From Trend to Event - Unraveling the Dynamics of Nitrate Export From Mesoscale Catchments Across Temporal Scales

DISSERTATION

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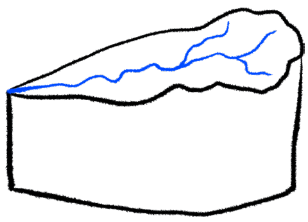

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Abstract

The invention of the Haber-Bosch process to synthesize reactive nitrogen has improved food security globally. However, the associated massive release of reactive nitrogen into the environment has disrupted the global nitrogen cycle with severe impacts on biodiversity, climate, and drinking water quality. To find an acceptable balance between the benefits and detrimental impacts of reactive nitrogen use, we need to understand the complexity of systems in which nitrogen is cycling. Catchments, as the main unit for water quality management, encompass numerous hydrological and biogeochemical processes that shape nitrogen retention in and nitrate export from catchments. Nitrogen retention and nitrate export are strongly controlled by catchment characteristics and hydro-meteorological conditions that vary in space and time. To mitigate nitrate pollution in a site-specific and targeted way, we need to identify the dominant processes and controls across spatiotemporal scales and the interlinkages between scales. Therefore, my overarching research question was:

How do hydrological and biogeochemical processes, operating across different temporal scales, shape the dynamics of nitrate concentrations and loads at the outlet of spatially heterogeneous catchments?

To disentangle the effects of spatial variability, I zoomed in on a heterogeneous mesoscale catchment in central Germany, analyzing data from three nested gauges (i.e., three sub-catchments). Furthermore, I zoomed out, comparing results from this catchment with neighboring catchments. The temporal scales investigated ranged from long-term trends over hydro-meteorological anomalies (a two-year drought) and seasonality to individual runoff events. My methodological approach encompassed data-driven analyses of concentration-discharge and load-discharge relationships combined with process-based modeling, hydro-meteorological runoff event characterization, and analysis of water and nitrogen transit times.

Results from the three studies in this thesis shed light on how the complex interplay of nitrate availability and transport shapes the signal of nitrate export at the catchment outlet. In Study 1, I disentangled the contributions of different sub-catchments to seasonality and long-term trends in nitrate export in response to an abrupt decline in nitrogen inputs after the German reunification. Building on the comprehensive understanding of (sub-)catchment functioning gained in Study 1, in Study 2, I investigated how a severe, two-year drought can affect sub-catchment-specific nitrate export patterns and nitrogen retention capacity. In Study 3, I focused on the temporal scale of runoff events, comparing results from the catchment analyzed in Studies 1 and 2 with those of neighboring catchments. Here, I assessed how hydro-meteorological event characteristics can affect event-driven nitrate export. In this thesis, I have synthesized the results of the three studies by dividing them into different temporal scales, highlighting the relevance of spatial heterogeneity and the interlinkages between spatiotemporal scales.

Long-term trend analyses revealed how changes in nitrate availability, which can be caused by strongly decreased fertilization (Study 1) or severe drought (Study 2), propagate through different sub-catchments. In both cases, sub-catchment differences in nitrogen transit times were crucial for understanding nitrate export dynamics at the catchment outlet.

The **hydro-meteorological anomaly** in the form of a severe drought, analyzed in Study 2, reduced the capacity of the catchment to retain nitrogen via biogeochemical processes. Additionally, summer drought conditions caused exceptionally long transit times, resulting in subsurface nitrate accumulation. Sub-catchment-specific transit times during rewetting determined whether accumulated nitrate was rapidly transported to the stream, causing peak nitrate concentrations, or whether it might have created a hydrological nitrogen legacy for the future.

All three studies revealed a pronounced **seasonality** in discharge and nitrate concentrations, driven by the seasonality in biogeochemical processes (uptake and removal) and catchment wetness. Biogeochemical processes controlled nitrate source availability, and catchment wetness controlled the hydrological connectivity of nitrate sources.

