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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):

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

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

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 $pQ(T,t)$ 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:

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

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

$$\omega(P_s,t) = beta(P_s,a,b) \tag{6}$$

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):

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

where $C_J(t\text{-}T,t)$ [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).

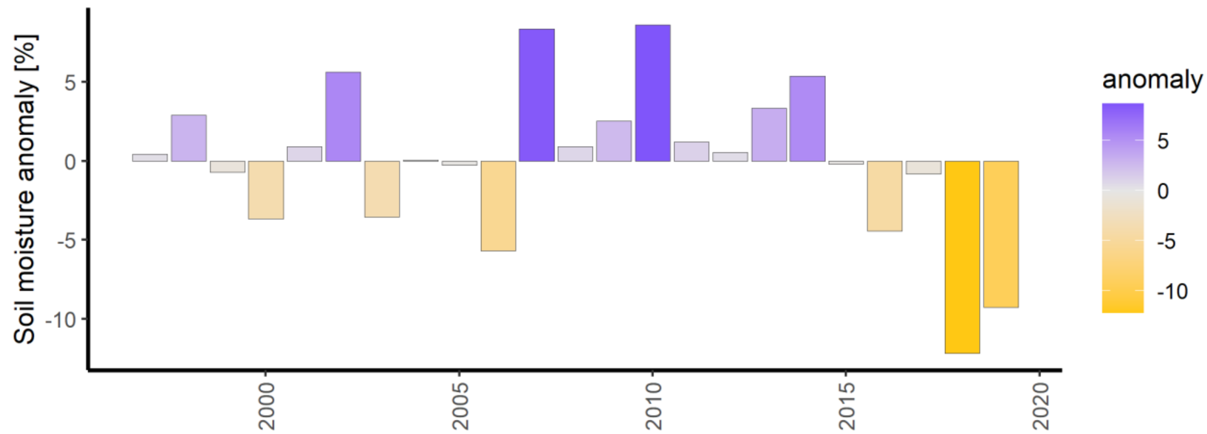

Figure S1 Soil moisture anomalies for the years (12-month period starting in May) from 1997 to 2019. Anomaly is shown as the difference between average soil saturation [%] for a specific year to the long-term mean.

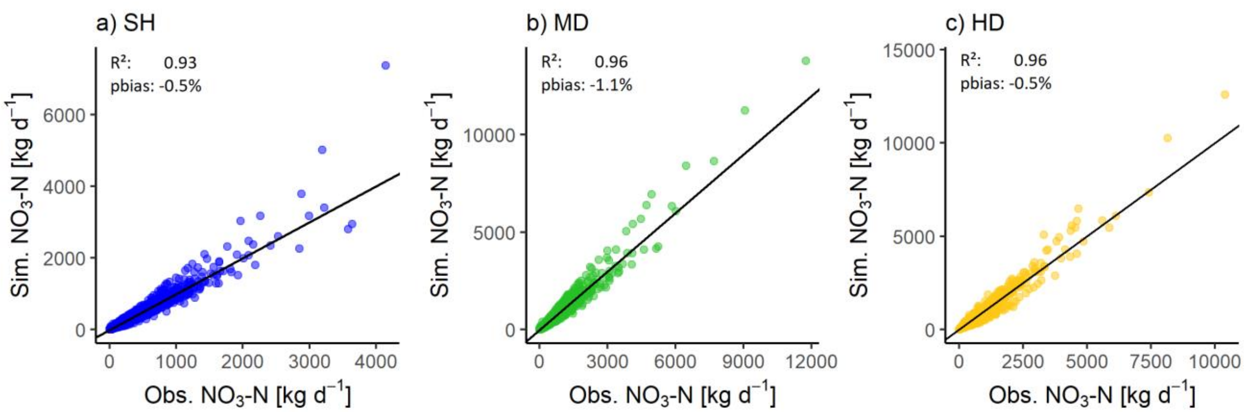

Figure S2 Observed versus simulated daily nitrate-N loads for the three sub-catchments of the Selke catchment (a-c). Observed nitrate-N loads refer to loads that were calculated from observed nitrate-N concentrations (daily averages of sensor measurements) and daily averages of observed discharge. Simulated 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^2) and the percentage bias (pbias) are shown as indicators for the goodness of fit.

