Droughts can reduce the nitrogen retention capacity of catchments

Carolin Winter[1], Van Tam Nguyen[1], Andreas Musolff[2], Stefanie Lutz[3], Michael Rode[4], Rohini Kumar[1], and Jan H. Fleckenstein[5]

[1]Helmholtz Centre for Environmental Research - UFZ
[2]UFZ - Helmholtz-Centre for Environmental Research
[3]Universiteit Utrecht
[4]Department Aquatic Ecosystem Analysis and Management, Helmholtz Centre for Environmental Research - UFZ, Germany
[5]Universität Bayreuth,Helmholtz-Zentrum für Umweltforschung UFZ

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In 2018–2019, large parts of Europe experienced an unprecedented multi-year drought with severe impacts on society and ecosystems. This study is among the first to analyze its impact on water quality by comparing long-term (1997–2017) nitrate export with 2018–2019 export in an intensively-monitored mesoscale catchment in Germany. We combined data-driven analysis of concentration-discharge and load-discharge relationships with process-based modelling to analyze the catchment nitrogen retention capacity and the underlying mechanisms of retention in the soils and during subsurface transport. Within the multi-year drought, we found a shift in the concentration-discharge relationship at the catchment outlet, reflecting exceptionally low riverine nitrate concentrations during dry periods and exceptionally high concentrations during subsequent wet periods. Nitrate loads during the multi-year drought were up to 70% higher than expected from the long-term relationship between discharge and loads. Model simulations suggested that this increase was driven by a decrease in denitrification and plant uptake in exceptionally dry soils and subsequent flushing of accumulated nitrogen during rewetting via fast, shallow flow paths. As a consequence, the overall capacity of the catchment to retain nitrogen was reduced, which was confirmed by model results for nitrate in the soil leachates. This observation was most evident in the upstream sub-catchments, which have relatively short transit times during wet periods (<2 months). Downstream, longer transit times (>20 years) inhibit a fast response of riverine water quality to drought conditions, which might result in a long-term drought legacy becoming visible in the future. Overall, our study reveals that a severe multi-year drought threatens water quality by intensifying nitrate pollution. This is crucial knowledge for water quality management in the face of climate change, as such droughts are predicted to become more frequent and prolonged across Europe.

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[1]Department for Hydrogeology, Helmholtz Centre for Environmental Research - UFZ, Germany

[2]Copernicus Institute of Sustainable Development, Utrecht University, Netherlands

[3]Department Aquatic Ecosystem Analysis and Management, Helmholtz Centre for Environmental Research - UFZ, Germany

[4]Department of Computational Hydrosystems, Helmholtz Centre for Environmental Research - UFZ, Germany

[5]Hydrologic Modelling Unit, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany

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Key words: drought, water quality, nitrate, catchment, biogeochemical cycling, nitrogen retention, data-driven analysis, process-based modelling

1 Introduction

In 2018–2019, large parts of Europe experienced a severe multi-year drought that was unprecedented in the last 250 years (Hari et al., 2020; Rakovec et al., 2022). This drought, caused by exceptionally low precipitation concurring with high temperatures, had detrimental impacts on vegetation during the growing season and caused massive forest diebacks (Hari et al., 2020; Schuldt et al., 2020). Besides the scarcity of water and its direct impact on ecosystems and society (Delpla et al., 2009; Fu et al., 2020; Stahl et al., 2010), there is first evidence that this drought could also have impacted fresh water quality in regard to nitrate concentrations. The Nitrate Report 2020 of the Netherlands (National Institue for Public Health and the Environment (RIVM), 2021) for example, found an increase in nitrogen (N) surplus in agricultural areas across the country and with it an increase in leachate nitrate concentrations below the root zone. This increase in N surplus and leachate nitrate concentrations in response to drought has been explained by the low water availability that might reduce crop growth and thus N plant uptake (Cramer et al., 2009; RIVM, 2021). However, high nitrate concentrations in the leachate do not necessarily reach the stream network, because catchments act as a filter and reactor that can delay the transit of N to the receiving stream or permanently remove it via denitrification (Van Meter & Basu, 2015). The extent of delays and removal strongly depends on the catchment characteristics and boundary conditions (e.g., Ehrhardt et al., 2021; Jawitz et al., 2020; Winter et al., 2021). Moreover, different N sources and their spatial distribution within a catchment can impact nitrate export at the catchment outlet (Casquin et al., 2021; Dupas et al., 2019). Therefore, both catchment characteristics and their spatial configuration might shape the response of riverine nitrate export to drought.

Diverse responses of stream water nitrate concentrations have been reported in different catchments for previous droughts and subsequent post-drought periods (Morecroft et al., 2000; Mosley et al., 2015). Several studies have found decreasing nitrate concentrations during droughts, which have been attributed either to disconnected shallow flow paths that normally allow for efficient transport of nitrate to the stream (J. Yang et al., 2018) or to increased in-stream retention efficiency and to increased uptake along with higher temperatures (Morecroft et al., 2000; Mosley, 2015; Oelsner et al., 2007). However, also increases or no changes in stream concentrations have been reported during droughts, mainly due to high nitrate concentrations in the baseflow or due to the presence of point sources, which increase in relative importance under low flow conditions (e.g. Andersen et al., 2004; Jarvie et al., 2003; Sprague, 2005; van Vliet & Zwolsman, 2008). With rewetting after the drought, many studies have reported high nitrate concentration peaks as a consequence of accumulated nitrate in the soil zone being flushed from the catchment via fast and shallow flow path (Górski et al., 2019; Morecroft et al., 2000; Mosley, 2015; Outram et al., 2014). This pattern can be explained by both remobilization of accumulated nitrate and stimulation of mineralization with the rewetting of dry soils (Campbell & Biederbeck, 1982; Haynes, 1986). Together, these findings imply that droughts can have profound impacts on nitrate availability and transport to the stream network, and that the catchment response to droughts seems to vary between catchments and potentially also with drought magnitude. Furthermore, recent studies have highlighted the role of different sub-catchments with different response times to changes composing the integrated signal of nitrate export at the catchment outlet (e.g. Ehrhardt et al., 2019; Nguyen et al., 2022; Winter et al., 2021). It can therefore be important to account for the spatial heterogeneity of a catchment and to look at sub-catchment specific contributions to better understand the overall catchment response to drought in terms of nitrate export.

To identify drought impacts on nitrate export, data-driven approaches have the advantage to give a direct reflection of real observations that are an integrated result of the complex biogeochemical and hydrological processes within the catchment. Data-driven approaches thus provide observation-based understanding without strong assumptions on the underlying processes, while allowing to build hypotheses on these processes. For example, the relationships of nitrate concentrations and discharge (C-Q) and of nitrate loads and discharge (L-Q) can serve as a robust characterization of catchment-specific nitrate export patterns under different flow conditions and allow for conclusions on N source availability and distribution and on catchment specific response times (e.g., Bieroza et al., 2018; Minaudo et al., 2019; Musolff et al., 2015). Moreover, a comparison of N input and output from a catchment allows for the quantification of catchment N retention resulting from hydrological and/or biogeochemical N legacies and denitrification (Ehrhardt et al., 2019; Van Meter et al., 2016; Van Meter & Basu, 2015; Winter et al., 2021). A tool complementary to data-driven analyses are mechanistic and process-based models, which explicitly aim at a physical description of the underlying processes causing the observed concentrations and loads and therefore provide detailed insights into the catchment internal N dynamics. For example, the mesoscale Hydrological Model with StorAge Selection functions (mHM-SAS; Nguyen et al., 2022) allows quantifying the rates of N uptake and removal in the catchment soils and lateral N transport at the sub-catchment scale. However, resulting simulations also rely on fixed assumptions and the distinct processes that these models entail. Therefore, combining data-driven analyses and mechanistic process-based modelling has several advantages: The data-driven analysis allows for a robust identification of drought impacts on nitrate export and a discussion on the underlying processes, while the process-based modelling allows testing if these processes can actually explain the observed behavior.

