Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales

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Abstract

Defining effective measures to reduce nitrate pollution in heterogeneous mesoscale catchments remains challenging if based on concentration measurements at the outlet only. One reason is our limited understanding of the sub-catchment contributions to nitrate export and their importance at different time scales. While upstream sub-catchments often disproportionally contribute to runoff generation and in turn to nutrient export, agricultural areas, which are typically found in downstream lowlands, are known to be a major source for nitrate pollution. To disentangle the interplay of these contrasting drivers of nitrate export, we analyzed seasonal long-term trends and event dynamics of nitrate concentrations, loads and the concentration-discharge relationship in three nested catchments within the Selke catchment (456 km^2), Germany. The upstream sub-catchments (40.4 % of total catchment area, 34.5 % of N input) had short transit times and dynamic concentration-discharge relationships with elevated nitrate concentrations during wet seasons and events. Consequently, the upstream sub-catchments dominated nitrate export during high flow and disproportionally contributed to overall annual nitrate loads at the outlet (64 %). The downstream sub-catchment was characterized by higher N input, longer transit times and relatively constant nitrate concentrations between seasons, dominating nitrate export during low flow periods. Neglecting the disproportional role of upstream sub-catchments for temporally elevated nitrate concentrations and net annual loads can lead to an overestimation of the role of agricultural lowlands. Nonetheless, in agricultural lowlands, constantly high concentrations from nitrate legacies pose a long-term threat to water quality. This knowledge is crucial for an effective and site-specific water quality management.

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Key Points:

- Analyzing the CQ-relationship across time scales allows to disentangle the impact of catchment heterogeneity on nitrate export.
- Mountainous upstream sub-catchments can dominate nitrate export during high flows and disproportionally contribute to nitrate loads.
- Agricultural downstream sub- catchments can dominate nitrate export during low flow and pose a long-term threat to water quality.

Abstract

Defining effective measures to reduce nitrate pollution in heterogeneous mesoscale catchments remains challenging if based on concentration measurements at the outlet only. One reason is our limited understanding of the sub-catchment contributions to nitrate export and their importance at different time scales. While upstream sub-catchments often disproportionally contribute to runoff generation and in turn to nutrient export, agricultural areas, which are typically found in downstream lowlands, are known to be a major source for nitrate pollution. To disentangle the interplay of these contrasting drivers of nitrate export, we analyzed seasonal long-term trends and event dynamics of nitrate concentrations, loads and the concentration-discharge relationship in three nested catchments within the Selke catchment (456 km²), Germany. The upstream sub-catchments (40.4 % of total catchment area, 34.5 % of N input) had short transit times and dynamic concentration-discharge relationships with elevated nitrate concentrations during wet seasons and events. Consequently, the upstream sub-catchments dominated nitrate export during high flow and disproportionally contributed to overall annual nitrate loads at the outlet (64.2 %). The downstream sub-catchment was characterized by higher N input, longer transit times and relatively constant nitrate concentrations between seasons, dominating nitrate export during low flow periods. Neglecting the disproportional role of upstream sub-catchments for temporally elevated nitrate concentrations and net annual loads can lead to an overestimation of the role of agricultural lowlands. Nonetheless, in agricultural lowlands, constantly high concentrations from nitrate legacies pose a long-term threat to water quality. This knowledge is crucial for an effective and site-specific water quality management.

Plain Language Summary

To efficiently remove nitrate pollution we need to understand how it is transported, mobilized and stored within large and heterogeneous catchments. Former studies show that upstream catchments often have a disproportional impact on nutrient export, while agriculture, a major nitrate source, is often located at downstream lowlands. To understand which parts of a catchment contribute most to nitrate export and when, we analyzed long-term (1983-2016) and high-frequency (2010-2016) data in the Selke catchment (Germany) at three locations. The mountainous upstream part dominated nitrate transport during winter, spring and rain events. It had a surprisingly high contribution to annual nitrate loads. The agricultural downstream part of the catchment dominated nitrate export during summer and autumn with relatively constant concentrations between seasons. Here, nitrogen inputs need more than a decade to travel through the subsurface of the catchment, which causes a time lag between measures to reduce nitrate pollution and their measurable effect. The resulting storage of nitrate in the groundwater threatens drinking water quality for decades to come. While the role of agricultural lowlands for nitrate export can be overestimated if neglecting the disproportional role of upstream sub-catchments, their impact poses a long-term threat to water quality.

1 Introduction

High nitrate concentrations in ground- and surface water are a long-known but still widespread problem in most developed countries (Bouraoui & Grizzetti, 2011; Kohl et al., 1971; Rockström et al., 2009). These high concentrations pose a threat to our drinking water quality and the integrity of aquatic ecosystems (Camargo & Alonso, 2006; Majumdar & Gupta, 2000). To most efficiently reduce nitrate pollution, a detailed understanding of the catchment-internal processes that drive nitrate mobilization, transport, storage and decay is needed. While good knowledge about these processes exists for rather uniform headwater catchments, understanding those in spatially more heterogeneous and complex mesoscale catchments (10^1 - 10^4 km², Breuer et al., 2008) is yet an open challenge, but vital for identifying management options. Upstream sub-catchments, on the one hand, often have a disproportional contribution to runof generation due to their higher drainage density and in turn they often disproportionally contribute to nutrient mobilization and transport (e.g. Alexander et al., 2007; Dodds & Oakes, 2008; Goodridge & Melack, 2012). Agricultural areas, on the other hand, are known to be a major source area for nitrate pollution (e.g. Padilla et al., 2018; Strebel et al., 1989). A typical setting for many mesoscale catchments in European uplands is, however, an elevated upstream area with no or a small percentage of agricultural land use and a downstream lowland area where agricultural land use dominates (e.g. Krause et al., 2006; Montzka et al., 2008). Hence, the different upstream and downstream sub-catchments can have quite different nitrate export dynamics, which are both relevant for nitrate export from the entire catchment and which may operate at very different times and time-scales. Their specific contribution, however, remains widely unknown if measuring only the integrated signal of nitrate export at the catchment's outlet, which makes it difficult to localize important source zones of nitrate and to identify important driving forces for their mobilization. To solve this issue, nested catchment studies are a promising approach to shed light on the contribution from sub-catchments to nitrate export (e.g. Dupas et al., 2017; Ehrhardt et al., 2019). They enable to analyze changes in nitrate transport along the river and to connect these changes to the specific characteristics of upstream and downstream sub-catchments and to interpret the integrated observations of concentration, Q and loads at the catchment outlet.

1.1 Time scales of nitrate export

The dynamics of water quality can be assessed on various time scales, which all have their specific relevance for understanding nitrate export dynamics at catchment scale. Long-term data are indispensable to assess trends in water quality over time and to assess transit times (TTs) and legacy stores, which can delay or buffer the catchment response to solute input at the catchment outlet (Dupas et al., 2016; Hirsch et al., 2010; Van Meter et al., 2017). Here, we refer to TTs as the time lag between a solute being introduced into the catchment and its riverine export. TTs of nitrate can vary between <1 year and up to >50 years, strongly dependent on the catchment characteristics and dominant flow paths (Ehrhardt et al., 2019; Van Meter et al., 2017). Legacy stores refer to the mass of solute – in our case nitrate – that has been retained and accumulated in the catchment. In the case of nitrate they are separated in organic N retained in the soil (biogeochemical legacy) and in inorganic N that is moving in the groundwater with long TTs (hydrological legacy). A precise understanding of these processes – TTs and legacy stores – is still missing. However, this knowledge is crucial to understand the response of riverine nitrate concentrations to land use changes and the time scale between measures to reduce nitrate reduction and their measurable success. Moreover, understanding the controls on the long-term persistence of pollutants - such as nitrate - within catchments was just recently framed to be one of the major unsolved problems in hydrology (Blöschl et al., 2019).

Long-term data are most often available at a low frequency (weekly to monthly), because methods to continuously measure high-frequency nitrate concentrations have been developed only recently (Burns et al., 2019). While these long-term low-frequency data are appropriate for the identification of long-term trends, TTs and legacy stores (e.g. Ehrhardt et al., 2019; Hirsch et al., 2010), the analysis of event dynamics can only be conducted with high-frequency data (Burns et al., 2019). The time scale of single events, however, is especially important for the analysis of nitrate dynamics, because most of the annual nitrate load to the stream is transported during events (Bernal et al., 2002; Inamdar et al., 2006). Event dynamics of nitrate concentrations (C) and Q can shed light on mobilization and transport processes that are masked if looking at long-term trends only (Duncan et al., 2017; Rose et al., 2018). For example, Dupas et al. (2016) found chemostasis (variability of nitrate concentrations is low compared to that of Q and there is no significant directional relationship between C and Q) in long-term trends in a mesoscale catchment, while dynamics at the scale of single discharge events conversely showed a decrease of nitrate concentrations with increasing Q. They argued that these event-scale patterns are one of the main drivers for the uncertainty in annual load estimations. Moreover, both long-term trends and event dynamics often show a strong seasonality (e.g. Dupas et al., 2017), which should be analyzed in parallel to accurately assess nitrate export patterns across time scales. Consequently, a combination of analyses of all - long-term trends, event dynamics and their seasonality - is needed to address the knowledge gap in driving forces of nitrate export dynamics.

1.2 Concentration-discharge relationship

The concentration-discharge relationship (CQ-relationship) is a simple data-driven concept that is commonly used to investigate export dynamics of nitrate or other solutes at various spatial and temporal scales (e.g. Godsey et al., 2009; Musolff et al., 2015; Rose et al., 2018). In general, the CQ-relationship allows to differentiate between three different export regimes: i) chemodynamic with accretion pattern, ii) chemodynamic with dilution pattern and iii) chemostasis (Godsey et al., 2009; Musolff et al., 2017). Export regimes i) and ii) are both summarized under the term “chemodynamic”, which means that a solute’s concentration variability is comparable or higher than the variability of Q, with concentrations either increasing (accretion) or decreasing (dilution) with increasing Q. Accretion patterns are generally explained by additional source zones getting connected during higher flow conditions, while dilution patterns are observed when higher Q causes a dilution of instream solute concentrations without further source zone activation (Basu et al., 2010). Chemodynamic nitrate export has often been found in relatively natural systems with no or only a small percentage of agricultural land use or urban areas, where nitrate sources are not ubiquitously available (Basu et al., 2010; Goodridge & Melack, 2012). On the contrary, chemostasis indicates constant nutrient concentrations in-stream that are not significantly correlated to Q and have a considerably lower variability (Basu et al., 2010; Bieroza et al., 2018). This pattern often emerges in catchments with a spatially uniform distribution of abundant solute sources, such as nitrate in agricultural areas, leading to a relatively constant release of solutes to the stream network (Basu et al., 2010; Bieroza et al., 2018). To assess the directional relationship between C and Q, Godsey et al. (2009) proposed a power law relationship between C and Q with the corresponding slope between ln(C) and ln(Q) – termed the CQ-slope. Subsequently, Thompson et al. (2011) established the CV_C/CV_Q metric to express the variability in C relative to the variability in Q (with CV being the coefficient of variation). Jawitz & Mitchell (2011) and Musolff et al. (2015) combined both approaches to a single conceptual framework as CQ-slope and CV_C/CV_Q are mathematically linked.