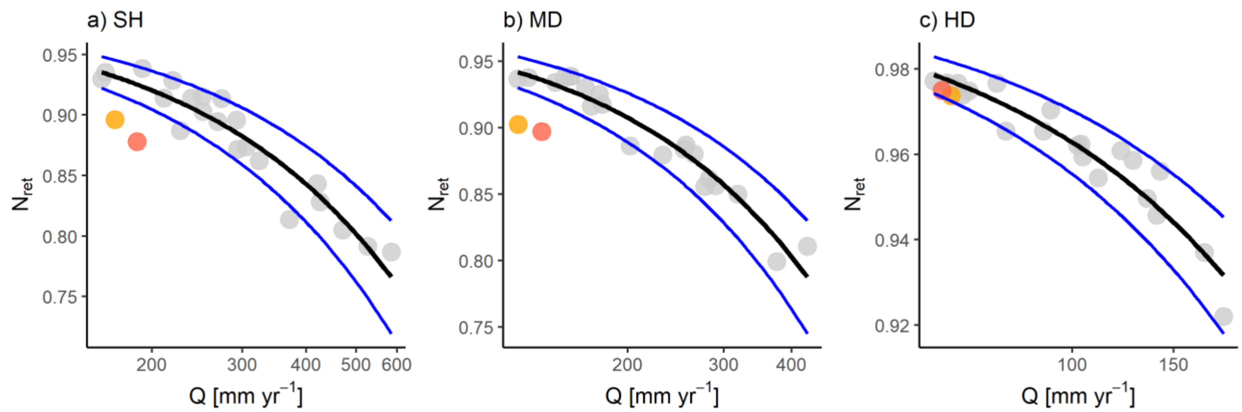

Figure S3 Relationship between the N retention capacity of catchments (N_{ret}) and log-scaled discharge (Q) at the nested catchment scale, given as annual averages (12-month period starting in May). Grey dots show the annual averages prior to the two-year drought (1997-2017); yellow and red dots show the averages over 2018 and 2019, respectively. Black lines represent the regression line between N_{ret} and log(Q) prior to the two-year drought, and blue lines show scenarios of +20% N input (upper line) -20% N input (lower line) in the form of fertilizer and manure 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} at high discharge, whereas its impact becomes small towards low discharge. Moreover, the years 2018 and 2019 clearly stand out in SH and MD. Hence, results on the impact of the two-year drought (characterized by exceptionally low discharge) on N_{ret} are sufficiently robust to uncertainty in N inputs.