In this study, we used data-driven analysis and process-based modelling to analyze the impact of the 2018-2019 multi-year drought on nitrate concentrations and loads compared to previous years (1997-2017) in a heterogeneous mesoscale catchment with three nested gauges, located in Germany. This setup allows us to disentangle sub-catchment specific drought-responses, while obtaining results at a larger and integral spatial scale that is relevant for water quality management. We hypothesize that droughts can cause a change in the nitrogen retention capacity of catchments, but with different impacts on riverine nitrate export at contrasting sub-catchments. Our specific objectives were to: i) identify changes in riverine nitrate concentrations and loads at the sub-catchment scale via data-driven analyses (using C-Q and L-Q relationships), and to ii) quantify changes in N cycling in the catchment soils and in the time scales of lateral N transport from the soil leachates to the stream network via process-based modelling (using mHM-SAS). This approach allows us to gain knowledge on drought impacts on catchment functioning in terms of retaining and releasing N, which is crucial for our ability to adapt to climate change and effectively mitigate nitrate pollution.

The 2018-2019 multi-year drought was an unprecedented event, but with accelerating climate change, such multi-year droughts are likely to become more frequent (Hari et al., 2020; IPCC, 2018; Rakovec et al., 2022; Samaniego et al., 2018). In this context, this study is one step towards a better understanding of the impacts of such droughts on nitrate export dynamics and the underlying mechanisms within a catchment.

2 Data and Methods

2.1 Study site

This study was conducted in the mesoscale Selke catchment, which is located in the Harz Mountains and Harz foreland in Saxony-Anhalt, Germany (Figure 1a). As a sub-catchment of the Bode basin, it is also part of the network of TERestrial ENvironmental Observatories (TERENO; Wollschläger et al., 2017). The Selke catchment is gauged with three nested stations: Silberhütte (SH), Meisdorf (MD) and Hausneindorf (HD, Figure 1a). The two upstream sub-catchments form the upper Selke with similar characteristics such as forest being the dominant land use and also in terms of relatively short TTs and comparable nitrate export dynamics (Nguyen et al., 2022; Carolin Winter et al., 2021). The downstream part forms the lowland area of the catchment, which is dominated by agricultural land use. Compared to the upper Selke, TTs are longer and the variability of export dynamics is reduced (Nguyen et al., 2022; Carolin Winter et al., 2021).

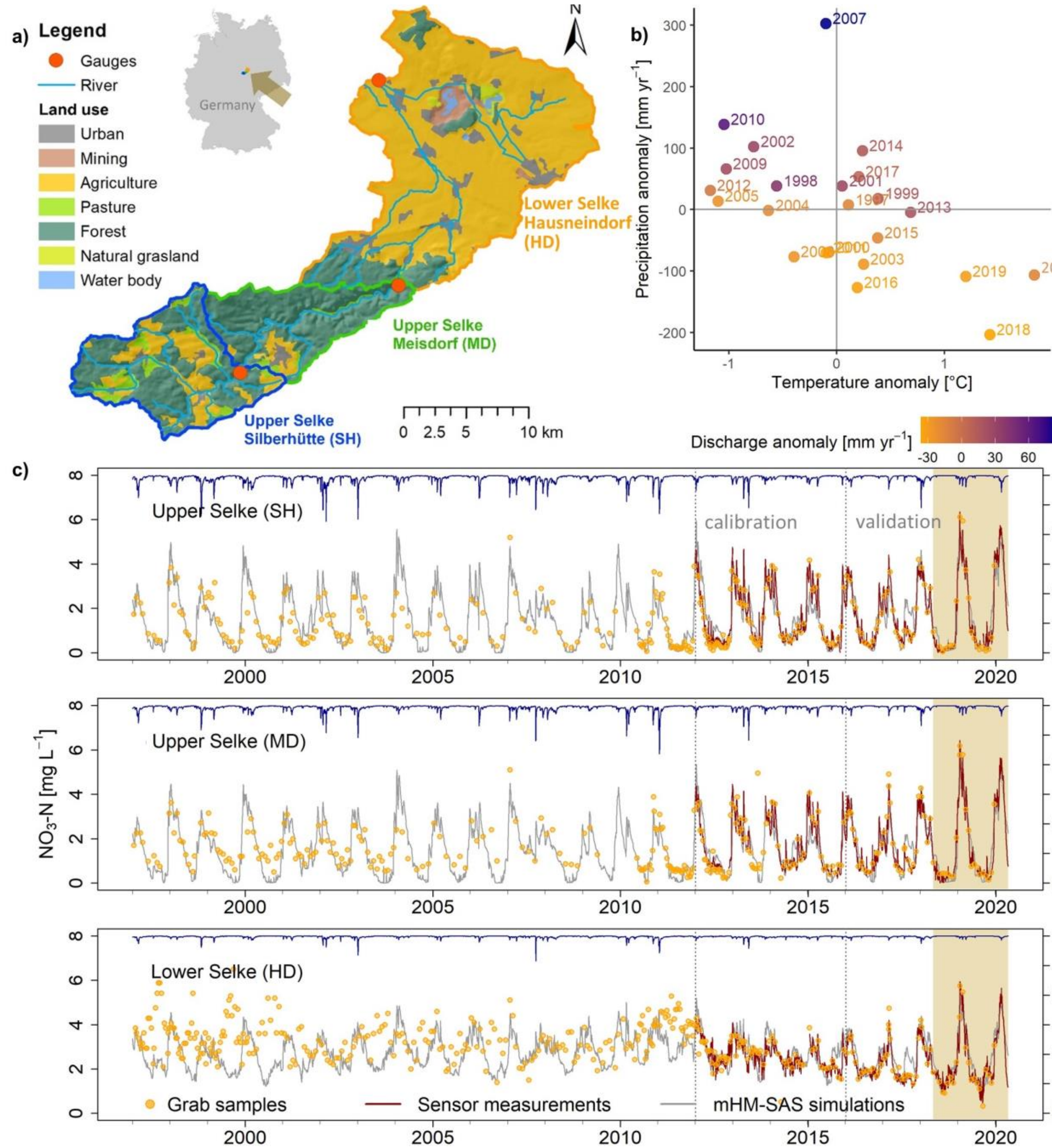

Figure 1 Study site, hydrometeorological conditions and nitrate concentration data. a) Land use map of the Selke catchment with its three gauging stations (SH, MD and HD). b) Climatic anomalies in the Selke catchment in terms of precipitation, temperature and discharge for the dying-wetting cycles (May–April) starting 1990–2019; and c) discharge and nitrate as nitrogen concentrations at the gauging stations of the three Selke sub-catchments (1997–2020) with low-frequency grab samples (orange dots), simulated

concentrations via mHM-SAS (grey line) and daily averages of high-frequency sensor measurements from 2012 on (red line). Dashed lines indicate the mHM-SAS calibration (2012–2015) and validation (2016–2020) periods, comparing simulated nitrate-N concentrations with daily averages of sensor measurements.

Sub-catchment characteristic	Unit	Upper Selke Silberhütte (SH)	Upper Selke Meisdorf (MD)	Lower Selke Hausneindorf (HD)
Area	(km²)	100.9	78.9	277.6
Mean Elevation	(m.a.s.l.)	448.9	370	164.8
Mean Slope	(%)	6.8	11.5	2.6
Mean annual precipitation	(mm)	718.6	646.9	537
Mean annual temperature	(°C)	8	8.4	9.9
Land use	(%)			
Forest		61.3	87.7	12.1
Agriculture		36.1	10	76.2
Others		2.6	2.3	10.7
Dominant soil type		Dystic/spodic cambisols		Haplic chernozem
Dominant geology		Paleozoic greywacke/ Denovian shale		Sedimentary

Table 1 Sub-catchment specific characteristics of the Selke catchment

Note. Catchment characteristics refer to spatially separated, not nested sub-catchments. Precipitation and temperature data was taken from the period 1997–2020.