So far, top down assessments of catchment export dynamics have mainly been focused on observations at the catchment outlet, largely neglecting catchment internal variabilities. Here we see a need for research on how the role of internal organization of catchments (i.e., nested sub-catchments) in term of nitrate inputs, reactive transport in the subsurface and the stream network, shapes the outlet observation seasonally and under varying flow conditions. To address this research gap, we conduct a nested catchment study in the mesoscale Selke catchment, which is an intensively monitored research site (Jiang et al., 2014; Wollschläger et al., 2017) and provides the unique opportunity to study long-term trends as well as event-scale nitrate concentrations and loads. We analyzed i) seasonal long-term trends and ii) event dynamics of nitrate concentrations, loads and the CQ-relationship for each nested sub-catchment. Furthermore, we iii) calculated sub-catchment specific transit time distributions (TTDs) from N inputs and riverine nitrate outputs to discuss the potential extent and effect of legacy stores and their impact on nitrate export dynamics and long-term trends. With this comprehensive approach, we aim at a better understanding of how nested sub-catchments i) compose the integrated response of nitrate concentrations, loads and CQ-relationships observed at the catchment outlet at different times scales (long-term, seasonal and event scale); and ii) affect the response of nitrate concentrations, loads and CQ-relationships to changes in N input.

2 Materials and Methods

2.1 Catchment description

The Selke catchment is located in the Harz Mountains and the Harz foreland of Saxony-Anhalt, Germany (Fig.1). It is a sub-catchment of the Bode catchment, which is an intensively monitored catchment within the network of TERrestrial ENvironmental Observatories (TERENO, Wollschläger et al., 2017). Within the Selke catchment, we consider three nested sub-catchments (Fig. 1), delineated by the following gauging stations: i) Silberhütte, with a drainage area of 105 km², ii) Meisdorf (184 km²) and iii) Hausneindorf (456 km²). Daily average specific Q is 0.90 mm d^{-1}, 0.65 mm d^{-1} and 0.32 mm d^{-1} for Silberhütte, Meisdorf and Hausneindorf, respectively.

Silberhütte and Meisdorf are located in the Harz Mountains and drain the upper part of the catchment. In the following, these two nested sub-catchments are summarized as the *upper Selke*. In the upper Selke, forests are the dominant land use (73 %), followed by agriculture (21 %), which is mainly located upstream of Silberhütte. Soils are dominated by Cambisols overlaying low permeable schist and claystone, resulting in relatively shallow groundwater systems (Jiang et al., 2014). Long-term mean precipitation is 694 mm a^{-1} (based on the gridded German Weather Service (DWD) datasets from Zink et al., 2017). There are three wastewater treatment plants (WWTPs) located in the upper Selke, of which one is located at the upper part draining to the gauge in Silberhütte.

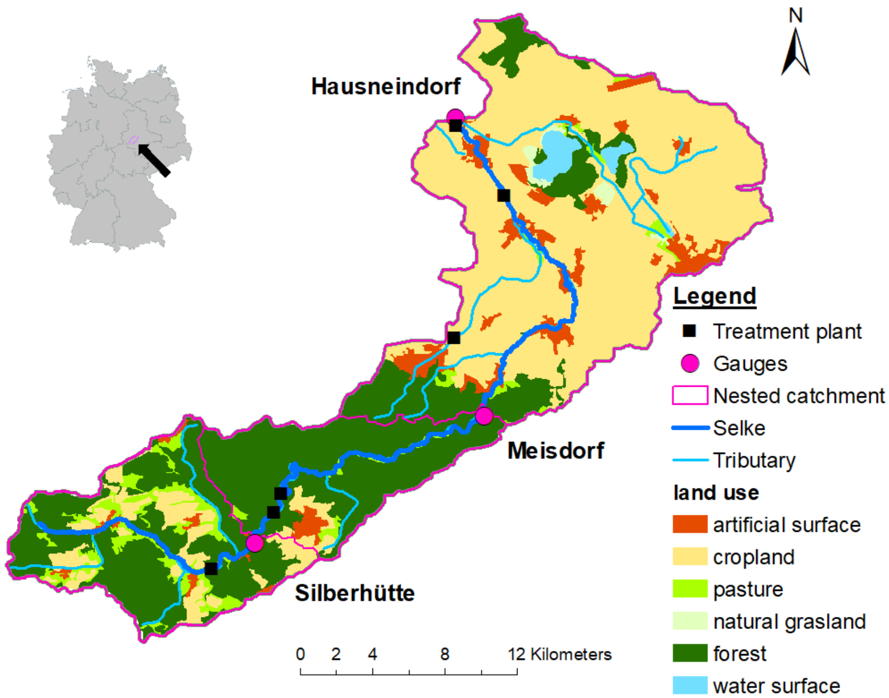

Figure 1. Land use map of the Selke catchment with gauging stations (pink dots) and wastewater treatment plants (black squares).

The transition from the upper to the lower part of the catchment marks a distinct change in landscape characteristics. The downstream part of the catchment is termed *lower Selk*e from here on. It is a fertile plain with productive soils in the foreland of the Harz Mountains dominated by agriculture (65 %) mainly in the form of arable crops. The long-term average precipitation is 519 mm. Soils are dominated by Chernozems above quaternary sediments and mesozoic sedimentary rocks (sandstone and limestone) that allow for considerably deeper groundwater systems, compared to the upper Selke (Jiang et al. 2014).

Another three WWTPs are located in the lower Selke, of which one is at a tributary to the Selke (Fig. 1). Furthermore, an opencast mine is located in the northeastern part of the lower Selke. After closing down the mine in 1991, Selke water was abstracted from 1998 on to fill the open pit with an average annual abstraction rate of 3.1 million m^3. In 2009 a landslide occurred from the banks of the pit-lake so that since 2010 water from the filling pit has been pumped into the Selke in order to stabilize the banks (annual rate of 10.4 million m^3).

Note that due to the nested catchment structure, all measurements from the lower Selke are an integrated signal from the upper and the lower Selke.

2.2 Data basis

Daily Q data are publicly available for all gauges from 1983 to 2016 on a daily basis and on a 15 min basis since 2010, provided by the State Office of Flood Protection and Water Management of Saxony-Anhalt (LHW; Fig. S1). Long-term data of nitrate concentrations for all three gauges were provided by the LHW from 1983 to 2009 and by the Helmholtz Centre for Environmental Research (UFZ) from 2010 to 2016, collected as grab samples at a biweekly to bimonthly basis and published previously by Yang et al. (2018). Continuous high-frequency data of nitrate were measured in more recent years at 15 min intervals, using TriOS ProPS-UV sensors, described in more detail by Rode et al. (2016). The data were collected by the UFZ as part of the TERENO monitoring program from 2013 to 2016 for Silberhütte, October 2010 to 2016 for Meisdorf and July 2010 to 2016 for Hausneindorf. Slight variations in the timing of measurements between Q and nitrate concentrations were corrected by aggregation to equal 15 min intervals.

2.3 Long-term trends of concentrations and concentration-discharge relationships

All analyses were carried out within the R software environment (R Core Team, 2019). Long-term trends in nitrate concentrations and loads were calculated using *'Weighted Regression on Time, Discharge and Season'* (WRTDS, Hirsch et al., 2010), implemented in the R-package *'Exploration and Graphics for RivEr Trends*' (EGRET). WRTDS requires time, Q and season as explanatory variables to simulate daily concentrations from sporadic measurements over long time series (Hirsch et al., 2010):

$$ln(C_i) = ß_{0,i} + ß_{1,i}t_i + ß_{2,i}ln(Q_i) + ß_{3,i}\, sin(2\pi t_i) + ß_{4,i}\, cos(2\pi t_i) + \varepsilon_i \qquad (1)$$

where subscript *i* indicates the specific day, *C* is the concentration in mg L^{-1}, *t* is the time in decimal years, *Q* is the discharge in $m^3\ s^{-1}$, $ß_1 – ß_4$ are fitted coefficients with $ß_2$ representing the CQ-slope and ε is an error term.

The regression in WRTDS is weighted via the tricube weight function (Tuckey, 1977), which gives an increasing relevance to observations close to the estimation point in terms of time, Q and season (Hirsch et al., 2010). Flow normalization is applied for an estimation of concentration that is unbiased by daily Q variation. Here, concentrations are flow-normalized (FN) in such a way that measured Q on a given date is assumed to have the same probability as all observed Q values of that date in all other years in the record. Thus, for every single date in the time series, eq. 1 is applied once with every Q record that was measured on the same date in all years and these values are finally averaged to one single FN concentration estimate for the specific day.

In order to analyze long-term trends of the CQ-relationship, we used a modification of the original EGRET codes to extract the daily parameter $ß_2$ from eq. 1, which was developed by Zhang et al. (2016). The parameter $ß_2$ represents the relationship between ln(C) and ln(Q) (CQ-slope), which enables a differentiation between export regimes: i) chemodynamic with an accretion pattern ($ß_2 > 0.1$); ii) chemodynamic with a dilution pattern ($ß_2 < -0.1$); and iii) chemostatic ($-0.1 < ß_2 < 0.1$). We chose the threshold for chemostatic at -0.1 and 0.1 according to Zhang et al. (2016) and Bieroza et al. (2018) being aware that this somewhat arbitrary threshold only indicates chemostatic patterns if $CV_C/CV_Q << 1$ (Musolff et al., 2015). For nitrate, the CQ-slope and the CV_C/CV_Q were found to be positively correlated (Musolff et al., 2015) as most of the variability in C is explained by variability in Q. In this case, the additional information gained by the CV_C/CV_Q metric is small. Methods and results of this study are therefore restricted the CQ-slope only.

Using daily streamflow data and low-frequency nitrate concentrations, we calculated seasonally averaged and FN nitrate concentrations, loads and FN CQ-slopes for all gauges from 1983 to 2016 in order to detect long-term trends and seasonal differences. Seasons were defined as spring lasting from March to May, summer from June to August, autumn from September to November and winter lasting from December to February. To quantify the uncertainty, all results were bootstrapped 200 times using the R package EGRETci (Hirsch et al., 2015) for FN nitrate concentrations and loads and a modification of the code from Zhang et al. (2016) for bootstrapping $ß_2$. As recommended by Hirsch et al. (2015), we used a block length of 200 (randomly selected with replacement) and show the 90 % confidence interval in all consequent figures (5 % - 95 % quantiles).