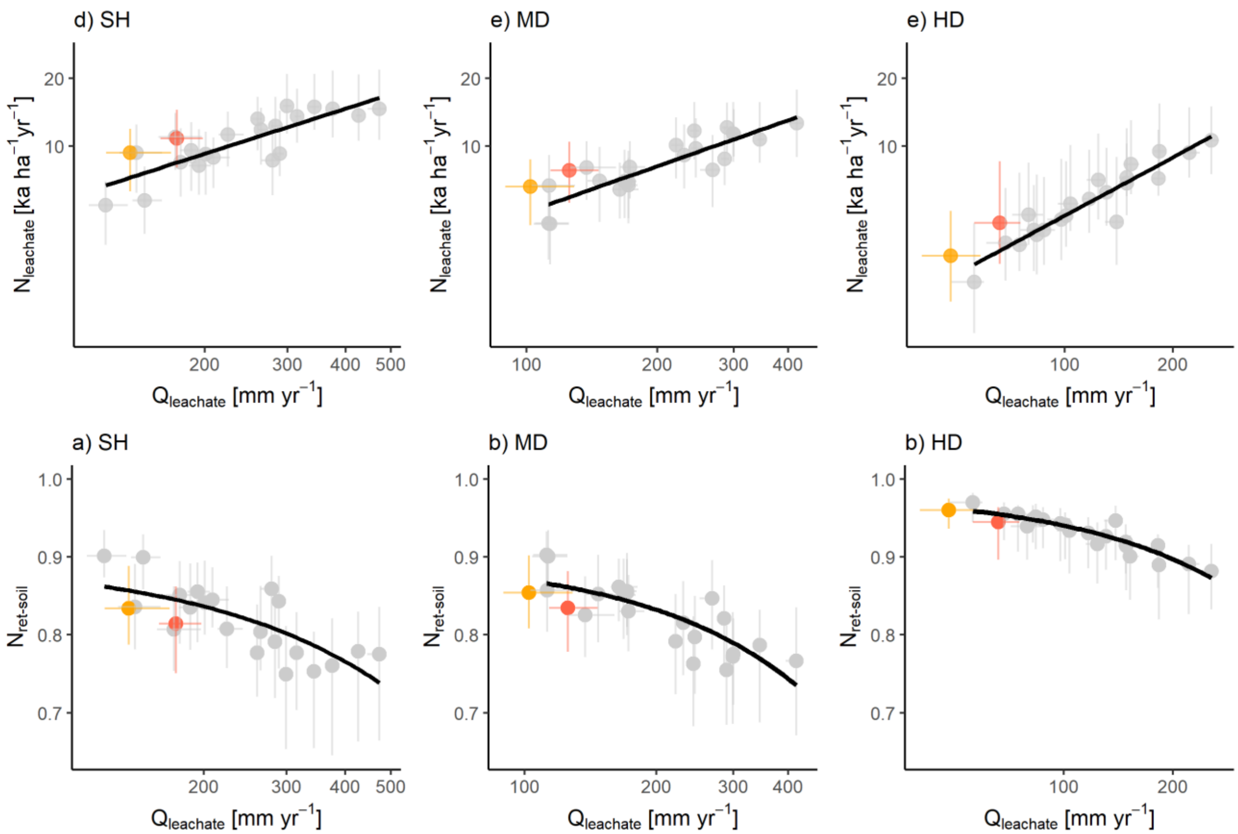

Figure S4 Long-term load-discharge (L-Q) relationship and the N retention capacity ($N_{ret\text{-}soil}$) calculated from annual (12-month period starting in May) averages of simulated soil leachate ($Q_{leachate}$) and nitrate-N loads in the soil leachates ($N_{leachate}$). Grey dots depict the annual averages of the long-term relationship from 1997 to 2017; colored dots represent the drought years 2018 (yellow) and 2019 (red). Error bars depict the 90% confidence intervals that result from parameter uncertainty in the mHM-SAS model (Nguyen et al., 2022). $N_{ret\text{-}soil}$ is calculated as 1 – (Nin/ $N_{leachate}$), with N_{in} being N input to the catchment. The depicted uncertainty does not allow for an unambiguous interpretation of the results. However, in tendency, the drought years 2018 and 2019 show higher Loads compared to the long-term L-Q relationship and a lower N retention capacity.

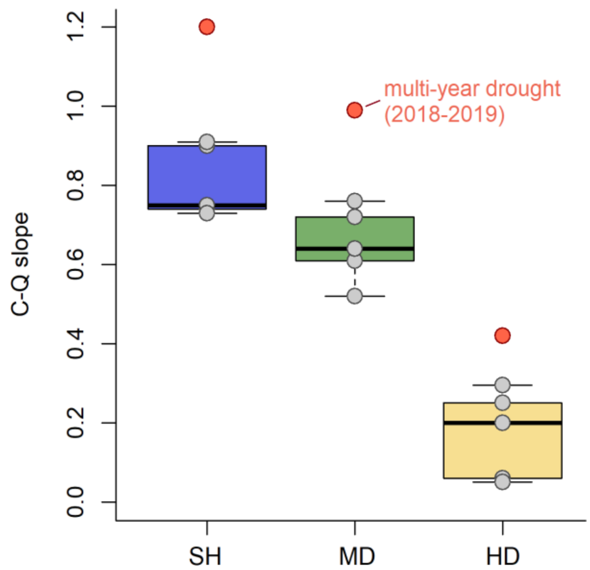

Figure S5 Block sampled concentration-discharge (C-Q) slopes (exponent of the power law relationship between C and Q) across all possible combinations of two consecutive years (12-month period starting in May) between 2012 and 2017 for the three sub-catchment of the Selke catchment (SH, MD, and HD from upstream to downstream), compared to C-Q slopes from the two-year drought (2018-2019; red dots).

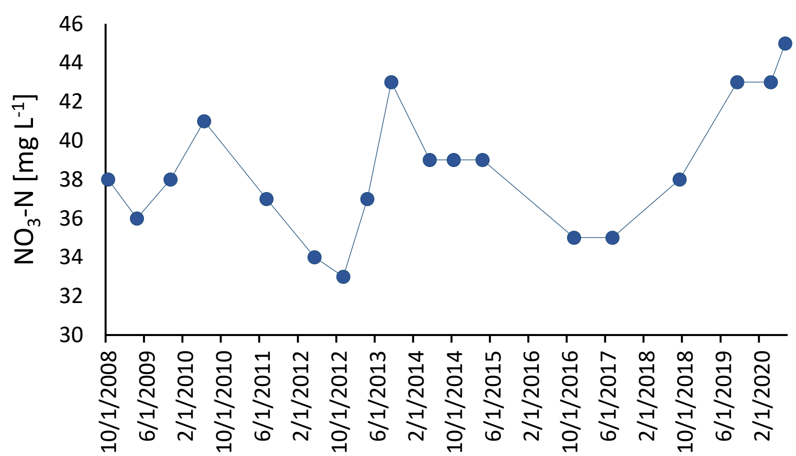

Figure S6 Groundwater observation well in Wilsleben (lower Selke catchment). Data provided by the State Office of Flood Protection and Water Quality of Saxony-Anhalt (LHW).

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