Hydro-meteorological conditions shaped nitrate export during **runoff events** by controlling nitrate availability and hydrological connectivity (Study 3). High-magnitude events, occurring mainly during wet conditions in winter and spring, exported disproportionately high nitrate loads with comparably constant nitrate export patterns and no sign of nitrate source limitation. In contrast, low-magnitude events, occurring mainly during dry conditions in summer and autumn, showed highly variable export patterns, reflecting the spatial heterogeneity in nitrate source availability and an increasing impact of biogeochemical retention processes.

By analyzing nitrate export across a range of spatiotemporal scales, I could break down the complexity of catchments to identify dominant processes and controls at their relevant scale and the interlinkages between scales. This allowed me to derive targeted suggestions for future research and water quality management. Future research can benefit from the process understanding gained in this thesis by incorporating it into mechanistic models to improve their ability to predict the impact of climate change on the export of nitrate or other pollutants. Regarding water quality management, I suggest to better account for the complexity of catchments by denser monitoring and differentiating site-specific mechanisms of nitrate export using C-Q relationships and transit times. These suggestions may help to find an acceptable balance between the societal benefits of reactive nitrogen and its harmful impacts.

Zusammenfassung

Die Erfindung des Haber-Bosch-Verfahrens zur Synthese von reaktivem Stickstoff hat zu einer Verbesserung der weltweiten Ernährungssicherheit geführt. Die damit verbundene massive Freisetzung von reaktivem Stickstoff in die Umwelt hat jedoch den globalen Stickstoffkreislauf gestört, mit schwerwiegenden Auswirkungen auf die Biodiversität, das Klima und die Trinkwasserqualität. Um ein akzeptables Gleichgewicht zwischen den Vor- und Nachteilen des Einsatzes von reaktivem Stickstoff zu finden, müssen wir die Komplexität der Systeme verstehen, in denen Stickstoff zirkuliert. Einzugsgebiete als primäre Einheit des Wasserqualitätsmanagements umspannen zahlreiche hydrologische und biogeochemische Prozesse, die den Stickstoffrückhalt in und den Nitratexport aus Einzugsgebieten beeinflussen. Stickstoffrückhalt und Nitratexport werden stark von Einzugsgebietsmerkmalen und hydrometeorologischen Bedingungen gesteuert, welche beide in Raum und Zeit variieren. Um die Nitratverschmutzung standortspezifisch und gezielt zu reduzieren, müssen wir die zugrundeliegenden Mechanismen auf verschiedenen räumlichen und zeitlichen Skalen und die Verbindung zwischen diesen Skalen verstehen. Meine übergeordnete Forschungsfrage lautete daher:

Wie prägen hydrologische und biogeochemische Prozesse, über verschiedene Zeitskalen hinweg, die Dynamik der Nitratkonzentrationen und -frachten am Auslass räumlich heterogener Einzugsgebiete?

Um die Auswirkungen der räumlichen Variabilität zu verstehen, teilte ich ein heterogenes, mesoskaliges Einzugsgebiet in Mitteldeutschland in drei Teileinzugsgebiete auf, indem ich die Daten drei aufeinanderfolgender Pegel analysierte. Außerdem erweiterte ich die räumliche Skala, indem ich die Ergebnisse aus diesem Einzugsgebiet mit den Ergebnissen angrenzender Einzugsgebiete verglich. Die untersuchten Zeitskalen reichten von Langzeittrends über hydrometeorologische Anomalien (eine zweijährige Dürre) und Saisonalität bis hin zu einzelnen Abflussereignissen. Mein methodischer Ansatz umfasste datengetriebene Analysen von Konzentrations-Abfluss- und Fracht-Abfluss-Beziehungen in Kombination mit prozessbasierter Modellierung, hydrometeorologischer Abflussereignis-Charakterisierung und die Analyse der Verweilzeiten von Wasser und Stickstoff.