2.4 Nitrogen input

Nitrogen (N) input into the Selke catchment was calculated following the procedure described by Ehrhardt et al. (2019). Here, N input refers to N surplus as the sum of three different input classes: i) agricultural N surplus, ii) atmospheric N deposition, and iii) N input from WWTPs, where i) and ii) are diffuse sources and iii) is a point source. To stay consistent with the nested catchment structure, N input data of Meisdorf represents N input for the entire upper Selke and N input from the lower Selke represents the entire Selke catchment, including the upper part.

We used agricultural N surplus data derived for the 403 counties in Germany, representing the annual surplus of N on agricultural areas that results from the difference between N sources (i.e., fertilizer and manure application, atmospheric deposition and biological N fixation by legumes) and N sinks in the form of N in harvested crops (Bach & Frede, 1998; Häußermann et al., 2019). Our study area is covered by two counties. The share of agricultural area for each county was taken from the CORINE Land Cover (CLC, EEA, 2012) for the years 1990, 2000, 2006 and 2012 and further corrected according to Bach et al. (2006 and pers. com), introducing a scaling factor for each county to adjust for the mismatch between the CLC derived agricultural share and that from statistical data sources (Bach et al., 2006).

Atmospheric N deposition represents the annual input from N emissions due to burning in private households, industry and traffic between 1980 and 2015, provided by the Meteorological Synthesizing Centre – West (MSC-W) of the European Monitoring and Evaluation Programme EMEP (e.g. Bartnicky & Benedictow, 2017; Bartnicky & Fagerli, 2004). From 1950 to 1980, a constant input is assumed, due to a lack of further data for that time. We considered N deposition for the non-agricultural land cover classes (e.g. forest, water bodies, wetlands, grassland) as the agricultural N surplus data already account for atmospheric deposition (see above) and added the biological N fixation according to Cleveland et al. (1999) and van Meter et al. (2017). Cities were neglected (except urban grassland like parks) under the assumption that nitrogen from sealed surfaces is directly discharged into the WWTPs.

Annual mean nitrate and ammonium concentrations from WWTP outflow between 2010 and 2015 were provided by the Ministry of Environment, Agriculture and Energy Saxony-Anhalt (MULE). We calculated nitrate input from WWTPs with the provided nitrate concentrations and an additional maximum estimate for the contribution of WWTPs to nitrate export under the assumption of a complete nitrification of wastewater-borne ammonium. For all years previous to 2010, nitrate concentrations from 2010 were assigned. We consider that these data and their extrapolation robustly represent the recent state of point source N loads but do not allow for describing the long-term evolution of N loads due to improvements in wastewater treatment and newly constructed WWTPs.

Finally, a harmonized and consistent dataset for each of the three different input types was created on county level (average area of 887 km²) for the period of 1950-2015 and combined to one single N input dataset that was clipped for all three nested sub-catchments. To this end, we used the weighted average, taking into account the areal fractions of involved counties and the respective (sub-)catchment boundaries.

2.5 Transit time distributions

Apparent transit time distributions (TTDs) for nitrate were calculated applying a methodology described by Musolff et al. (2017) and Ehrhardt et al. (2019). We assumed a log-normal form for the TTDs because this allows to account for the long tails in the TTD needed to adequately reflect legacy effects. First, we scaled N input and mean annual FN nitrate concentrations from the long-term low-frequency data in order to compare the temporal dynamics of input and output independently from their absolute value. Then, we calibrated the parameters μ and σ of the log-normal distribution by minimizing the sum of squared errors between simulated and measured scaled FN nitrate concentrations. We used these TTDs to compare the response of the nested catchments to changes in N input and to improve our estimate of N legacies in the period from 1983 to 2015. More specifically, we calculated the total conservative N export for each sub-catchment by convolving the annual N input for each year with the calibrated TTDs, extracting the fractions that would be exported by 2015, and summing up these annual estimates to derive the cumulative N export until 2015. We then compared this estimate of conservative N export to the measured nitrate export over the same period to get an estimate of the *missing N*. We assume that missing N was either removed via denitrification or it is still in the catchment as hydrological or biogeochemical legacy. A clear separation of these two forms of legacies is challenging (Ehrhardt et al., 2019) and beyond the scope of this study. Nevertheless, we used the long-term trends in the CQ-slope to discuss the likely domination of either hydrological or biogeochemical legacies and compared the difference between TTD-derived and measured N export to literature data on potential denitrification.

2.6 Event dynamics

We used the high-frequency data from 2010 to 2016 to analyze storm events at all three gauges. To identify events, we converted Q from $m^3\ s^{-1}$ to mm, smoothed it with a running average and separated it into a base flow and fast flow component following the methodology described by Gustard (1983) and WMO (2008). This methodology linearly interpolates between turning points in Q that are defined as local minima within a non-overlapping 5-day window, which are at least 1.11 times smaller than their neighboring minima. Despite its simplicity, this base flow separation method was chosen because it allows for an unambiguous identification of event starting points (Tarasova et al., 2018). We defined the start of an event as the point in time when fast flow increases to at least 2.5 % of base flow and Q has increased by a minimum of 5 % over the previous 5 hours. Events were defined to end when fast flow decreases to less than 2.5 % of base flow. The final selection of the event was based on the criterion that the event included a minimum of 20 data points, peak Q reached at least the 5 % percentile of all Q measurements, fast flow contribution at the peak of the event was at least 30 % of total flow and Q decreased at least to one third of its former increase. Events with data gaps larger than 5 hours were discarded from the analysis. These criteria and thresholds were chosen as they allowed for a good balance between the separation of clearly evident events from scatter in Q and the detection of a sufficient number of small-scale events that occurred during low flow seasons (LFSs) to obtain a fairly equal number of events during all four seasons.

Next, we fitted equation (2) to each selected event (Eder et al., 2010; Krueger et al., 2009; Minaudo et al., 2017) to analyze the event-specific CQ-slope and the hysteresis direction and extent:

$$C = a * Q^b + c * \frac{dq}{dt} \qquad (2)$$

where *a*, *b* and *c* are parameters that were fitted for each event individually. Parameter *a* gives the event-specific intercept and *b* the CQ-slope, which is comparable to the parameter $ß_2$ from the long-term analysis (eq. 1). Consequently, parameter *b* was used to differentiate between chemodynamic-accretion (b > 0.1), chemodynamic-dilution (b < -0.1) and chemostatic (-0.1 < b < 0.1) nitrate transport during storm events. Parameter *c* was used to identify the extent and direction of event-specific hysteresis with c > 0.1 indicating clockwise hysteresis, c < -0.1 indicating counterclockwise hysteresis and -0.1 < c < 0.1 indicating no or complex hysteresis. Note that dQ/dt was scaled for the individual event to allow a better comparison of c between the events. The season of an event was defined as the season in which the event starts. To assure the quality of results, parameters *b* and *c* were only used for further analysis if the coefficient of determination (R^2) for the event-specific fit of eq. 2 was larger than 0.5.

3 Results

3.1 Seasonal and long-term patterns in nitrate concentrations

Referring to the regular monitoring results between 1983 and 2016, the upper Selke showed a pronounced seasonality, with lower nitrate concentrations during low flow seasons (LFSs, summer and autumn) and higher concentrations during high flow seasons (HFSs, winter and spring), while nitrate concentrations in the lower Selke were more stable between seasons. In general, the fitted nitrate concentrations increased from the upper to the lower Selke (Fig. 2), but due to the differences in seasonality, this increase was especially pronounced during LFSs. Here, FN nitrate concentrations (NO_3-N) ranged between 0.5 – 1.8 mg L^{-1} in the upper Selke and between 2.0 – 3.7 mg L^{-1} in the lower Selke. During HFSs, the difference between upper and lower Selke nitrate concentrations was relatively small. Here, FN nitrate concentrations ranged between 1.6 – 3.4 mg L^{-1} in the upper Selke and between 2.4 – 3.7 mg L^{-1} in the lower Selke. Using WRTDS to fit daily nitrate concentrations resulted in a small bias of 1.7 %, 0.5 % and -0.5 % for Silberhütte, Meisdorf and Hausneindorf, respectively, with respect to the measured long-term data.

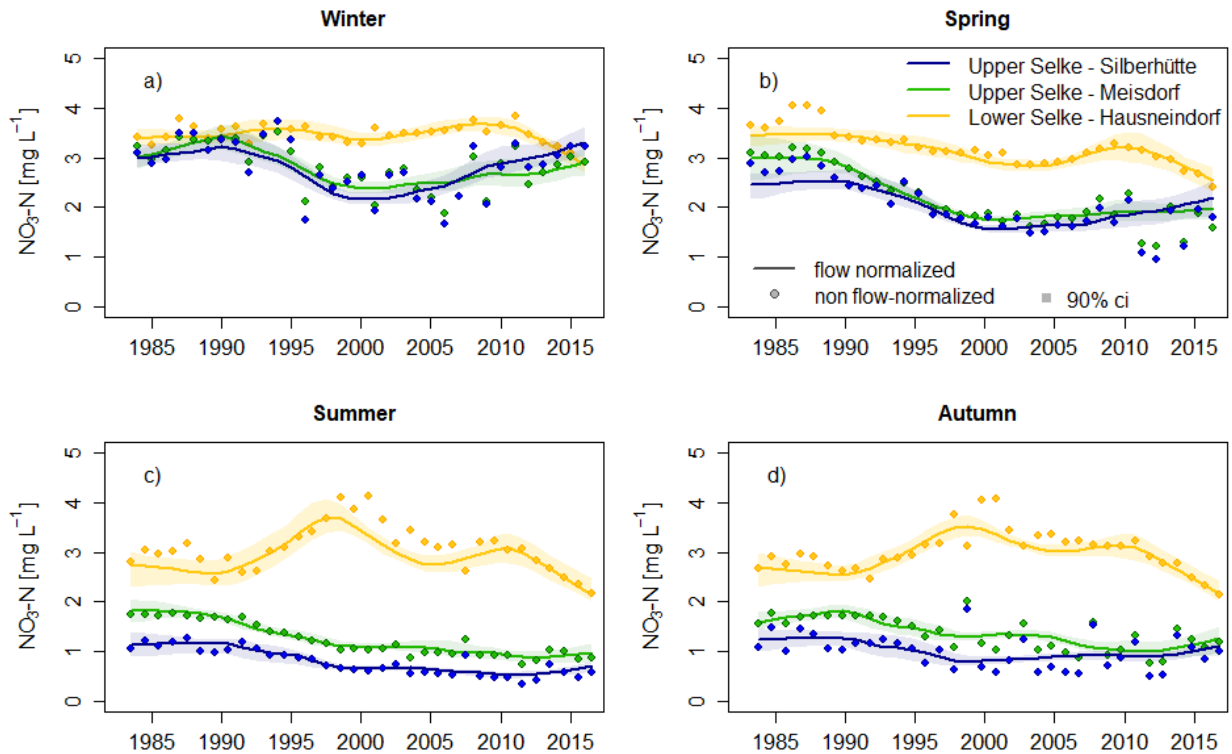

Figure 2. Long-term trends of annual flow normalized (FN, lines) and annual non-FN (dots) nitrate concentrations from three nested sub-catchments of the Selke catchment, separated by season. Uncertainty bands in the sub-catchment specific color indicate the 90% confidence intervals from bootstrapping FN values.

