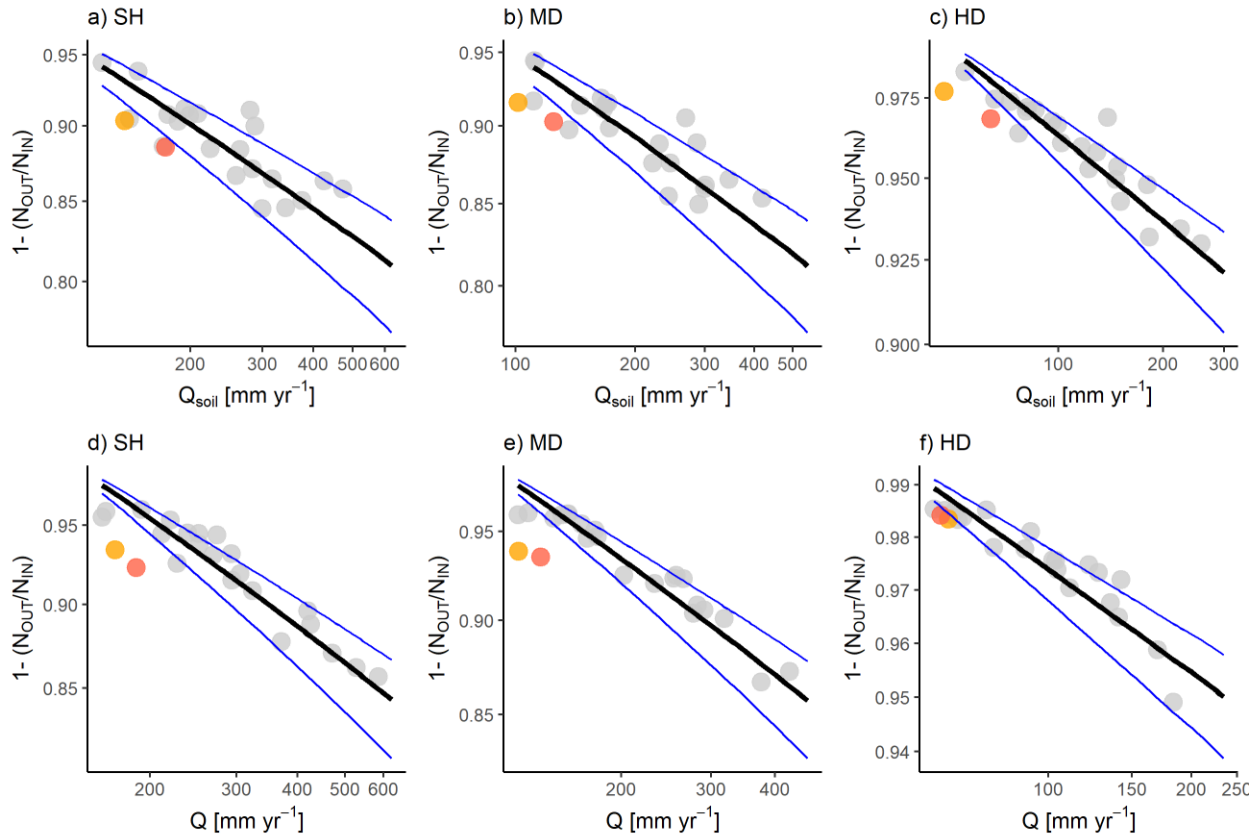
where  $C_J(t-T, t)$  [ $ML^{-3}$ ] is the nitrate concentration in the inflow  $J$  at time  $t-T$ . More details of the model description are given Nguyen et al. (2022).