2.2 Characterization of different hydroclimatic conditions and anomalies

We adopted the definition of annual wet, drying, dry and wetting periods from J. Yang et al. (2018), based on the catchment subsurface storage condition in a headwater catchment of the Selke catchment. Accordingly, wet periods last from January to April, drying periods (i.e., the transition from wet to dry) last from May to June, dry periods last from July to October and wetting periods (i.e., the transition from dry to wet) last from November to December. Instead of annual averages or averages over a hydrological year, we calculated averages of discharge and N fluxes over 12-month periods starting with the drying period in May and ending with the wet period end of April. This was done under the rationale that nitrate starts accumulating in a catchment over the drying and dry period, when fast flow paths are deactivated (J. Yang et al., 2018), and that, subsequently, accumulated nitrate is more efficiently exported from the catchment during wetter conditions. Under this rationale, comparing annual statistics of nitrate export is more meaningful if comparing 12-month periods starting in May instead of January or November, considering the seasonality in climatic conditions in central Germany. Throughout the manuscript, we therefore calculate averages of 12-month periods (drying-wetting cycles) starting in May. We differentiate drying-wetting cycles by the year in which they started, for example, the drying-wetting cycle 2018 started on 1st May 2018 and ended on 30th April 2019. In the same manner, we refer to the multi-year drought as the drying-wetting cycles 2018 and 2019, spanning a period from May 2018 until the end of April 2020.

To compare the drying-wetting cycles 2018 and 2019 with the ones from previous drying-wetting cycles (1990–2017), we calculated their anomalies in hydroclimatic conditions compared to the long-term average. To this end, we calculated the drying-wetting cycle averages in observed temperature, precipitation, discharge and in modelled soil moisture (see section 2.5) for the study catchment. We then calculated the long-term average over all cycles and subtracted the single drying-wetting cycle averages from those long-term averages. The divergence of single drying-wetting cycles from the long-term average is considered the climatic anomaly. In the Selke catchment for the 2018-2019 drought, drying-wetting cycles starting in May 2018 and May 2019 are characterized by exceptionally low precipitation (anomaly of -205mm yr^{-1} and -110 mm yr^{-1} in 2018 and 2019, respectively, compared to the long-term average of 602 mm yr^{-1} over the period 1997-2020), high temperatures (+1.6°C and +1.4°C in 2018 and 2019, compared to the long-term average of 9.0°C) and low discharge (-37.0 mm yr^{-1} and -39.2 mm yr^{-1} compared to the long-term average of 98.5 mm yr^{-1}) (Figure 1b). In terms of soil moisture, these two drying-wetting cycles were the driest cycles in the Selke catchment since the start of our time series in May 1997, with 2018 being even drier than 2019 (Figure S1). Consequently, the multi-year drought that affected large parts of Central Europe (Hari et al., 2020) can also be characterized as an exceptional drought in the Selke catchment.

2.3 Data

Daily long-term temperature and precipitation data (1997–2020) were provided by the German Meteorological Service (Deutscher Wetterdienst, DWD). N input data (i.e., fertilizer, manure and plant residues) and land use management (i.e., crop rotation) and atmospheric deposition were based on agricultural authority data obtained from X. Yang et al. (2018) and Jomaa et al. (2018). Accordingly, N input to agricultural fields in mHM-SAS follows a two- or three-year crop rotation, as typical in this area and as implemented in X. Yang et al. (2018) and Nguyen et al. (2022). Daily discharge data and biweekly–monthly grab samples of nitrate concentrations were provided by the State Office of Flood Protection and Management of Saxony-Anhalt (LHW; Figure 1c). Sensor measurements (using TriOS Pro-UV sensors; Rode et al., 2016) of nitrate concentrations at a 15-minute resolution (2012–2020) were provided by the TERENO facilities of the Helmholtz Centre for Environmental Research (UFZ). To match the temporal resolution of long-term data, nitrate concentrations were aggregated to daily averages

(Figure 1c). Part of this data was previously used by (Musolff et al., 2021; Rode et al., 2016; Winter et al., 2021, 2022; X. Yang et al., 2018). Therefore, for the detailed processing of nitrate concentration data, we refer to Rode et al. (2016) and the other references above. With a coefficient of determination (R^2) between 0.8 for MD and HD and 0.9 for SH, processed high-frequency nitrate concentration data from sensor measurements showed a good agreement with concentrations from grab samples analyzed in the lab.

Nitrate-N concentrations differed between the upper and the lower Selke and between normal (i.e., drying-wetting cycles 2012–2017) and drought periods (drying-wetting cycles 2018–2019; Figure 1c). Median concentrations in the upper Selke measured before the multi-year drought ranged from 0.6 mg L^{-1} and 0.7 mg L^{-1} during dry periods in SH and MD respectively, to a median of 2.6 mg L^{-1} and 2.5 mg L^{-1} during wet periods. Median nitrate-N concentrations measured at HD were higher and less variable with a median of 2.1 mg L^{-1} during dry periods and 3.0 mg L^{-1} during wet periods. During the multi-year drought, nitrate-N concentrations generally showed a higher seasonal variability (Figure 1c). During dry periods 2018 and 2019, nitrate-N concentrations were lower than during previous dry periods, with a median of 0.2 mg $L^{-1}$and 0.4 mg L^{-1} and 1.3 mg L^{-1} in SH, MD and HD, respectively. During the subsequent wet periods (January-April 2019 and 2020), nitrate-N concentrations were exceptionally high with a median of 4.2 mg L^{-1}, 3.8 mg L^{-1}, and 3.7 mg L^{-1}. In the upper Selke (SH and MD) nitrate-N concentrations reached the highest value observed since the start of measurements in 1983, with 6.4 mg L^{-1} in January 2019. Peak concentration in the lower Selke (HD) during that time was 5.9 mg L^{-1}, which was also among the highest values measured at this gauge (Fig. 1c).

2.4 Data driven analysis using concentration-discharge relationships

To characterize nitrate export in the Selke catchment, we performed a data driven analysis using concentration-discharge (C-Q) relationships from daily averages and load-discharge (L-Q) relationships from drying-wetting cycle averages. A simple but efficient way to describe the C-Q relationship, is a power-law relationship of the form

$$C(t) = \alpha Q(t)^{\beta} \tag{1}$$

with t standing for the respective time step. The parameters α and β describe the intercept (α) and the slope of the relationship in the log-log space (β), also termed C-Q slope (Musolff et al., 2015; Thompson et al., 2011). A positive C-Q slope indicates an increase of nitrate concentrations with discharge (enrichment pattern), whereas a negative C-Q slope indicates decreasing nitrate concentrations with increasing discharge (dilution pattern). Both patterns imply a directional relationship between concentrations and discharge with nitrate concentrations either increasing or decreasing with increasing discharge. On the contrary, a C-Q slope around zero indicates that nitrate concentrations are not or poorly correlated with the dynamics of discharge. Since nitrate loads (L) are the product of nitrate concentrations (C) and discharge (Q), the L-Q slope can be described using β+1, with the differentiation in this study that the C-Q slope and the L-Q slope were calculated with data of different temporal resolutions and are thus not directly comparable.

The C-Q relationship was calculated from daily averages of measured data only and is therefore restricted to the period 2012–2020. To test if the C-Q slope for the multi-year drought was different than the long-term average, we compared both slopes and their standard errors. To account for the different sample sizes between the pre-drought and drought periods, we applied additional block sampling across all possible combinations of two consecutive drying-wetting cycles and compared the resulting pre-drought C-Q slopes with the one from the multi-year drought.

Instead of restricting our analysis to observed daily data, as done for C-Q relationships, we calculated L-Q relationships with the sums of daily load and discharge data over drying-wetting cycles starting in May

1997. To this end, we used the continuous daily discharge measurements and filled the gap in daily nitrate concentration measurements by interpolating from biweekly–monthly grab samples via Weighted Regression on Time Discharge and Season (WRTDS; Hirsch et al., 2010). The fit between daily loads calculated from interpolated and measured nitrate concentration data (2012-2019) was high, with an R^2 between 0.93 and 0.96 and a small percentage bias between -0.5% and -1.1% (Figure S2).

2.5 Process-based nitrogen export modeling with Storage Selection Functions

To get a deeper insight into catchment processes that cause the observed nitrate export patterns during and after the multi-year drought, we simulated daily nitrate concentrations at the three gauging stations using the mesoscale Hydrological Model with StorAge Selection functions (mHM-SAS, Nguyen et al., 2021, 2022). The mHM-SAS model is explained in detail in Nguyen et al. (2022) and in the supplements (Text S1). Briefly, mHM-SAS provides a spatially distributed (1x1 km^2) representation of hydro-climatic inputs, N pools and fluxes in the soil zone based on a combination of mHM and the soil nitrogen model (X. Yang et al., 2018). Nitrate pools and fluxes in the saturated and unsaturated zone below the soil are represented for each sub-catchment using the nitrate transport model with SAS functions (van der Velde et al., 2012, Nguyen et al., 2022).