Besides general differences in nitrate concentrations and their different seasonality, long-term trends also showed a different behavior between upper and lower Selke, again most pronounced during LFSs. Here, a marginal decrease from 1990 on occurred in the upper Selke, while in the lower Selke, FN nitrate concentrations increased substantially, with a maximum value of 3.7 and 3.5 mg L^{-1} in summer and autumn 1997, respectively. A secondary peak occurred during 2010 with 3.1 mg L^{-1} in both seasons (Fig. 2 c,d). In the most recent years (2011 – 2016), nitrate concentrations in the lower Selke during LFSs decreased to an average value of 2.6 mg L^{-1}. During HFSs, nitrate concentrations in the upper Selke decreased more strongly after 1990 but increased again from 2000 on. In the lower Selke, however, only slight temporal changes occurred during HFSs and the decrease in most recent years - observable during LFSs - occurred to a lesser extent also during HFSs (Fig. 2 a,b).

3.2 Seasonal and long-term behavior of nitrate loads

Nitrate loads showed a strong seasonality with highest nitrate loads during HFSs and lowest during LFSs (Fig. 3). This seasonality was more pronounced in the upper Selke than in the lower Selke and, consequently, the relative contribution from sub-catchments to nitrate loads varied seasonally. Overall, highest loads occurred during winter with an average of 515.5 kg d^{-1} in Silberhütte, 607.8 kg d^{-1} in Meisdorf and 774.8 kg d^{-1} in Hausneindorf (average from non-FN values). If neglecting in-stream losses of nitrate, this implies that the upper Selke transported 78.4 % of the catchment’s nitrate loads during winter. Lowest loads occurred during summer with 39.5 kg d^{-1}, 77.4 kg d^{-1} and 207.6 kg d^{-1} for Silberhütte, Meisdorf and Hausneindorf, respectively. Contrarily to winter, the upper Selke had a much smaller contribution to the catchments loads of only 37.3 % during summer. On an annual scale, the upper Selke contributed approximately 64.2 % to the total catchment's nitrate loads. If accounting for the sub-catchment area, consequently, the average of annual loads were highest in Silberhütte with 8.6 kg ha^{-1} a^{-1}, followed by Meisdorf with 6.3 kg ha^{-1} a^{-1} and smallest in Hausneindorf with 3.9 kg ha^{-1} a^{-1}.

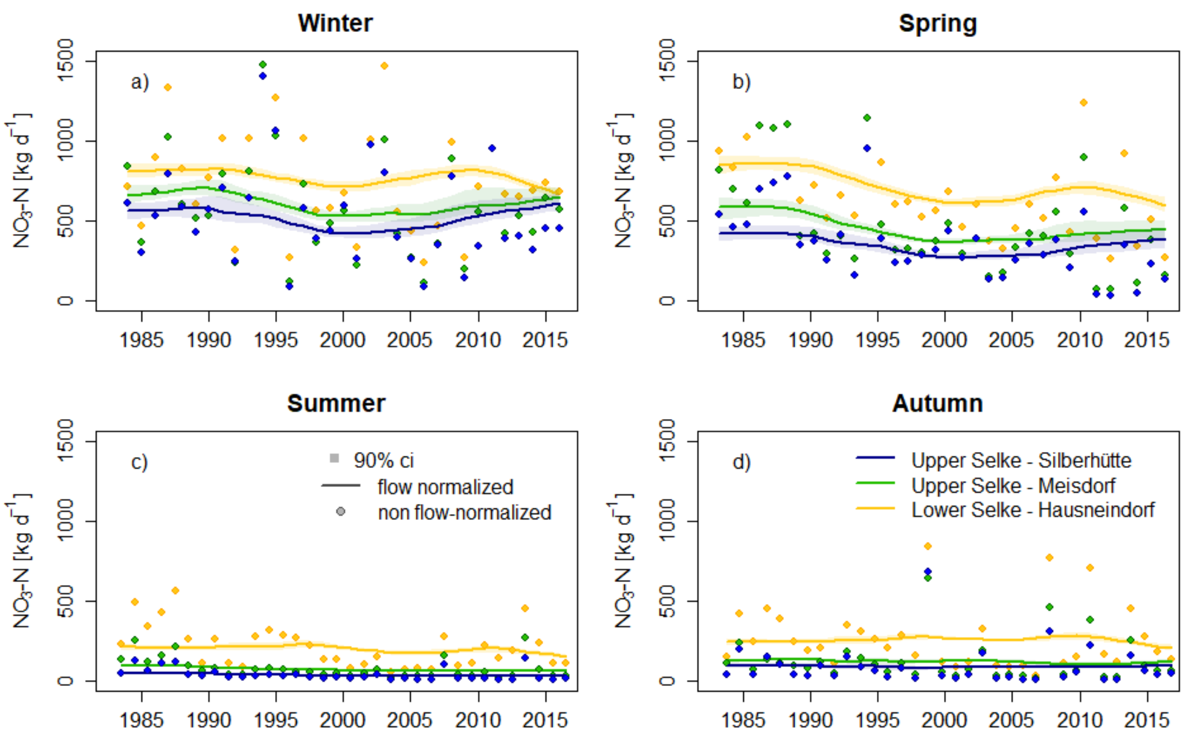

Figure 3. Long-term trends in annual FN nitrate loads (lines) and annual non-flow normalized nitrate loads (dots) from three nested sub-catchments of the Selke catchment, separated by season (a-d). Uncertainty bands in the sub-catchment specific color indicate the 90% confidence intervals from bootstrapping FN values.

3.3 Concentration-discharge relationships

Long-term CQ-slopes in the upper Selke were positive, indicating chemodynamic nitrate export with an accretion pattern (Musolff et al., 2017), which was observed in seasonal (Fig. 4) as well as in annual CQ-slopes (Fig. S2 c). The only exception was Meisdorf during LFSs between 1983 and 1990, where nitrate export was chemostatic with a CQ-slope close to zero (Fig. 4 c,d). CQ-slopes in Silberhütte were higher than the ones in Meisdorf, except for HFSs from 2010 on, where CQ-slopes were both around 0.45 (Fig. 4 a,b). During LFSs, CQ-slopes in the upper Selke peaked in 1999 and, following a minimum around 2005, leveled out afterwards. Uncertainty assessed via bootstrapping was highest for LFSs, but the generally positive CQ-slopes from 1990 on were still evident (Fig. 4 c,d).

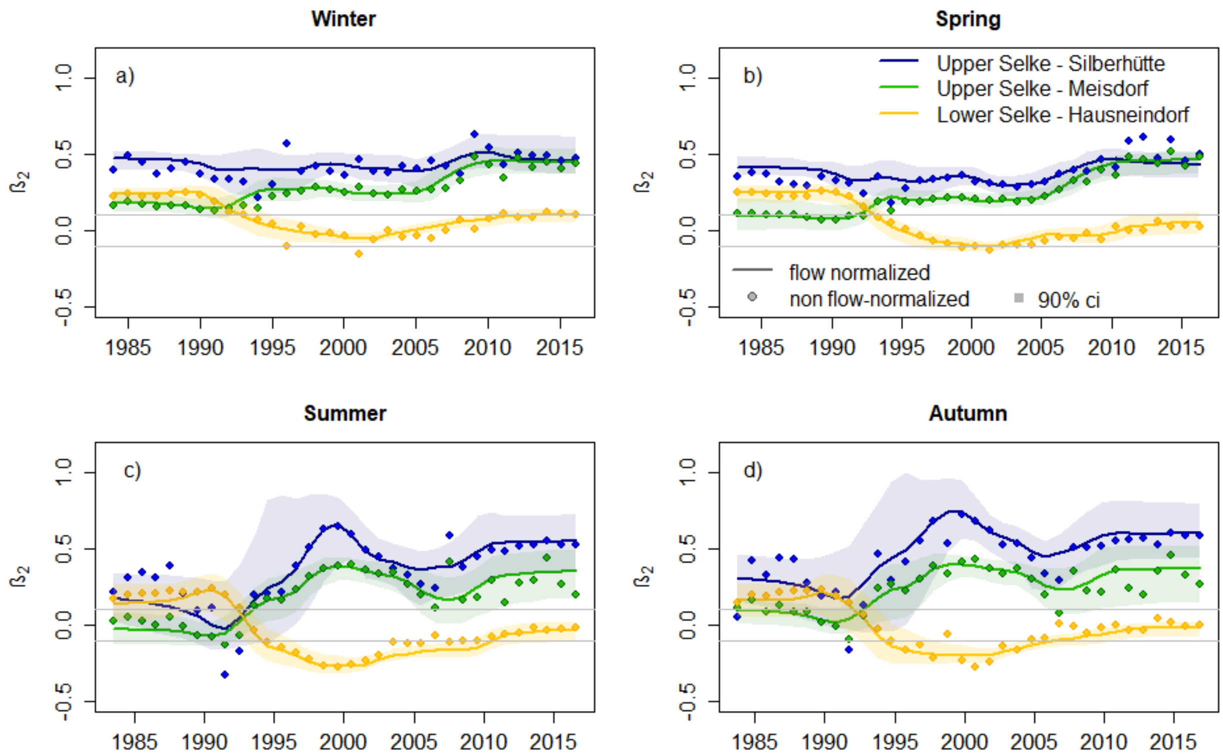

Figure 4. Long-term trends of the fitted parameter ß$_2$, indicating the annual flow normalized (FN) and annual non-FN ln(concentration)-ln(discharge) relationship (CQ-slope) from three nested sub-catchments in the Selke catchment, separated for each season. Uncertainty bands in the sub-catchment specific color indicate the 90% confidence intervals from bootstrapping FN values.