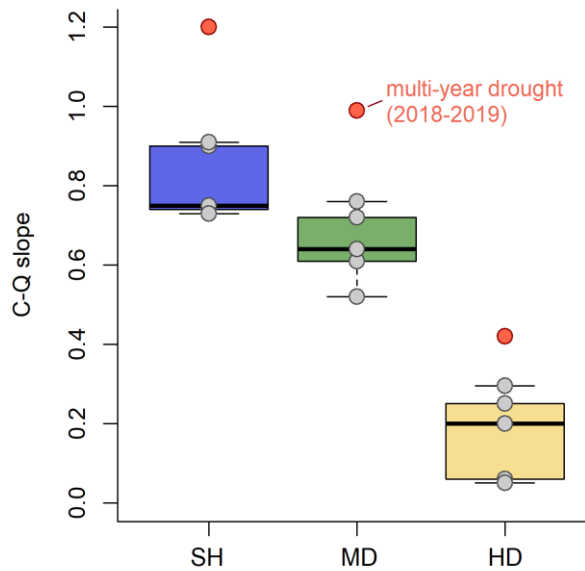
**Figure S1** Soil moisture anomalies for the drying-wetting cycles from 1997 to 2019 (12-month period starting in May). Anomaly is shown as the difference between average soil saturation [%] for a specific drying-wetting cycle to the long-term mean.



**Figure S2** Observed versus simulated daily nitrate-N loads for the three sub-catchments of the Selke catchment (a-c). Observed nitrate-N loads refer to loads that were calculated from observed nitrate-N concentrations (daily averages of sensor measurements) and daily averages of observed discharge. Simulated Nitrate-N loads were calculated from nitrate-N concentrations that were interpolated between biweekly to monthly grab samples via Weighted Regression on Time Discharge and Season (WRTDS; Hirsch et al., 2010) and observed daily discharge. The coefficient of determination (R<sup>2</sup>) and the percentage bias (pbias) are shown as indicators for the goodness of fit.



**Figure S3** Relationship between the N retention capacity of soils ( $N_{ret-soil}$ ) or catchments ( $N_{ret}$ ) and log-scaled discharge ( $Q$ ) at the nested catchment scale, given as drying-wetting cycle averages (12 month period starting in May). Grey dots show the drying-wetting cycle averages prior to the multi-year drought (1997-2017); yellow and red dots show the averages over the 2018 and 2019 drying-wetting cycle, respectively. Black lines represent the regression line between  $N_{ret}$  or  $N_{ret-soil}$  and  $\log(Q)$  prior to the drought, blue lines show scenarios of +20% N input (upper line) -20% N input (lower line) in form of fertilizer, manure and plant residues to test the sensitivity of results to uncertainties introduced by imprecise information on N input and crop rotation. This sensitivity analysis shows that the variability in N input mainly affects  $N_{ret}$  and  $N_{ret-soil}$  at high discharge, whereas its impacts becomes small towards low discharge. Hence, results on the impact of the multi-year drought (characterized by exceptionally low discharge) on  $N_{ret}$  and  $N_{ret-soil}$  are sufficiently robust to uncertainty in N inputs.