Nguyen et al. (2022) calibrated the model in the Selke sub-catchments for the years 2012–2015 with a Nash-Sutcliffe Efficiency (NSE) of 0.81, 0.81 and 0.57 over the validation period (2016–2019), which includes parts of the multi-year drought. Using the same set-up, here we extended the model simulations to the 1997–2020 time period (Figure 1c). We used these extended simulations to contrast average conditions with the 2018–2019 drought-induced changes in the C-Q relationships in the different sub-catchments of the Selke catchment. Despite distinct climatic conditions during the 2018-2019 drought period, simulated nitrate concentrations via mHM-SAS showed a good fit to the measured sensor data with a NSE of 0.89, 0.88 and 0.77 in SH, MD and HD respectively (Figure 1c). With this setup, the mHM-SAS model allows for a separation of the contribution of each sub-catchment to the overall catchment responses, to account for sub-catchment specific N cycling in the soil zone (denitrification, plant uptake, mineralization and leaching), instream uptake, denitrification along the groundwater flow paths and for dynamic transit times.

To additionally estimate the potential impact of forest dieback during the multi-year drought (Schuldt et al., 2020), we ran scenarios with a 5%, 10%, 20% and 100% reduction of N uptake from forested areas and compared simulated nitrate concentrations of the different scenarios with the baseline scenario.

2.6 Catchment retention capacity

We estimated the capacity of a catchment to retain N (N_{ret}) during a drying-wetting cycle by the ratio of average nitrate-N load export (N_{OUT}) against average atmospheric deposition during an drying-wetting cycle and long-term average N inputs from fertilizer, manure and plant residues (N_{IN}):

$$N_{ret} = 1 - \frac{N_{OUT}}{N_{IN}} \tag{2}$$

We used the long-term average N input across crop rotations, as precise information on which crop is applied to which field in which year is not available and thus a long-term average is more robust. Additionally, we assessed the sensitivity of our results to uncertainty in N input through crop rotation, by variying N inputs by ±20%, which confirmed the overall robustness of our results (Figure S3).

We distinguish two forms of N retention capacity: i) *the catchment N retention capacity* (N_{ret})*,* which is the ratio of observed riverine nitrate-N load exported at the (sub-)catchment outlet to the corresponding N input and ii) *the soil N retention capacity* ($N_{ret\text{-}soil}$), where N_{OUT} is replaced by nitrate-N loads in the leachate from the root zone, simulated via mHM-SAS. Consequently, N_{ret} or $N_{ret\text{-}soil}$ equal to zero indicate that the same amount of N entering a catchment is also exported from the catchment soils or leaving the catchment at its outlet within one drying-wetting cycle. N_{ret} or $N_{ret\text{-}soil}$ equal to one indicate 100% retention of N input within the catchment or the catchment soils, respectively. $N_{ret\text{-}soil}$ is a direct estimate of N retention in the catchment soil, because N that entered the soil but is not leached, is eventually retained or processed within the soil compartment. Instead, N_{ret} is a combination of soil N retention and its consecutive transport via hydrological flow paths to the stream network, which is additionally affected by N transit times and denitrification along the subsurface flow paths.

Because observed nitrate-N loads and discharge at the (sub-)catchment outlet are inherently an integrated signal of all upstream sub-catchments, we also aggregate the simulated water and nitrate leaching from the soils to nested values for the calculation of $N_{ret\text{-}soil}$. To estimate changes in the N retention capacities relative to the hydrological conditions, we calculated a linear regression between N_{ret} and observed log-transformed discharge and between $N_{ret\text{-}soil}$ and simulated log-transformed leachate for the drying-wetting cycles previous to the multi-year drought (1997-2017).

3 Results

3.1 Concentration-discharge and load-discharge relationship

Nitrate concentrations during the multi-year drought show an accelerated seasonality (see section 2.3) that is reflected in a more chemodynamic C-Q relationship (Figure 2a-c). All three sub-catchments show a positive C-Q relationship for daily averages of pre-drought (January 2012 – April 2018) nitrate-N concentrations and discharge, with the highest slope in SH, followed by MD and the lowest slope in HD. During the multi-year drought, the C-Q slope for all sub-catchments increased by values that are multiples of the standard error of the pre-drought regressions for the entire period (Figure 2a-c), but also for block sampled C-Q slopes that account for the smaller samples size of the drought period (Figure S4).

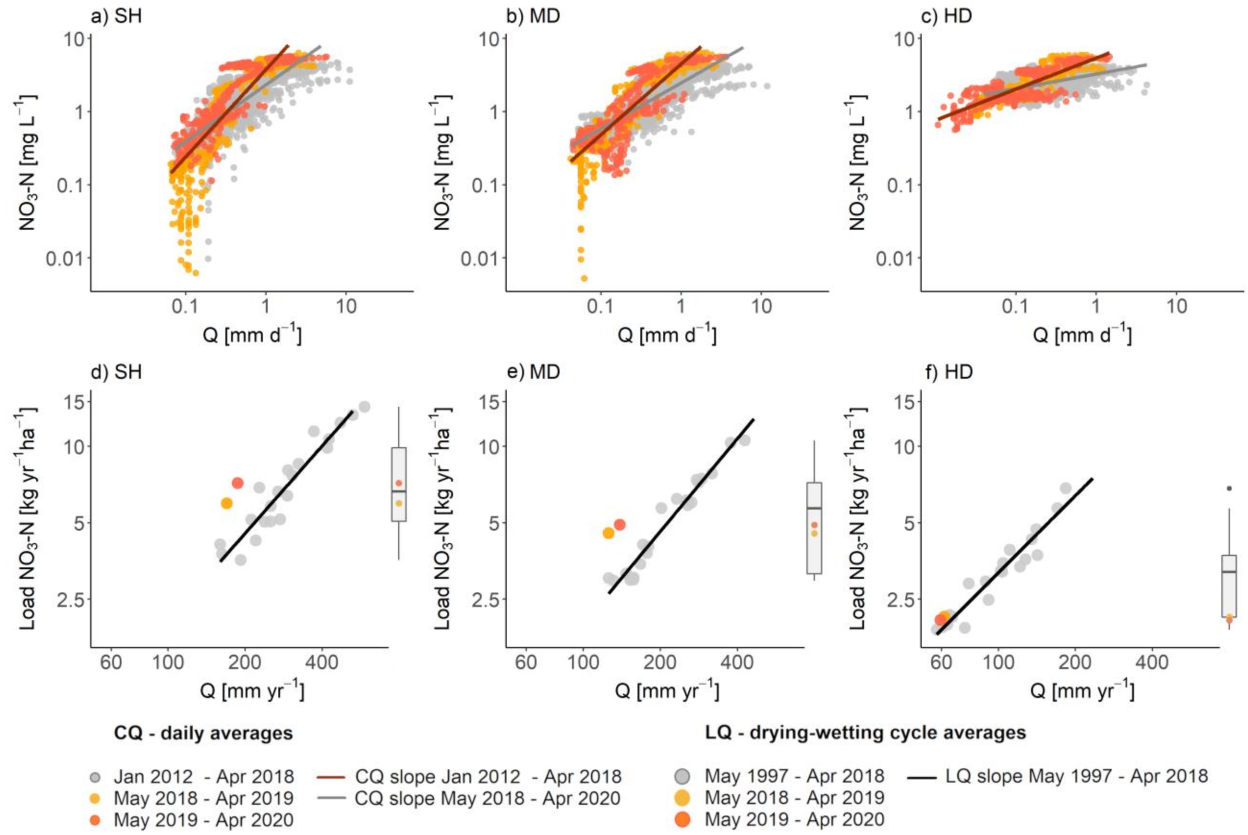

Figure 2 Concentration-discharge (C-Q) and load-discharge (L-Q) relationships for the three sub-catchments of the Selke catchment (SH, MD and HD). a-c) Daily averaged nitrate concentration and discharge data with log-transformed axes. The lines show the C-Q slope for daily averages before the multi-year drought (grey) and since the start of the multi-year drought (dark red). d-f) Drying-wetting cycle averages for loads and discharge in the log-log space since 1997. Black lines show the L-Q slope previous to the multi-year drought. Boxplots at the right side of each panel (d-f) show the distribution of data points within the pre-drought load range and drought cycles indicated as colored dots.