In contrast to the upper Selke, the export regime in the lower Selke changed significantly over time (Fig. 4, Fig. S2). CQ-slopes in the lower Selke were positive between 1983 and 1990 for all seasons, which indicates chemodynamic nitrate transport with accretion patterns. After 1990, CQ-slopes decreased towards values around zero during HFSs (Fig. 4 a,b), which indicates chemostatic transport, and towards negative CQ-slopes during LFSs (Fig. 4 c,d), which indicates chemodynamic nitrate export with a dilution pattern. From around 2010 on, nitrate transport in the lower Selke was chemostatic during all seasons with a tendency to slightly higher CQ-slopes during HFSs compared to LFSs.

3.4 Nitrogen budget

Since the start of the time series in 1950, N input strongly increased until 1976 and fluctuated between 1976 and 1989 around an average N input of 57.3 kg ha^{-1} a^{-1} in the upper Selke and 79.4 kg ha^{-1} a^{-1} in the lower Selke. Maximum N input was reached in the year 1988. In 1990, after the reunification of Germany and the associated break down of the intensive agriculture in East Germany (Gross, 1996), N input decreased drastically within one year and then stabilized again on a lower level around 33.9 ± 3.3 kg ha^{-1} a^{-1} (upper Selke) and 37.7 ± 5.2 kg ha^{-1} a^{-1} (lower Selke) from 1995 onwards (Fig. 5, Table 1).

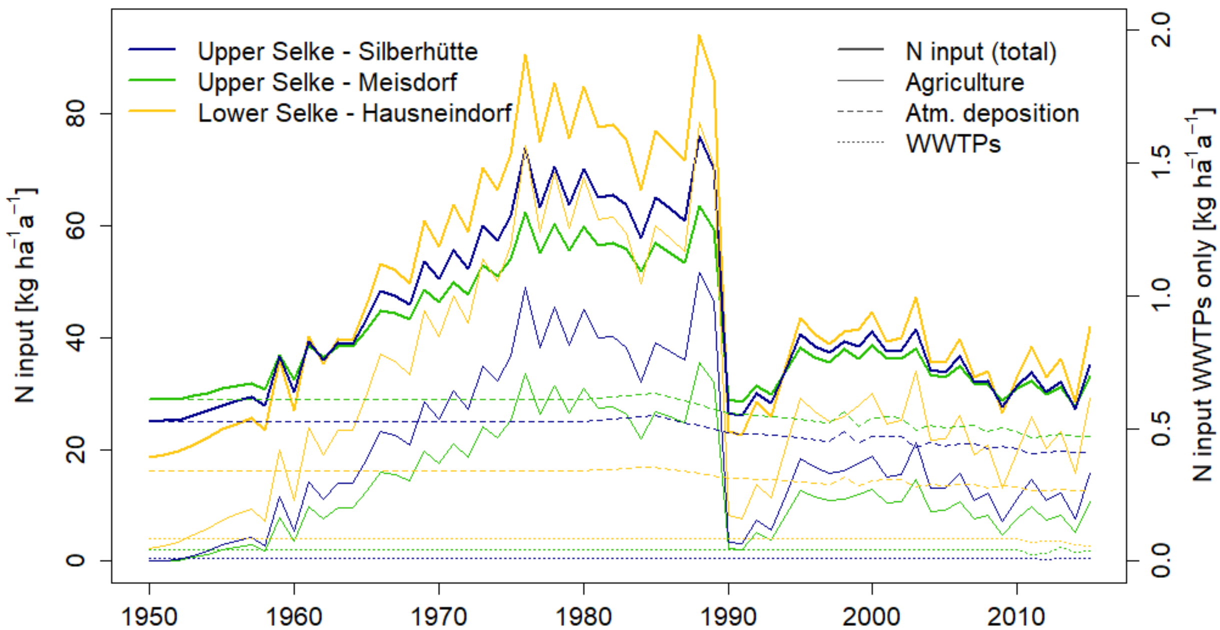

Figure 5. Total N input per hectare and year for all three nested sub-catchments of the Selke catchment and N input divided into its components i) from agricultural areas, ii) atmospheric deposition and biological fixation on non-agricultural areas, and iii) outflow from wastewater treatment plants (WWTPs, second y-axis).

Annual N input per hectare (ha) was generally lower for the upper Selke (representing the catchment area draining to the gauge at Meisdorf) than for the lower Selke (representing the entire catchment area draining to the gauge at Hausneindorf; Fig. 5; Table 1). The only exceptions were found during years, when the total N input was especially low (e.g. 1990/91). In these years, the scenario reversed with highest N input in the upper Selke and lowest N input in the lower Selke, due to a relatively high atmospheric N deposition over the Harz Mountains and biological N fixation in the forests (Fig. 5, Table 1). Between 1983 and 2015, approximately one third (34.5 %) of N input stemmed from the upper Selke and most of this from the upstream area draining to the gauge at Silberhütte (Table 1). N surplus from agriculture in this period was around 33 % and 68 % of the total N input for the upper and lower Selke, respectively. The remaining part mainly stemmed from natural areas (mainly forests and grasslands), while the contribution from WWTPs was small. If assuming constant N input from WWTPs over the year, they contributed on average 0.8 % - 1.6 % to exported annual nitrate loads in the upper Selke and 2.4 % - 3.6 % in the lower Selke (assuming no or a complete nitrification of wastewater-born ammonium). During LFSs, the contribution from WWTPs to nitrate export was on average 3.4 % - 7.4 % and 6.2 % - 9.5 % for the upper and lower Selke, respectively.

3.5 Nitrate retention and transit time distributions

Modes and μ-values of the lognormal TTDs fitted as a transfer function between annual N input and annual FN nitrate concentrations show that TTs in the upper Selke were considerably shorter than those in the lower Selke (Table 1). The convolution model was accurate for the upper Selke at Meisdorf ($R^2 = 0.92$) and acceptable for Silberhütte ($R^2 = 0.57$) as well as for the lower Selke ($R^2 = 0.40$; Table 1).

TTD derived conservative N export over the period from 1983 to 2015 was higher than N input for this period (Table 1), because it integrated parts of the high N input from before 1983. We refer to the TTD derived conservative N export that was not exported in form of measured annual nitrate loads as the *missing N* (Van Meter et al., 2016; Table 1), which is either still in the catchments as legacy or removed via denitrification. All sub-catchments of the Selke catchment showed a considerably percentage of missing N (80 – 92%). This number is smallest for the upper Selke, especially for the upstream area draining to the gauge at Silberhütte, and largest for the lower Selke, with 10.8-11.5 kg ha^{-1} a^{-1} more N being missing than in the upper Selke.

Table 1. Transit time distributions (TTDs) and the balance between nitrogen (N) input and its riverine export as nitrate loads

			upper Selke		**lower Selke**
		unit	**Silberhütte**	**Meisdorf**	**Hausneindorf**
TTDs	μ	[a]	2.12	1.59	2.91
	σ	[a]	1.15	1.10	0.73
	R^2	[-]	0.57	0.92	0.40
	Mode (year of peak travel time)	[a]	3	3	12
N input vs. export (1983 – 2015)	Cumulative N input	[t]	14078.7	23195.4	67146.9
	N $export_{conv}$ (conservative)	[kg ha^{-1} a^{-1}]	44.3	41.2	50.3
	Cumulative N $export_{conv}$ (conservative)	[t]	15352.9	25045.3	75753.0
	Cumulative N export, (measured)	[t]	3052.1	3912.0	6094.3
	Missing N (conservative - measured)	[kg ha^{-1} a^{-1}]	35.5	34.8	46.3
		[t]	12300.7	21133.3	69658.6
		[%]	80.1	84.4	92.0

Note. TTDs follow a log-normal distribution with fitted parameters μ and σ and the R^2 as the coefficient of determination. Conservative N export is the N input convolved with TTDs as indicated by subscript *conv*. *Missing N* refers to the difference between conservative N export and measured N export in form of riverine nitrate loads.

3.6 Storm events

We identified a total of 200 storm events, with 59 for Silberhütte (over the period from 2013 to 2016), 72 for Meisdorf and 69 for Hausneindorf (both over a period from 2010 to 2016). From all these events, 56 % could be described adequately with the empirical formula defining the hysteresis loop (eq. 2) with $R^2 > 0.5$. This corresponds to 40 events in Silberhütte, 44 in Meisdorf and 29 in Hausneindorf, with at least seven events per season and gauge. Fitted parameters *b* and *c* for event-specific CQ-slopes and hysteresis behavior of these events are displayed in Fig. 6. Upper Selke CQ-slopes were dominantly positive, indicating chemodynamic nitrate export during storm events with an accretion pattern (Fig. 6 a,b). Some exceptions were found during autumn in Silberhütte, where some small events during November showed negative CQ-slopes and caused a large variability in CQ-slopes during this season (Table S1) and during summer in Meisdorf. Event-specific hysteresis in the upper Selke was dominantly counterclockwise, indicated by the negative parameter *c* (Fig. 6 d,e). In contrast to the upper Selke, event-specific CQ-slopes in the lower Selke were negative during LFSs, indicating chemodynamic nitrate transport with a dilution pattern (Fig. 6 c). During HFSs however, event specific CQ-slopes were dominantly positive, indicating an accretion pattern, similar to the upper Selke. Hysteresis during summer was clockwise, and dominantly counterclockwise during all other seasons, again similar to the upper Selke. For all three sub-catchments, variability in hysteresis behaviour was most pronounced during autumn. If looking at all identified events – regardless of their R^2 (Fig. S3) – the described patterns in CQ-slopes and hysteresis stayed evident, with the only exception that CQ-slopes in the lower Selke during spring were dominantly around zero or negative.