Die Ergebnisse der drei Studien in dieser Arbeit geben Aufschluss darüber, wie das komplexe Zusammenspiel zwischen der Nitratverfügbarkeit und dem -transport das Signal des Nitratexports am Einzugsgebietsauslass prägt. In Studie 1 entschlüsselte ich die Beiträge der verschiedenen Teileinzugsgebiete zur Saisonalität und den Langzeittrends des Nitratexports in Reaktion auf einen abrupten Rückgang der Stickstoffeinträge nach der deutschen Wiedervereinigung. Aufbauend auf dem in Studie 1 gewonnenen, umfassenden Verständnis der Funktionsweise der Teileinzugsgebiete, untersuchte ich in Studie 2, wie sich eine schwere zweijährige Dürre auf die Nitratexportdynamiken und die Stickstoffrückhaltekapazität unterschiedlicher Teileinzugsgebiete auswirken kann. In Studie 3 konzentrierte ich mich auf die zeitliche Skala von Abflussereignissen und verglich die Ergebnisse aus dem in den Studien 1 und 2 analysierten Einzugsgebiet mit denen benachbarter Einzugsgebiete. Dabei untersuchte ich, wie die hydrometeorologischen Charakteristiken verschiedener Abflussereignisse die Nitratexportdynamiken beeinflussen können. In dieser Dissertation habe ich die Ergebnisse der drei Studien basierend auf verschiedenen Zeitskalen zusammengefasst, um die Bedeutung der räumlichen Heterogenität und der Verknüpfungen zwischen den räumlichen und zeitlichen Skalen hervorzuheben.

Die Analysen von **Langzeittrends** haben gezeigt, wie sich Veränderungen in der Nitratverfügbarkeit, die durch stark verringerte Düngung (Studie 1) oder schwere Dürre (Studie 2) verursacht werden können, in verschiedenen Teileinzugsgebiete ausbreiten. In beiden Fällen waren die Unterschiede zwischen den Stickstoffverweilzeiten der Teileinzugsgebiete entscheidend, um die Nitratexportdynamik am Einzugsgebietsauslass zu verstehen.

Die in Studie 2 analysierte **hydrometeorologische Anomalie** in Form einer schweren Dürre verringerte die Fähigkeit des Einzugsgebiets, Stickstoff über biogeochemische Prozesse zurückzuhalten. Darüber hinaus verursachte die Trockenheit im Sommer außergewöhnlich lange Verweilzeiten, was zu einer unterirdischen Nitratakkumulation führte. Die teileinzugsgebietsspezifischen Verweilzeiten während der Wiedervernässung bestimmten, ob das akkumulierte Nitrat schnell zum Fließgewässen transportiert wurde und dort Spitzen-Nitratkonzentrationen verursachte, oder ob das akkumulierte Nitrat möglicherweise ein hydrologisches Stickstoff-Vermächtnis für die Zukunft schuf.

Alle drei Studien zeigten eine ausgeprägte **Saisonalität** im Abfluss und in den Nitratkonzentrationen, welche durch die Saisonalität biogeochemische Prozesse (Stickstoffaufnahme und -abbau) und der Einzugsgebietsfeuchte bedingt war. Biogeochemische Prozesse kontrollierten die Nitrateverfügbarkeit und die Einzugsgebietsfeuchte steuerte die hydrologische Konnektivität der Nitratquellen.

Die hydrometeorologischen Bedingungen beeinflussten den Nitratexport während den **Abflussereignissen**, indem sie die Nitratverfügbarkeit und die hydrologische Konnektivität kontrollierten (Studie 3). Abflussereignisse hoher Größenordnung, die hauptsächlich zu Zeiten feuchter Bedingungen im Winter und Frühjahr auftraten, exportierten unverhältnismäßig hohe Nitratfrachten mit vergleichsweise konstanten Nitratexportmustern, ohne Anzeichen einer Limitierung der Nitratverfügbarkeit. Im Gegensatz dazu zeigten Abflussereignisse niedriger Größenordnung, welche überwiegend während trockener Bedingungen im Sommer und Herbst auftraten, sehr variable Exportmuster, welche die räumliche Heterogenität der Nitratverfügbarkeit und einen vergleichsweise starken Einfluss biogeochemischer Rückhalteprozesse widerspiegeln.