Median nitrate-N loads per area over the drying-wetting cycles 1997–2017 were 6.6 kg yr^{-1} ha^{-1}, 5.7 kg yr^{-1} ha^{-1} and 3.2 kg yr^{-1} ha^{-1} in SH, MD and HD, respectively. During the multi-year drought, nitrate-N loads were in a similar range in SH (6.0 and 7.2 kg yr^{-1} ha^{-1}, in 2018 and 2019 respectively) and lower but still within the interquartile range in MD (4.5 and 4.9 kg yr^{-1} ha^{-1}) (Figure 2d-f). They were clearly lower in HD with a load of 2.1 kg yr^{-1} ha^{-1} in both drying wetting cycles (Figure 2d-f).

In terms of L-Q relationships, nitrate-N loads increased with increasing discharge with an L-Q slope close to 1 in all sub-catchments (Figure 2d-f). During the drought cycles 2018 and 2019, loads exported from the upper Selke were clearly above the loads expected from the long-term L-Q relationship. So, relative to discharge that was naturally low during the drought, loads were unexpectedly high. More specifically, exported loads at SH were 2.2 and 2.9 kg ha^{-1} yr^{-1} higher in 2018 and 2019 than expected from the long-term L-Q relationship, and at MD loads were 1.9 kg ha^{-1} yr^{-1} higher in both years. In relative numbers, this is an increase by 58%-70%, compared to the predicted export from the L-Q relationship from previous years. In the lower Selke (HD) on the contrary, the difference between observed and expected nitrate-N export was marginal during the multi-year drought (0.2 kg ha^{-1} yr^{-1} in both drying-wetting cycles, equivalent to an increase by 10%). However, exported nitrate loads in the lower Selke have generally decreased since 2011 (Winter et al., 2021). Therefore, 2013–2017 loads are the once plotting clearly below the long-term L-Q slope (Figure 2d); as such, the L-Q relationships from the multi-year drought can be seen as slightly increased if compared to the most recent years only. To illustrate, exported nitrate loads at HD during the multi-year drought are around 0.5 kg ha^{-1} yr^{-1} higher than expected from the 2013–2017 L-Q relationship (Figure 2f).

3.2 Simulated internal nitrogen fluxes

The sub-catchment specific N fluxes, simulated via mHM-SAS and averaged over the drying-wetting cycles are summarized in Table 2. They show that particularly in the drying-wetting cycle starting in May 2018, which was the driest cycle of the multi-year drought (Figure 1b), N fluxes clearly differed from the long-term average (1997–2017). Notably, mineralization rates in 2018 increased by 23%, 39% and 67% in SH, MD and HD, respectively. In the same drying-wetting cycle, denitrification in the soils of the sub-catchments was 27%–34% lower than the long-term average, whereas plant uptake was reduced by around 10% in the upper Selke (SH and MD), but not in the lower Selke (HD), likely due to differences in the soil type (Table 1). N in the leachates were relatively low in both cycles (2018 and 2019), especially in MD and HD, due to the dry soil moisture content (Figure S1).

Table 2. Nitrogen (N) fluxes simulated via mHM-SAS, separately for the three Selke sub-catchments.

Site	Drying-wetting cycle	Mineralization [kg ha^{-1} yr^{-1}]	Denitrification [kg ha^{-1} yr^{-1}]	Plant uptake [kg ha^{-1} yr^{-1}]	Leachate [kg ha^{-1} yr^{-1}]
SH	May 1997 - April 2018	20.9 ±8.2	23.1 ±3.7	45.1 ±3.9	10.5 ±2.9
SH	May 2018 - April 2019	29.0	16.8	40.4	8.8
SH	May 2019 - April 2020	14.2	26.5	43.9	10.6
MD	May 1997 - April 2018	8.8 ±2.6	12.1 ±1.9	25.1 ±1.8	5.5 ±2.1
MD	May 2018 - April 2019	11.9	8.9	22.4	3.0
MD	May 2019 - April 2020	8.2	13.4	26.7	3.3
HD	May 1997 - April 2018	43.5 ±23.6	48.3 ±7.6	94.2 ±5.6	3.6 ±2.3
HD	May 2018 - April 2019	72.6	31.7	96.4	0.8
HD	May 2019 - April 2020	14.7	46.0	98.5	2.0

Note. Long-term time periods (May 1997–April 2018; grey background) show the average of drying-wetting cycle averages (12-month period starting in May) and their respective standard deviation (±).

3.3 Transit times and storage selection preference

Similar to nitrate concentrations and loads, the simulated a/b ratio for SAS functions (indicative of young versus old water preference) and median TTs showed a different behavior during the multi-year drought compared to previous years, with clear contrasts between upper and lower Selke (Figure 3). Upper Selke sub-catchments showed a young water preference (a/b ratio < 1) with shorter median TTs during the wet periods (January-April; median of 41 and 53 days in SH and MD, previous to the drought and median of 22 and 36 days during the drought). During dry periods (July-October) previous to the drought, the median of median TTs in the upper Selke was 2.5 and 6.7 yrs in SH and MD, respectively (Figure 3d-e). Nevertheless, more than half of all drying-wetting cycles still showed a young water preference even during dry periods (Figure 3a-b). However, during the dry periods of the multi-year drought, median TTs were very long (median of median TTs was 46 yrs in both sub-catchments) with a pronounced old water preference, particularly in 2018. Note that the maximum transit time in the simulations is restricted to the number of years since the start of simulations, which explains the July–December plateau (Figure 3). Long median TTs during the dry season can therefore be interpreted as >46yrs. This cutoff likely causes an underestimation of the median of previous years as well and creates some additional uncertainty in the absolute numbers. However, this does not affect the general result of exceptionally high median TTs during the dry periods in 2018–2020 compared to previous drying-wetting cycles (1997–2017).

In the lower Selke sub-catchment, there is a clear selection preference for old water throughout all drying-wetting cycles and periods (Figure 3c). Even during wet periods, median TTs were relatively long (median 20 yrs), compared to the upper Selke sub-catchments (Figure 3d-f). Similar to the upper Selke sub-catchments, median TTs during the dry periods in 2018 and 2019 were longer than normal with a median of 32 yrs compared to 24 yrs in previous drying-wetting cycles.