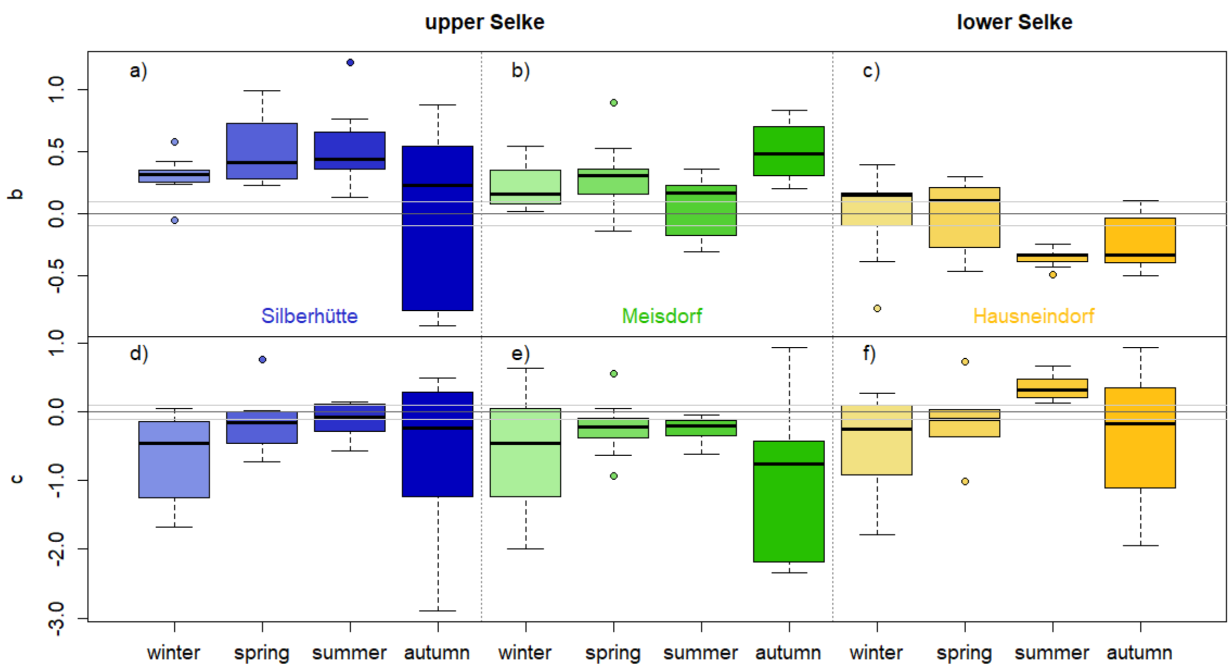

Figure 6. Boxplots of the event-specific fitted parameters b (CQ-slope) and c (hysteresis) in eq. 2 with $R^2 > 0.5$. Parameters were separated by seasons and gauging stations within the Selke catchment, displayed from upstream (left) to downstream (right).

4 Discussion

4.1 Long-term trends in nitrate export

To understand how nested sub-catchments affect the response of nitrate export to changes in N-surplus, the drastic N input change in 1990 together with the nested catchment structure gave an ideal setting to analyze the long-term response from different sub-catchments (Ehrhardt et al., 2019). The question of how long these input changes need to propagate through the catchment subsurface until they are measurable in the stream, can mainly be answered by the sub-catchment specific nitrate TTDs, which showed a clear difference between the upper and the lower Selke. While in the upper Selke, the TTDs showed a peak after three years indicating a dominance of short transit times, the TTD in the lower Selke showed a peak after 12 years and therefore had a considerably longer tailing (Table 1). Consequently, N input in the upper Selke is transported rapidly to the stream network and the response of instream nitrate concentrations to changes in N input becomes visible almost immediately, while in the lower Selke, N input is transported far more slowly and the response of nitrate concentrations to changes in N input is delayed by more than a decade. Long-term persistence of nitrate pollution is, therefore, rather an issue in the agriculturally dominated lower Selke than in the upper Selke.

The sub-catchment specific differences in TTDs helped to explain the different long-term trends in nitrate concentrations, loads and CQ-slopes (Fig. 2 and 4). In the upper Selke, short TTs mainly explain the immediate decrease of nitrate concentrations and loads after 1990 as a response to the drastic N input decrease, which is supported by a study from J. Yang et al. (2018) who found short TTs of around 79 days for a small headwater catchment in the upper Selke (1.44 km^2) and by other studies that report short TTs in typical upland catchments with a responsive hydrological regime (e.g. Hrachowitz et al., 2009; Soulsby et al., 2015). The increase in nitrate concentrations and loads from 2000 on, however, cannot be explained by TTDs and N input; instead, it coincided with an increase in CQ-slopes (Fig. 4), reflecting that nitrate concentrations increased during HFSs but stayed similar during LFSs (Fig. 2). One possible explanation is that local changes in agricultural practices, forest management or land use arrangement, which were not accounted for in the county-level N input data, might have changed the amount and connectivity of nitrate sources to streams and the consequent degree of nitrate mobilization during high flow conditions.

In contrast to the upper Selke, long TTs in the lower Selke led to a delayed reaction of instream nitrate concentrations to changes in N input, such as the drastic decrease in 1990. Directly after this input decrease, nitrate concentrations during LFSs contrarily increased in the lower Selke (Fig. 2 c,d). Most likely, this increase reflects the delayed response to the peak in N input from before 1990 (Fig. 5), while the decrease in N input in 1990 became measurable in riverine nitrate concentrations only about a decade later (Figs. 2 and 3). However, the two emerging peaks in nitrate concentrations during LFSs (1997 and 2000) in the lower Selke and the striking decrease after 2010 during all seasons (Fig. 2) cannot be explained by transit times alone. Agricultural and more densely populated catchments are typically exposed to a large number of different nitrate sources and anthropogenic impacts (Caraco & Cole, 1999; Silva et al., 2002). In the lower Selke, the starting operation of WWTPs around 1996/1997 and the activities around the mining pit close to the catchment outlet are likely drivers for individual peaks in the analyzed long-term trends. Furthermore, the water that was added to the Selke River since 2009 to keep the water level in the mining lake constant, likely caused a dilution of riverine nitrate concentrations and might have been one reason for the decrease of nitrate concentrations in recent years (Fig. 2, Fig. S4). Another possible reason might be a decline in groundwater recharge due to climate change that caused a lower mobilization of nitrate from the groundwater to the stream network. Hence, although the decrease in nitrate concentrations in the lower Selke is generally a good sign for water quality, the driving forces are related to considerable uncertainty. Nitrate concentrations might have decreased due to a delayed reaction from the decrease in N input 1990, due to a decline in groundwater recharge or due to the dilution with water from the flooded mining pit with lower nitrate concentrations. We assume that a combination of all these processes was responsible for the observed concentration declines.

CQ-slopes in the lower Selke changed from i) an accretion pattern before 1990 to ii) dilution in LFSs and chemostasis in HFSs and finally towards iii) chemostatic nitrate export during all seasons in recent years (Fig. 4). A very similar dynamic of CQ-slopes was reported by Ehrhardt et al. (2019) for a nearby mesoscale catchment. They explained this by the vertical stratification of nitrate storage in the subsurface as a consequence of the downward transport of nitrate with time (Dupas et al., 2016) and different active flow paths during HFSs and LFSs. During LFSs, Q is dominated by base flow that originates from deeper groundwater, while during HFSs, shallower subsurface flow paths are activated that access a younger fraction of groundwater (Ehrhardt et al., 2019; Musolff et al., 2016). As N input gradually increased until 1976, deeper groundwater in the lower Selke in the first years of our time series still showed lower nitrate concentrations than shallow groundwater. Consequently, nitrate concentrations during low flow conditions were lower than concentrations during high flow, leading to the observed accretion pattern. After the German reunification in 1990, N input drastically decreased leading to a decrease of nitrate concentrations in shallow groundwater and higher concentrations in deeper groundwater due to the downward percolation of the high N inputs from before 1990 (Fig. 5). Consequently, nitrate concentrations in the lower Selke were higher during low flow conditions than during high flow conditions, leading to the observed dilution pattern. Another reasonable explanation for the dilution pattern is the impact from upper Selke nitrate export. Due to the shorter TTs in the upper Selke, long-term trends in riverine nitrate concentrations showed an immediate decrease after 1990, while concentrations still increased in the lower Selke. This diverging long-term trends were especially pronounced during LFSs (Fig. 2 c,d). Lower nitrate concentrations from the upper Selke during LFSs could have, therefore, diluted the higher nitrate concentrations downstream, leading to the observed dilution pattern in CQ-slopes in the lower Selke (Figs. 4 c,d and S2 c). Most plausibly, a mixture of both vertical layering of groundwater nitrate concentrations and the impact of the upper Selke led to the observed dilution pattern. In recent years, chemostatic nitrate export during all seasons developed in the lower Selke, likely due to a mixture of both vertical equilibration of groundwater nitrate concentrations after a prolonged period of stable N inputs (Fig. 5; Dupas et al., 2016; Ehrhardt et al., 2019) and a less pronounced dilution effect from the upper Selke due to converging nitrate concentration levels between the sub-catchments (Fig. 2).

Similar to Ehrhardt et al. (2019), we could show that CQ-relationships transitionally shift with changes in N input and further that these changes can be different between seasons. Thus, chemostatic nitrate export is not exclusively an indication for intensive agriculture but also for homogenously distributed N stores, both vertically in the subsurface and between different sub-catchments. In fact, chemodynamic export at the catchment outlet can also indicate ‘not equilibrated systems’, where changes in N input have not yet propagated through the whole system, causing a vertical layering of nitrate concentrations in the subsurface and/or diverging nitrate concentration between sub-catchments due to different sub-catchment specific TTDs. Defining one unique CQ-slope for nitrate concentrations at the catchment outlet across longer time series and seasons can be misleading as may it integrates input and mobilization patterns as well as transport times that are not necessarily the same over space and time (Fig. S5). For example a temporal transition from accretion patterns towards dilution - as observed in the lower Selke during LFSs from 1990 to 2000 - might be interpreted as constantly chemostatic if not accounting for these transitional changes and for seasonal differences.

4.2 N legacies and potential denitrification

Measured nitrate export accounted for approximately 15.4 % and 8.0 % of the TTD derived conservative estimate of N export for the upper and lower Selke, respectively. This translates into 34.8 kg N ha^{-1} a^{-1} and 46.3 kg N ha^{-1} a^{-1} missing N (Table 1) and is a first evidence for considerable N retention in both sub-catchments, especially in the lower Selke. Fast TTs in the upper Selke indicate a dominance of biogeochemical legacies and only a minor impact of hydrological legacies. CQ-slopes and the pronounced seasonality, furthermore, indicate that N sources are either stored in the shallower zones of the sub-surface or in the more distant zones to the stream network, which could both be partially activated during high flow conditions such as storm events during winter. This explanation is supported by J. Yang et al. (2018), who proposed that an expansion of Q generating zones during high flow conditions in a small headwater catchment in the upper Selke enables the mobilization of additional N sources. In contrast in the lower Selke, long TTs and the shifts in CQ-relationships indicate a dominance of hydrological legacies over biogeochemical ones, as nitrate export patterns are driven by the seasonal activation of different N source zones with different ages, as discussed above (Ehrhardt et al., 2019).