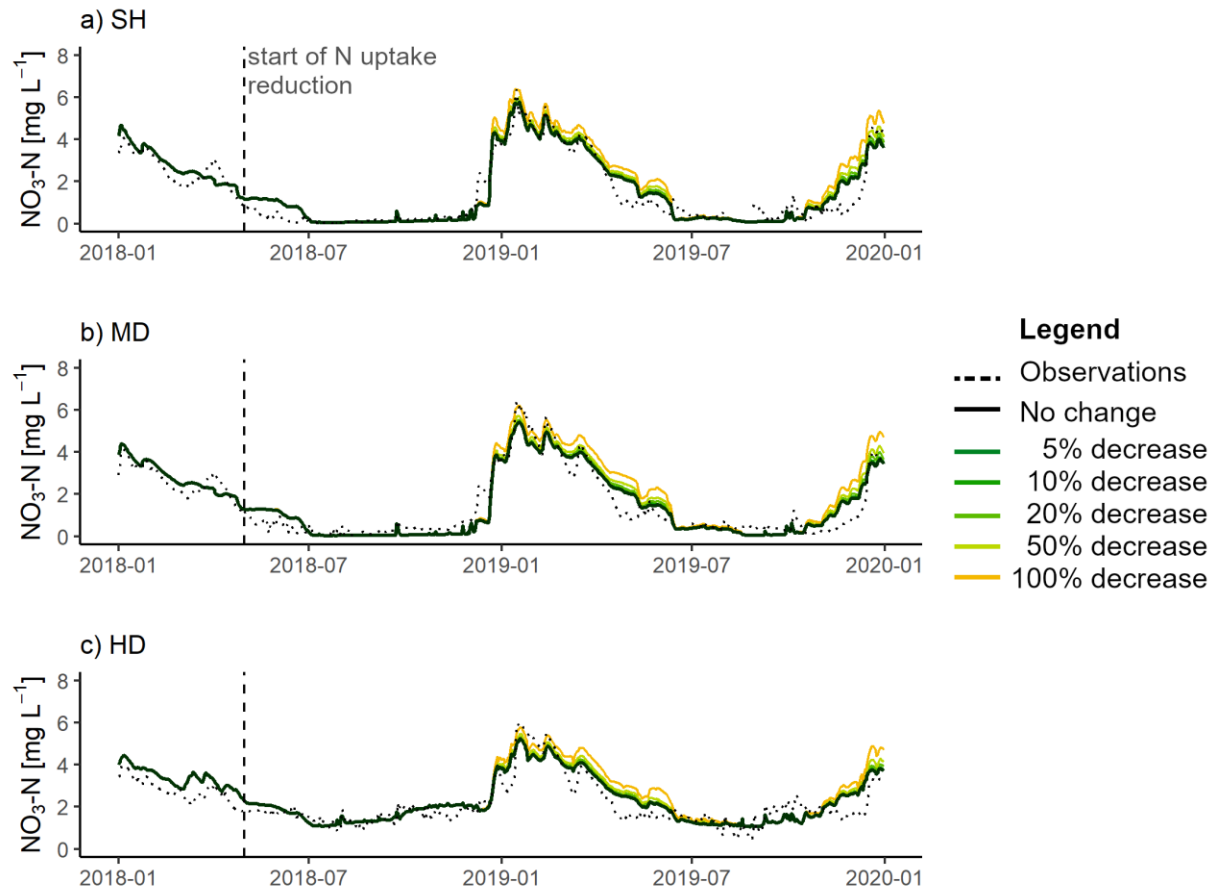
**Figure S4** Block sampled concentration-discharge (C-Q) slopes (exponent of the power law relationship between C and Q) across all possible combinations of two consecutive drying-wetting cycles between 2012 and 2017 for the three sub-catchment of the Selke catchment (SH, MD and HD from upstream to downstream), compared to C-Q slopes from the multi-year drought (2018-2019; red dots). A drying wetting cycle is a 12-month period starting in May.

## Text S2

### Reduced plant N uptake due to drought impacts on forests and agricultural crops

The multi-year drought had detrimental impacts on forests across Europe (Schuldt et al., 2020). As large parts (87.7%) of the upstream area of the Selke catchment are covered by forests, long-term consequences from forest dieback on stream nitrate export might apply (see main manuscript, section 4.2). To estimate the potential effect of forest dieback on stream nitrate export, we manually manipulated N uptake in forested areas and ran five different scenarios of a 5%, 10%, 25%, 50% and 100% reduction in N uptake (Figure S4). Unsurprisingly, results show negligible effects on stream nitrate-N concentrations during the drought, when storage selection preference was dominated by old water from pre-drought periods. During the wet period an increase in nitrate concentrations occurred; the stronger the higher the plant uptake reduction (Figure S4).

The scenario of a 100% reduction of forest N uptake, although not being a very realistic scenario, gives an estimate of the maximum impact possibly induced by forest dieback. For this scenario, highest riverine nitrate concentration increase were simulated for the wetting period after the dry summer in 2019, where nitrate-N concentrations were 42%, 45% and 16% ( $1.0 \text{ mg L}^{-1}$ ,  $0.9 \text{ mg L}^{-1}$  and  $0.5 \text{ mg L}^{-1}$ ) higher than without an additional reduction of forest N uptake in SH, MD and HD, respectively.



**Figure S5** Scenarios of nitrate-N concentrations under reduced N uptake from trees in the forested areas, simulated with mHM-SAS for the nested sub-catchments of the Selke catchment (a-c). Note that sub-catchment-specific contributions are not separated and thus nitrate-N concentrations reflect the integrated signal from the entire upstream catchment.

## References

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