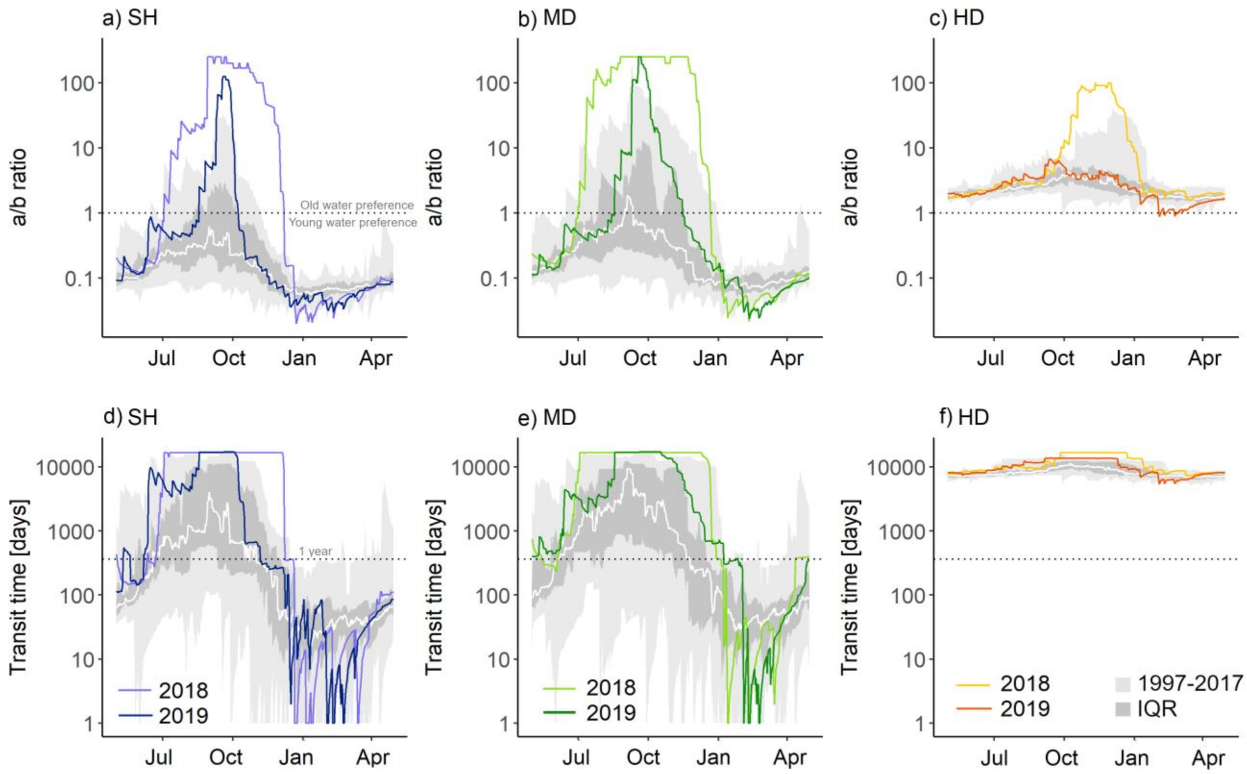

Figure 3 Simulated sub-catchment-specific water age selection preference (a-c) as the ratio of the fitted parameters a and b, and (d-f) median transit times given in days. Grey areas indicate the range of all pre-drought (1997–2017) drying-wetting cycles and their interquartile range and white lines the median of all pre-drought cycles. Colored lines indicate the multi-year drought with the two drying-wetting cycles starting in May 2018 and 2019.

3.4 Catchment retention capacity

In all cases, soils and catchments retained the largest part of N input (>0.8), most pronounced in HD, where retention capacity was always >0.9 (note that these values account for the nested catchment). On average, $N_{ret\text{-}soil}$ was 0.02-0.04 lower than N_{ret} (Figure 4a-f), which can be explained by additional N loss occurring during the transit of N from the leachates to the stream network. Both $N_{ret\text{-}soil}$ and N_{ret} show a clear decrease with decreasing drying-wetting cycle discharge averages in all sub-catchments. In the upper Selke (SH and MD), $N_{ret-soil}$ decreased with increasing discharge with a slope of -0.06, and N_{ret} decreased with a slope of -0.08 and -0.07. In the lower Selke, $N_{ret-soil}$ an N_{ret} decreased with increasing discharge with a slope of -0.03 and -0.02, respectively.

In the upper Selke, the relationship between N retention capacity and discharge during the multi-year drought (drying-wetting cycles 2018 and 2019) was clearly lower than that of previous cycles (1997-2017). N_{ret} and $N_{ret-soil}$ dropped by around 0.02 – 0.03 compared to the long-term regression line, which can be translated into 1.6-2.6 kg N ha^{-1} yr^{-1} that are not retained but exported. In the lower part of the catchment (HD), $N_{ret-soil}$ dropped by 0.01 in both drying-wetting cycles, whereas N_{ret} was very close to the long-term regression line (difference of 0.002).

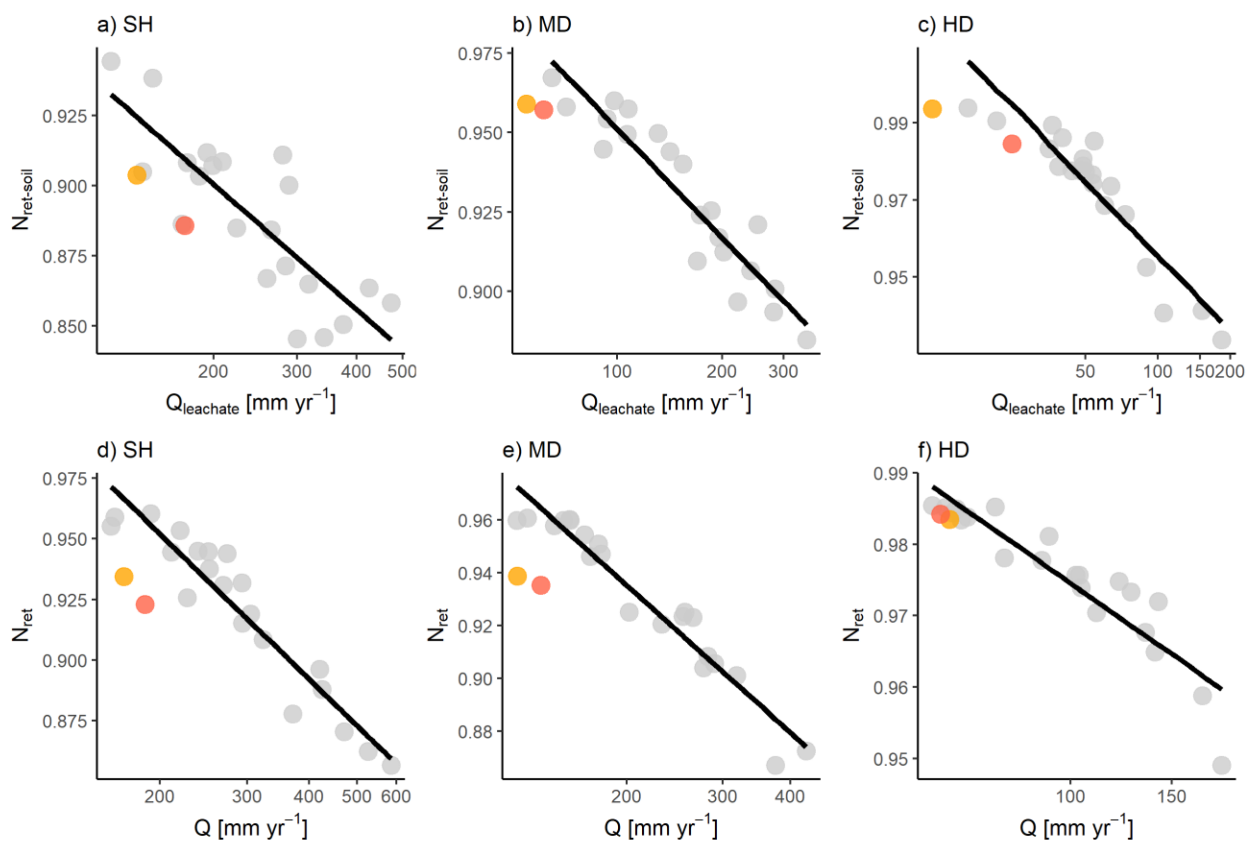

Figure 4 Relationship between the N retention capacity of soils ($N_{ret-soil}$) or catchments (N_{ret}) and log-scaled discharge (Q) at the nested catchment scale, given as drying-wetting cycle averages (12 month period starting in May). Black lines represent the regression line between N_{ret} or $N_{ret-soil}$ and log-transformed discharge prior to the multi-year drought (1997–2017).

4 Discussion

4.1 Inter-annual variability of nitrate concentrations

The presented results show that the multi-year drought spanning the years 2018 and 2019 and across Central Europe can have strong impacts on catchment water quality in terms of nitrate export. The increased inter-annual variability of nitrate export, with lower concentrations during the dry periods (July-October) and exceptionally high concentrations during the subsequent wet periods (January-April). It shows that the drought did not only affect nitrate fluxes in the soil leachates as discussed in the 2020 Nitrate Report from the Netherlands (National Institue for Public Health and the Environment (RIVM), 2021), but it can also propagate through catchments affecting in-stream nitrate concentrations at the catchment outlet within a relatively short time period. These results are in close agreement with previous studies that similarly reported low nitrate concentrations during a drought and high concentrations during subsequent rewetting (e.g. Górski et al., 2019; Morecroft et al., 2000; Mosley, 2015). Such high nitrate concentrations following drought pose a threat to water quality and the health of aquatic ecosystems (Carpenter et al., 1998).