Denitrification is the only process leading to permanent nitrate removal from the catchment. It accounts for a part of the missing N and prevents it from being stored in the catchment (Seitzinger et al., 2006). Kuhr et al. (2014) simulated average denitrification rates for soils in Saxony-Anhalt using the process-based DENUZ transport model (Köhne and Wendland, 1992; Kunkel and Wendland, 2006) and showed that denitrification rates in the unsaturated zone in and around the Selke catchment are low to very low (9 – 13 kg ha^{-1} a^{-1}), which is considerably lower than the rates of missing N for the Selke catchment mentioned above (Table 1). Even assuming the upper range denitrification rate, missing N would still be >20 kg N ha^{-1} a^{-1} in the upper and >30 kg N ha^{-1} a^{-1} in the lower Selke.

The potential for denitrification in the groundwater is largely depleted in Saxony Anhalt, according to a recent study from Hannappel et al. (2018). From the seven observation wells within the Selke catchment, only one showed evidence for ongoing denitrification, which was located in the upper Selke. Hence, denitrification in the groundwater likely removed a part of N input in the upper Selke. However, from all observation wells in Saxony-Anhalt located on a similar geologic setting as the upper Selke (Palaeozoic), less than 5% showed evidence for ongoing denitrification. This is a warning sign for the upper Selke, indicating that essential electron donors such as pyrite for autolithotrophic denitrification have been largely consumed or might get depleted in the near future. In the lower Selke, none of the observation wells showed a potential for denitrification in groundwater (Hannappel et al., 2018). We, therefore, argue that denitrification in groundwater played only a minor role for the fate of N input in the lower Selke, which is in line with findings from Ehrhardt et al. (2019) in a nearby mesoscale catchment. Nevertheless, there is evidence for significant denitrification in the riparian zones, especially during LFSs. Recent studies by Lutz et al. (2020) and Trauth et al. (2018) reported a removal by riparian denitrification of up to 12 % of nitrate from groundwater entering the Selke River along a 2 km section downstream of Meisdorf. Additionally, a stable isotope study of Müller et al. (2015) in the Bode catchment, which includes the Selke catchment, found evidence for significant denitrification in the stream beds during LFSs while denitrification in the groundwater was not evident, in line with Hannappel et al. (2018). The studies agree that riparian zone and stream bed denitrification are more likely to occur in the downstream part of the river where flow velocities are reduced, which suggests that this type of denitrification might be an important process for the lower but not evidently for the upper Selke.

Assimilatory uptake in the stream is another important process for nitrate export dynamics, which could, according to Rode et al. (2016), have removed around 5 % of nitrate in the upper Selke and 13 % in the lower Selke. Nevertheless, the permanent removal via denitrification accounts for only a small percentage of assimilatory uptake. Hence, we suggest that assimilatory uptake does only account for a small percentage of the missing N. Moreover, following the argument of Ehrhardt et al. (2019), the change in seasonal patterns in the lower Selke and the high nitrate concentrations in LFSs around 1997 (Fig. 2 c,d) indicate that assimilatory uptake was not a key process causing the observed nitrate export patterns at longer time scales, as this would imply a more steady seasonality.

In summary, a large portion of N was not exported from the Selke River and is therefore missing. It is unlikely that denitrification alone is responsible for all missing N, which means that parts of it were stored as legacies. We argue that biogeochemical legacies dominate in the upper Selke, while long TTs and deeper aquifers lead to a dominance of hydrological legacies in the lower Selke. As N input and the percentage of missing N in the lower Selke was higher, extensive N legacies and especially long-term nitrate pollution are more of an issue in the agriculturally dominated lowland parts of the catchment than in the mountainous upstream part. Groundwater dominated catchments like the lower Selke are generally more prone to hydrological legacies (Van Meter & Basu, 2017). As these (sub-)catchments are typically associated with agricultural land use, they are most prone to developing nitrate legacies.

4.3 Seasonality in nitrate export

The contribution from different sub-catchments to nitrate export in the Selke catchment was highly seasonal, with significant differences between HFSs and LFSs. While the upper Selke dominated nitrate export during HFSs, the lower Selke dominated during LFSs. This seasonal shift in the dominant sub-catchment for nitrate export was driven by the seasonally different dynamics of mobilization and transport in the different sub-catchments.

Nitrate concentrations in the upper Selke showed a pronounced seasonality with high concentrations during HFSs and low concentrations during LFSs, a dynamic that was reflected also by positive the CQ-slope, indicating a chemodynamic-accretion pattern (Fig. 4). This accretion pattern can be explained by the activation of additional N sources with efficient transport to the stream during wet conditions (J. Yang et al., 2018). In contrast to chemostatic patterns, N sources are not uniformly distributed but rather distinct sources become activated during certain flow conditions. Therefore, accretion patterns hint at patchy N sources and spatially limited N legacies. This might be a common situation in mountainous upstream catchments that include only patches of agriculture or other relevant N sources. The consequent increase in nitrate concentrations during high flows can cause high nitrate loads, as observed in the upper Selke. Although it is known that upstream catchments can have an important role for nutrient transport (Alexander et al., 2007; Goodridge & Melack, 2012), the contribution from the upper Selke to 78.4 % of overall nitrate loads during winter and 64 % on the annual scale was unexpectedly high, given the fact that the upper Selke comprises only 17 % of the catchment's agricultural area and contributed on average only 37 % of total N input. We explain this disproportional contribution to nitrate loads by the high nitrate concentrations during HFSs (reflected by the described accretion pattern) together with a disproportional contribution to Q, which is typical for upstream catchments (Alexander et al., 2007; Dupas et al., 2019).

Nitrate concentrations in the lower Selke generally showed a less pronounced seasonality compared to the upper Selke, especially since 2010, when nitrate export became chemostatic during all seasons (Fig. 4). Chemostatic export was often found for catchments like the lower Selke that are dominated by agricultural land use, indicating a considerable amount of nitrate legacy stores (Basu et al., 2010, 2011) and a prolonged period of relatively stable N inputs (Ehrhardt et al., 2019). Due to the decreasing contribution from the upper Selke during LFSs and base flow conditions, the relatively constant nitrate input (around 3.1 mg L^{-1}) in the lower Selke kept nitrate concentrations high during these periods and consequently dominated nitrate export under dry conditions when surface waters are subject to an increased risk of eutrophication and a consequent loss of aquatic biodiversity (Whitehead et al., 2009). Another factor that could have caused high or non-decreasing nitrate concentrations during LFSs, is the constant contribution from WWTPs that have a relatively higher impact when stream Q is low. However, their overall contribution to nitrate export in the lower Selke was low even during LFSs (6.2 - 9.4 %) and the dilution pattern during events indicates no significant impact from rainwater overflow basins. Outflow from WWTPs were therefore certainly not the dominant driving force for elevated nitrate concentrations during LFSs.

In conclusion, the pronounced seasonality in the upper Selke leads to a dominance of nitrate export during HFSs and a disproportional contribution to annual nitrate loads. During LFSs, the contribution to nitrate export from the upper Selke is small and consequently the relatively constant nitrate export from the lower Selke dominates. The integrated signal of nitrate export patterns, measured at the catchment outlet, is not a constant mixture of sub-catchment specific signals but reflects a seasonal dominance of different sub-catchments. These results emphasize the importance of analyzing seasonal dynamics in different parts of larger catchments in order to identify the patterns of most dominant N sources at different times of the year (under different hydrological conditions) and thus the temporal interplay between different high-risk zones for N pollution.

4.4 Event dynamics and their seasonality

To examine the integrated signal of nitrate export across time scales, we analysed not only long-term trends and seasonal patterns, but also the CQ-slopes and hysteresis behaviour during single events. Because high-frequency data for event analysis were available between 2010 and 2016, we could directly compare long-term trends and event dynamics during this common period. Event-specific as well as long-term CQ-slopes in the upper Selke were dominantly positive, indicating chemodynamic export with an accretion pattern that is time-scale independent (Fig 6 a,b). Large storm events, therefore, can mobilize and transport large amounts of nitrate and contribute disproportionally to annual nitrate loads. The counterclockwise hysteresis found for most events (Fig. 6 d,e) indicates that N sources are mobilized with a delay to Q, which can be explained by distant N sources and higher nitrate concentrations in riparian floodplain aquifers that dominate the falling limb of event-Q (Rose et al. 2018; Sawyer et al. 2014).

In the lower Selke, long-term CQ-slopes between 2010 and 2016 showed a chemostatic pattern, while event specific CQ-slopes were more dynamic (Fig. 4; Fig. 6 c). The event-specific dilution patterns (negative CQ-slopes) in LFSs in the lower Selke can be explained by lower nitrate concentrations from the upper Selke (Fig. 2 c,d) that diluted lower Selke nitrate concentrations or by a direct dilution from shallow flow paths that were activated during events and diluted the more highly concentrated base flow. During HFSs, event specific CQ-slopes in the lower Selke became dominantly positive (Fig. 6 c), indicating a chemodynamic export with an accretion pattern same as in the upper Selke. It is also during HFSs that- in recent years - nitrate concentrations from the upper Selke were similary high than nitrate concentrations in the lower Selke (Fig. 2 a,b). It is, therefore, reasonable to assume that higher nitrate concentrations from the upper Selke during storm events caused an increase in concentrations also in the lower Selke and led to the described accretion pattern during winter-events. The observed counterclockwise hysteresis during winter confirms this assumption, because it was also observed in the upper Selke and indicates more distant nitrate sources (Musolff et al., 2017) which, in this case, might represent the impact from the upper Selke. For both dilution from spring to autumn and accretion during winter, the event dynamics in the lower Selke are considerably influenced by the upper Selke nitrate export.

Event specific CQ-slopes estimated at the catchment outlet (lower Selke) are in accordance with findings from Bowes et al. (2015), who reported a dominance of dilution patterns during storm events at the outlet of a mesoscale catchment that integrates different types of land use (39 % arable, 27 % grassland and 23 % woodland). Similarly to our study, the only accretion pattern was observed during winter. Bowes et al. (2015) related this accretion pattern to an additional mobilization of distant agricultural N-sources, which are comparable to our findings with respect to mobilization form the upper Selke. Furthermore, they argued that diffuse N-sources become depleted throughout large storm events in winter and spring, which might also apply to a lesser extend in the upper Selke catchment and explain its lower export of nitrate during spring compared to winter (Fig. 2, 4). Moreover, Dupas et al. (2016) found a similar dilution pattern during most storm events at the outlet of a mesoscale catchment in Thuringia (Saxony-Anhalt, Germany), while long-term trends increasingly showed chemostasis, as observed in the lower Selke. These comparisons show that nitrate export patterns observed at the Selke catchment are not an isolated phenomenon. Taking advantage of the nested catchment study design in the Selke catchment that allowed to identify sub-catchment specific contributions, we suggest that the contrast between long-term and event specific CQ-slopes in the lower Selke reflects the upstream sub-catchment export patterns and therefore serves as an indicator to disentangle sub-catchment specific contributions to nitrate export and its dynamics.

4.5 Conceptual framework and implications for management

A key objective of this study was to analyze how the integrated response of nitrate concentrations, loads and CQ-relationships at the outlet of a mesoscale catchment is composed by the specific contributions from its nested sub-catchments. While upstream sub-catchments are known to have a disproportional impact on nutrient transport (e.g. Alexander et al., 2007; Dodds & Oakes, 2008; Goodridge & Melack, 2012), agricultural areas, which are more likely to occur in downstream lowlands, are known to be a major source for nitrate pollution (e.g. Padilla et al., 2018; Strebel et al., 1989). The available long-term and high-frequency data for 3 nested catchments within the Selke catchment allowed to disentangle these contrasting drivers of nitrate export and allowed for a detailed analysis of the relative impact of more mountainous upstream sub-catchments (upper Selke) versus more intensively cultivated downstream lowlands (lower Selke) across time scales. The general findings are summarized in Fig. 7, illustrating that TTs for nitrate in the upper Selke were relatively short (Fig. 7 a) and transport patterns were quite dynamic with nitrate concentration increasing with Q (Fig. 7 b,c). These dynamics led to relatively short-term impacts of temporally elevated nitrate concentrations during HFSs and events and a disproportional contribution to annual nitrate loads. On the contrary, the lower Selke showed long TTs (Fig. 7 a) and a less dynamic export behaviour with relatively constant nitrate concentrations (Fig. 7 b,c). Due to the long TTs, the imbalance between TTD derived conservative N export and measured N export and the low potential for denitrification, legacy stores in the downstream part are expected to be significant. Consequently, nitrate pollution in the lower Selke is a rather long-term and persistent problem that likely dominate nitrate exports during LFSs and base flow conditions for years to come. This differentiation between a more mountainous upper part of a catchment and an agriculturally dominated lowland part is not exclusive to the Selke, but very common for many mesoscale catchments in temperate climates (e.g. Krause et al., 2006; Montzka et al., 2008). Hence our findings have far reaching consequences for the management of nitrate pollution in such catchments.

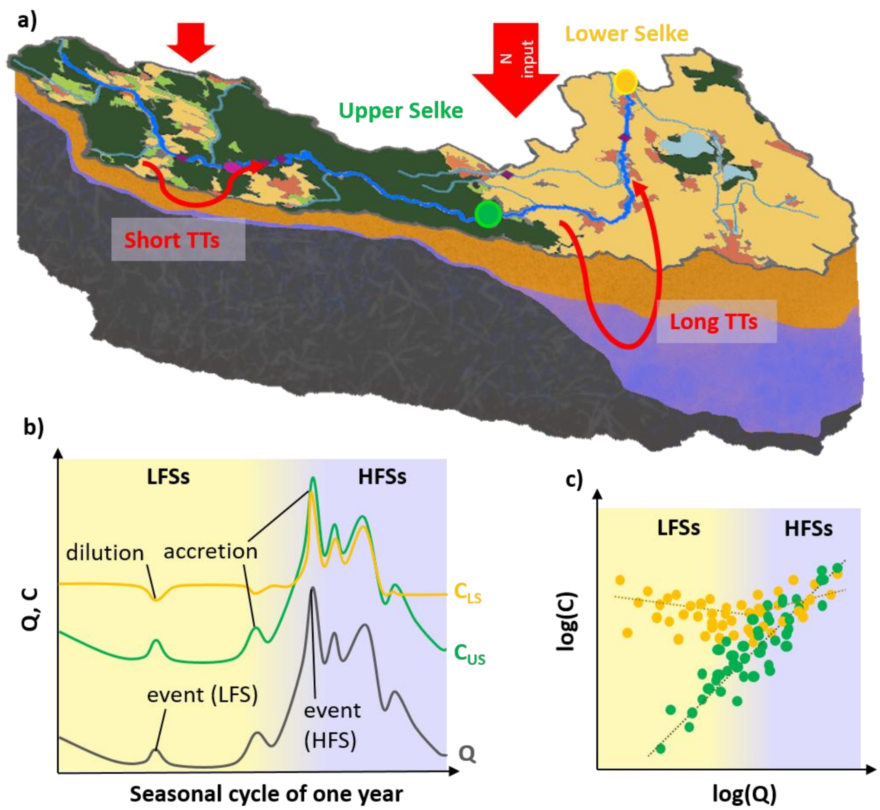

Figure 7. Conceptual framework explaining the sub-catchment specific contribution from the upper Selke (green) and the lower Selke (yellow) to nitrate export from the Selke catchment during low flow seasons (LFSs, yellow background) and high flow seasons (HFSs, blue background). Note that nitrate export from the lower Selke always is an integrated signal from the entire catchment. Subfigure a) shows the Selke catchment with its land use, its relative N input (not true to scale) and effective travel times of nitrate (TTs), b) shows the seasonal and event dynamics of nitrate export and c) the long-term CQ-relationships. Note that long-term CQ-relationships, as depicted in c) do not account for temporal shifts but represent the integrated signal.

Water quality managers should be aware of these potential differences between sub-catchments. If the aim is to reduce high nitrate loads, the focus must be on the upstream sub-catchments with short TTDs and dynamic transport patterns. As nitrate concentrations are especially high during winter and spring, an application of nitrate fixing crops during these seasons is a promising measure to reduce nitrate leaching (Askegaard et al. 2005, Constantin et al. 2009). Furthermore, large buffer stripes (> 50m) can decrease connectivity between agricultural fields and the stream network (Mayer et al., 2005). Unfortunately, high N loading via atmospheric deposition, as apparent in the Harz Mountains (Kuhr et al., 2014) cannot be addressed on site but would require a large-scale reduction of fertilizer application and fossil fuel combustion. Nevertheless, a substantial reduction of N-surplus from agriculture and measures to decrease nitrate leaching are believed to have the potential for a significant and relatively fast reduction of nitrate export to the streams, as the riverine concentration decrease after 1990 suggests.

If the aim is to reduce low flow nitrate concentrations to protect drinking water resources and aquatic ecosystems on the long-term, lowland areas with extensive agricultural land use and long TTs need to be the target for remediation measures. However, long TTs and legacy stores will impede a fast success of nitrate reduction measures and will likely affect drinking water quality and low-flow instream concentrations for years to come. For such groundwater-dominated systems, long-term management strategies to reduce fertilizer application at a large scale will be needed to effectively address nitrate pollution (Bieroza et al., 2018; Ehrhardt et al., 2019).

In any case, to address short-term *and* long-term nitrate pollution, water quality managers should neither solely focus on upstream areas of catchments nor solely on the lowland areas where most of the agricultural land use typically occurs. Instead, they need to integrate all characteristic landscape units and their interaction.

5 Conclusions

A key goal of this study was to characterize the spatial variability in nitrate export dynamics across nested sub-catchments and to disentangle their respective contributions to the integrated signal of nitrate export at the catchment outlet. Taking advantage of a comprehensive dataset that includes long-term and high-frequency data from three nested sub-catchments in the Selke catchment, we could show that sub-catchments can have very different nitrate export dynamics that lead to seasonally different sub-catchment contributions to nitrate concentrations and loads. The mountainous upstream part of the catchment (here the upper Selke) transports temporally elevated nitrate concentrations during HFSs and events and has therefore a disproportional contribution to nitrate loads. This imbalance underlines the important role of upstream sub-catchments for effective measures to reduce nitrate pollution. Hence, nitrate export from hydrologically responsive upstream catchments can be a serious threat to water quality, especially with respect to exported loads. At the same time, short TTs emphasize a fast response to changes in N input and dedicated mitigation measures are likely to show effects relatively quickly. In contrast, lowland sub-catchments with long TTs and a dominance of agricultural land use (here the lower Selke) pose a long-term and persistent problem of nitrate pollution, which can threaten the quality of drinking water for decades. Nitrate export from these sub-catchments is relatively steady and dominates during LFSs and base flow conditions. Its impact on nitrate concentrations during HFSs and events and especially on nitrate loads, however, might be overestimated if neglecting the impact from upstream sub-catchments. We do not aim at prioritizing individual measures to reduce nitrate pollution between sub catchments, but we emphasize the importance of sub-catchment-specific characteristics in order to place nitrate reduction measures most effectively and to assume realistic timescales for their success.

We could further show that CQ-relationships for nitrate concentrations can change as a reaction to changes in N input. While chemodynamic patterns can indicate ‘not equilibrated systems’ that are still in transition towards a new equilibrium, chemostasis can indicate homogenously distributed N sources - both vertically in the subsurface and between sub-catchments – after a prolonged period of stable N inputs. To detect these changes, it is crucial to account for temporal changes and seasonality in CQ-relationships. Furthermore, we found that the combined analyses of long-term trends and event scale CQ-slopes is a promising approach to disentangle the impact from sub-catchments on nitrate export at the catchment outlet as it can reveal short-term impacts from more dynamic upstream catchment export that is relevant for load estimations and a more precise detection of N sources. Examining the whole range of time scales – from long-term trends to the event scale – is therefore crucial to assess the full range of sub-catchment impacts on nitrate export, as the times and time scales relevant for nitrate export can vary substantially between sub-catchments.

Findings from this study should be further tested by applying our or similar approaches to other mesoscale catchments with different characteristics and in different settings. Including the knowledge gained from such studies on sub-catchment contributions to nitrate export into spatially distributed water quality models would eventually lead to more precise projections and, in turn, to more robust management strategies for water quality.

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Data availability:

Supplementary figures and tables are available as Supplementary Information. Datasets on i) FN and non-FN nitrate concentrations, loads and CQ-slopes, ii) N iput and iii) event characteristics are available under: doi:10.4211/hs.c3ea08faa88a46a4a3ce596a09686198.

Raw data on discharge and water quality is freely available on the website of the State Office of Flood Protection and Water Quality of Saxony-Anhalt (LHW), from gldweb.dhi-wasy.com/gld-portal/.

High frequency data of nitrate concentrations are archieved in the TERENO data base and will be available upon request through the TERENO-Portal (www.tereno.net/ddp).

Atmospheric deposition data can be accessed on the website of the Meteorological Synthesizing Centre – West (MSC-W) of the European Monitoring and Evaluation Programm (EMEP) (http://emep.int/mscw/index_mscw.html, Norwegian Meteorological Institute, 2017), which is assigned to the Meteorological Institute of BNorway (MET Norway).

The raw meteorological datasets can be obtained freely from German Weather Service (DWD); and gridded products based on Zink et al. (2017) from https://www.ufz.de/index.php?en=41160

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