The shift in the C-Q relationship towards a steeper C-Q slope (Figure 2a-c) reflects that the intensification in the seasonality of nitrate export was not solely driven by low discharge due to the drought. Instead, nitrate concentrations during dry periods were even lower than expected from the C-Q relationship and higher during wet periods, showing an increased inter-annual variability compared to that of discharge. This increased concentration variability indicates that biogeochemical and hydrological processes within the catchment changed during the drought, which are affecting the availability and transport of nitrate. The exceptionally low nitrate concentrations during the dry periods of the multi-year drought can be explained by the strong old water preference during these periods (Figure 3a-c). Nguyen et al. (2022) showed that old water in the upstream Selke catchment is considerably affected by denitrification (Damköhler number >10), which can explain the very low nitrate concentrations. The pronounced old water preference in the upstream catchment during the multi-year drought is in agreement with a study from X. Yang et al. (2021). Using water stable isotopes as age tracers in a small (1.44 km^2) headwater catchment of the Selke catchment, they found a large increase in stream water ages, driven by a decrease in younger surface runoff and stream discharge. Differences in the median TTs between this and our study (8 yrs and 46 yrs) can be explained by the difference in the catchment area of around two orders of magnitude and by uncertainty in the estimation of longer TTs, especially as annually cycling isotope tracers show only limited applicability towards long TTs (Seeger & Weiler, 2014).

In the downstream sub-catchment, the potential for denitrification in groundwater is very low (Damköhler number <1; Nguyen et al., 2022). Therefore nitrate concentrations do not significantly decrease with water ages and could, instead, still show signs of historically higher N inputs (Carolin Winter et al., 2021). Hence the low nitrate concentrations during the dry periods are likely driven by the upstream catchment area. However, also the efficiency of instream N uptake is enhanced with higher temperatures (Nguyen et al., 2022), which is an additional factor explaining part of the low nitrate concentrations during drought, even more so in the lowland part of the catchment where light availability is higher and flow velocity is reduced (Rode et al., 2016). Therefore, a combination of both, dilution of old and largely denitrified water from upstream and increased in-stream uptake efficiency, mainly downstream, are responsible for the low nitrate concentrations during the dry periods 2018 and 2019.

While predominately old (pre-drought) water was exported during dry periods, the rates of denitrification and plant N uptake from the soils during the drying-wetting cycle 2018 decreased across the catchment. This decrease can be attributed to the very low soil moisture during the drought that inhibits denitrification (as implemented in the soil routines in HYPE; Lindström et al., 2010) and plant growth. Together with the deactivation of shallow flow paths, the reduced N removal can lead to an accumulation of inorganic N in the catchment soils. Similarly, the rewetting of dry soils in autumn can cause a peak in mineralization that transforms accumulated organic material into mobile inorganic N (Campbell & Biederbeck, 1982; Haynes, 1986), in agreement with the simulated high mineralization rates for the drying-wetting cycle 2018 (Table 2). Furthermore, Maxwell et al. (2022) showed that the rate of depolymerization (i.e., breaking down of large organic-N molecules into smaller ones), which is rate-limiting for mineralization (Jan et al., 2009; Schimel & Bennett, 2004), increased under drought in a montane grassland in Austria. With the shift towards younger water fractions and median TTs < 2 months during the wetting and wet periods in the upstream sub-catchments, the accumulated and mineralized N pool can be rapidly transported to the stream network, which can explain the high nitrate-N concentration peaks (Figure 1c, 2a-c). In contrast, in the downstream sub-catchment, old water fractions dominate all year round (Figure 3f), and therefore most of the accumulated N cannot reach the stream network within the subsequent wetting- and wet period. Note that the 'wetting-' and 'wet periods' 2018 and 2019 are part of the multi-year drought, and in relative terms were also exceptionally dry compared to previous wetting and wet periods, but they typically show a higher catchment wetness compared to 'dry periods' due to pronounced hydroclimatic seasonality over the study region (Sinha et al., 2016; J. Yang et al., 2018).

The changes in N cycling were only evident for the drying-wetting cycle in May 2018, not for the one starting in May 2019 that was dry, but not as dry as in 2018 (Figure 1b, Table 2). This indicates that the described perturbation in N cycling does only occur under severe drought conditions. In a small

(0.6 km²) catchment, Burt et al. (2015) found evidence that post-drought mineralization can supply sufficient N to sustain increased nitrate concentrations through the next high-flow season. Hence, such drought legacies might have also built up in the larger Selke catchment and impact nitrate export in subsequent years. One indication for this is that although the drying-wetting cycle in 2018 was drier and had a stronger impact on soil-N fluxes (Table 2), nitrate export dynamics for the drying-wetting-cycle in 2019 were comparable to the ones observed in 2018 (Figure 2).

4.2 Sub-catchment-specific contributions to the intgral nitrate response to the drought

The spatial configuration of land use and other characteristics within a catchment can play an important role for nitrate export from the entire catchment and its temporal variability (Casquin et al., 2021; Dupas et al., 2019; Carolin Winter et al., 2021). In the Selke catchment, previous studies showed that the upstream area contributed disproportionally to annual nitrate loads, despite having a lower N input; whereas the downstream part contributed most to nitrate export during low-flow periods (Nguyen et al., 2022; Winter et al., 2021). During the multi-year drought, this difference in the sub-catchment-specific contributions became even more pronounced. Water from the upstream catchment area during the dry periods was very low in nitrate and therefore had the potential to dilute the higher concentrations from the downstream agricultural areas. Nonetheless, the contribution from the downstream area maintained nitrate-N concentrations at levels >1 mg L^{-1} even under low flow conditions during summer, when aquatic ecosystems are most vulnerable to eutrophication (Jeppesen et al., 2010; Whitehead et al., 2009). With rewetting, the ability of the forested upstream area to dilute downstream nitrate concentrations has been almost entirely lost, as nitrate concentrations reached similar or even higher levels than the downstream area (Figure 1c, 2a-c). Therefore, the observed changes in immediate response to the drought with regard to the seasonal dynamic of nitrate concentrations at the catchment outlet were almost entirely controlled by the upstream area due to its shorter TTs and young water preference. The sub-catchment differences in median TTs and storage selection preferences can be explained by differences in landscape characteristics within the catchment. The upstream area is located in the Harz Mountains with higher precipitation, steeper slopes and shallower soils and in turn a faster transit of water and shorter flow paths to the streams, which typically results in faster TTs and is reflected in a selection preference for younger water (Jiang et al., 2014; Tetzlaff et al., 2009; Table 1).

Considering the important role of the upstream, largely forested (87.7%; Table 1), part of the catchment for the overall nitrate export, one should also consider the potential long-term impacts of the multi-year drought on forest ecosystems. Schuldt et al. (2020) showed that especially the dry summer in 2018 caused severe tree mortality in Central Europe, whereas Schnabel et al. (2021) could show in a German floodplain forest that the drought impact on trees was even stronger in 2019, due to an accumulated drought effect. Moreover, there is evidence that droughts can negatively affect tree growth several years after the actual drought event (Anderegg et al., 2013). Such forest dieback can cause increased nitrate concentrations (Kong et al., 2022; Mikkelson et al., 2013), but its effect on water quality can again be delayed for several years (Huber, 2005). The strongest modelling scenario, with a 100% decrease in N uptake from forested areas, showed up to 45% increase in simulated nitrate-N concentrations in the rewetting phase of 2019 (see supplements Text S2, Figure S5). While a 100% decrease in N uptake is not a realistic scenario, it can give an indication of possible future impacts of forest dieback on nitrate export and shows that ongoing and future forest dieback as a drought legacy (Anderegg et al., 2013) should be considered as an additional drought-induced threat to stream water quality.

4.3 Exported nitrate loads and catchment retention capacity

The overall discharge during the multi-year drought was very low. Nitrate loads, however, were only low in the downstream part of the catchment (HD). In the upstream area (SH and MD), nitrate loads were up to 70% higher than expected from the long-term L-Q relationship. This can be explained by the exceptionally high nitrate concentrations during the wetting- and wet periods of the multi-year drought (November-April, Figure 2). As discussed above, these high nitrate concentrations are the result of reduced plant uptake and denitrification of N in the soils during the previous dry periods and short TTs during wet periods. Hence the increase of exported loads relative to discharge, but also relative to N input to the catchment, show that under severe drought a catchment can lose a part of its functionality to retain N. We differentiate between the capacity of the entire catchment (or sub-catchment) and the catchment soils to retain N (N_{ret} and $N_{ret\text{-}soil}$), which can both be affected by drought, but at different, catchment specific time scales as discussed in the following.

We identified two drivers of a decrease in N_{ret} and $N_{ret\text{-}soil}$, i.e., an increase in discharge and the multi-year drought (Figure 5). The discharge-driven decrease in the N retention capacity can be explained by hydrologic mobilization and transport dominating over biogeochemical processes such as N uptake and removal. In contrast, under dry (but not drought) conditions, the role of nitrate uptake and removal gains in relative importance and with that the retention capacity of the catchment increases. However, extreme climate events, such as the 2018–2019 multi-year drought can cause a perturbation of those biogeochemical processes, if soils are too dry to maintain functionality in terms of N cycling. The decrease of N uptake and removal can result in a divergence from the retention-discharge relationship, as it was apparent for the soil leachates in all three sub-catchments (Figure 4a-c) and also for other years with very low discharge (Figure 4, 5). Until the end of the data record available for this study, no recovery from this loss in $N_{ret\text{-}soil}$ could be observed, but also there has not yet been a specifically wet year since the drought in 2018. Therefore, the resilience of the sub-catchments (Hashimoto et al., 1982), in terms of their ability to recover from such loss in catchment-soil N retention capacity after the multi-year drought, remains uncertain.

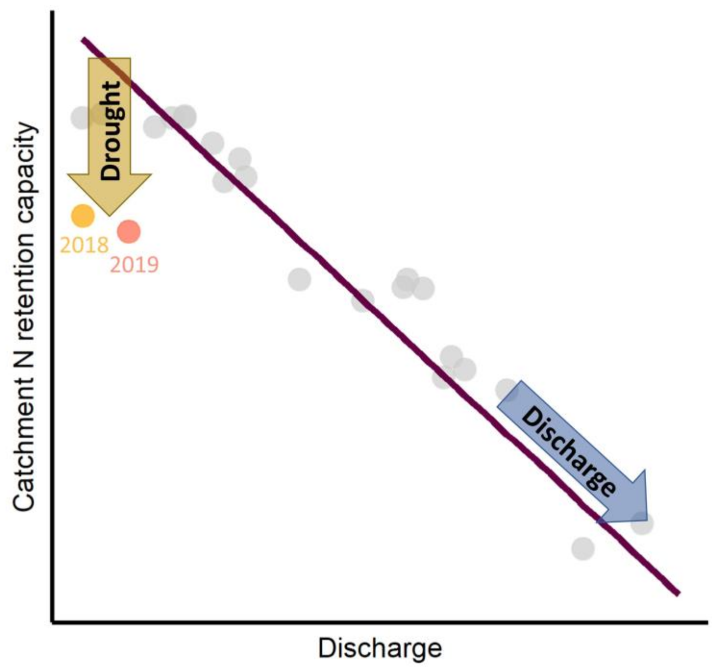

Figure 5 Conceptual framework of the capacity of a catchment to retain N in relation to average discharge. The framework illustrates two potential drivers that cause a reduction in the catchment retention capacity. Those are either an increase in discharge (blue arrow) or a drought event (yellow arrow). Data was taken from the gauge at MD that gives an integrated signal of the upper Selke catchment, which is characterized by a relatively fast reaction in riverine nitrate export to drought.

When looking at N export at the sub-catchment gauges, the decrease in the catchment retention capacity is only evident in the upstream sub-catchments. This difference in catchment-soil and overall catchment retention capacity can be explained by different sub-catchment-specific TTs. Whereas short median TTs in the upstream sub-catchments during the wet period allow for a rapid response of stream nitrate concentrations to drought, long median TTs in the downstream sub-catchment (even under wet conditions) dampened such a fast drought response. Instead, increased N in the soil leachates together with long median TTs potentially generate a hydrological N legacy that might become visible at the catchment outlet years to decades later (Van Meter et al., 2016; Van Meter & Basu, 2015), especially under the assumption of a low denitrification potential in groundwater (Nguyen et al., 2022).

5 Conclusion

The presented study is among the first to assess the impact of the 2018-2019 multi-year drought in Central Europe on nitrate concentrations in a heterogenous mesoscale catchment. We found that such an exceptional drought can have significant impacts on water quality in terms of nitrate concentrations, load export and catchment N retention capacity.

C-Q relationships revealed an increased inter-annual variability in nitrate concentrations, with low concentrations during dry periods and exceptionally high concentrations during wet periods, mainly driven by the more responsive upstream part of the catchment. Low concentrations could be explained by a selection preference for old and largely denitrified water, whereas high concentrations reflect a reactivation of shallow and young flow paths that transport accumulated N from the catchment soils. The accelerated inter-annual variability was not only driven by a stronger temporal shift in N transport but also by a decrease in N uptake and removal via denitrification and plant uptake during dry periods. Thus also the overall provision of exportable nitrate increased, which was reflected in a decrease in the capacity of the catchment soils to retain N and an increase in nitrate loads at the (sub-)catchment outlets relative to the long-term L-Q relationship. We identified two drivers for a decrease in the catchment- and catchment-soil N retention capacity i) a decrease with increasing discharge that reduces the relative importance of soil N cycling compared to hydrological transport, or ii) a severe drought that decreases N cycling by drying out the catchment soils. The subsequent transport of increased nitrate leaching from the soil zone to the stream network is dependent on the sub-catchment specific TTs and the denitrification potential in the groundwater. In catchments with short median TTs, the catchment-retention capacity can decrease within the observation period. Instead, long transit times can dampen such a short-term response, but potentially form a hydrological N legacy that might become visible at the catchment outlet years to decades later.

Hotter multi-year droughts are likely to become more frequent and more prolonged with climate change (Hari et al., 2020; IPCC, 2018). Our study shows that such climatic extremes are a threat not only to water quantity but also to water quality in terms of nitrate pollution, as they can reduce the capacity of the catchment soils and entire catchments to retain N. Moreover, such droughts have the potential to override positive effects of measures to improve water quality (e.g. two-stage ditches; Bieroza et al., 2019). Consequently, droughts need to be considered as an additional risk to water quality that can intensify the existing anthropogenic pressures. To counteract the additional risk, one should consider intensified restrictions on manure and fertilizer applications. Furthermore, our study emphasizes the role of catchment heterogeneity and TTs for a catchment's vulnerability to drought impacts on nitrate export and the timing of such impacts. Whereas fast-reacting sub-catchments with short TTs can contribute to immediate drought responses, slowly-reacting sub-catchments (long TTs) might build up drought-induced N legacies that could impact future water quality on the long term, depending on the subsurface denitrification potential. We could show that a severe drought can potentially amplify such sub-catchment specific differences. The increased variability of nitrate export on both temporal and spatial scales calls for an increased spatiotemporal frequency of water quality monitoring and more site-specific management plans for site-specific problems. This also means that more studies on drought effects on water quality in different catchments and also for other pollutants are needed to assess the additional risk that is posed by longer and hotter droughts.

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Data availability statement

The source code and input data for mHM-SAS are available under https://git.ufz.de/nguyenta/mhm-sas and https://git.ufz.de/yangx/mHM-Nitrate. The raw discharge data can be downloaded from the State Office of Flood Protection and Water Quality of Saxony Anhalt (LH) under https://gld.lhw-sachsen-anhalt.de/. The raw meteorological data can be downloaded from Germanys National Meteorological Service (DWD) at https://opendata.dwd.de/climate_environment/CDC/grids_germany/daily/regnie/ and gridded products based on Zink et al. (2017) are available under https://www.ufz.de/index.php?en=41160. Raw nitrate-N concentration data are archived in the TERENO database, available upon request through the TERENO-Portal (www.tereno.net/ddp).

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