Durch die Analyse des Nitratexportes auf verschiedenen räumlichen und zeitlichen Skalen konnte ich die Komplexität von Einzugsgebieten aufschlüsseln, und wichtige Kontrollmechansismen auf der jeweiligen Skala sowie die Verbindungen zwischen diesen Skalen ermitteln. Daraus konnte ich gezielte Vorschläge für die zukünftige Forschung und das Wasserqualitätsmanagement ableiten. Zukünftige Forschung kann von dem in dieser Arbeit gewonnenen Prozessverständnis profitieren, indem dieses Verständnis in mechanistische Modelle eingebaut wird, um dadurch deren Fähigkeit zu verbessern, die Auswirkungen des Klimawandels auf den Export von Nitrat oder anderen Schadstoffen vorherzusagen. Bezüglich des Wasserqualitätmanagements schlage ich vor, die Komplexität von Einzugsgebieten durch ein dichteres Monitoringnetz und die Differenzierung standortspezifischer Mechanismen des Nitratexports mit Hilfe von C-Q-Beziehungen und Verweilzeiten besser zu berücksichtigen. Diese Vorschläge könnten dazu beitragen, ein akzeptables Gleichgewicht zwischen dem gesellschaftlichen Nutzen von reaktivem Stickstoff und seinen schädlichen Auswirkungen zu finden.

1 Introduction

Nitrogen (N) is an essential nutrient for all life on earth. However, human interference with nitrogen cycling has drastically increased the availability of reactive nitrogen in the biosphere, with detrimental impacts on biodiversity, climate, and drinking water quality (Elser, 2011; Vitousek et al., 1997). High concentrations of reactive nitrogen in the groundwater and surface water, mainly in the form of nitrate (NO_3^-), threaten the health of aquatic ecosystems (Schindler et al., 1985) and human health if ending up in our drinking water (Majumdar and Gupta, 2000). Despite great mitigation efforts, nitrate pollution remains a pervasive problem (Bijay-Singh and Craswell, 2021; SRU, 2015). Therefore, it is of utmost importance to understand the spatiotemporal integration of processes that shape the availability and transport of reactive nitrogen at the catchment scale, i.e., the relevant scale for water quality management (SRU, 2015). It is the main objective of this thesis to contribute to this understanding by unraveling the dynamics of nitrate export from mesoscale catchments across temporal scales. In the following, I introduce the overarching problem of a global excess of reactive nitrogen (1.1) and the resulting amplification of the nitrogen cycle and increased nitrate availability for hydrological transport (1.2). I then present the current state of our knowledge of the processes in a catchment that can control nitrate availability and hydrological nitrate transport (1.3) at different spatial (1.4) and temporal scales (1.5).

1.1 Global Excess of Reactive Nitrogen

The largest global nitrogen-pool is dinitrogen (N_2) in the atmosphere, with a volumetric fraction of about 78% (Elser, 2011). However, dinitrogen is inert and, therefore, inaccessible to most organisms (Elser, 2011; SRU, 2015). Therefore, to initiate nitrogen cycling in the biosphere, atmospheric dinitrogen needs to be transformed into reactive nitrogen compounds that are available for primary producers, such as plants. Naturally, dinitrogen is fixed by microorganisms that are capable of producing nitrogenase or by lightning strikes. However, due to the high energy demand of dinitrogen fixation, most ecosystems are naturally nitrogen-limited (Vitousek et al., 1997; Elser, 2011). Hence, the availability of reactive nitrogen strongly controls the structure and species composition of ecosystems (Vitousek et al., 1997).

In the early 20th century, Fritz Haber and Carl Bosch developed a method to synthesize ammonia (NH_3) from atmospheric dinitrogen, providing a literally inexhaustible source of reactive nitrogen for plant fertilization. This invention enabled a tremendous increase in agricultural productivity and food security across the globe (Elser, 2011). Another development was the invention of combustion engines that release nitrogen from fossil fuels and, together with other industrial burning processes, fix atmospheric dinitrogen in a similar way lightning strikes do (Elser, 2011). Both inventions mark milestones in the development of our modern civilization. However, human interference with the natural nitrogen cycle has also come with severe downsides: nitrogen oxides in the atmosphere contribute to global warming, depletion of the ozone layer, and air pollution (Vitousek et al., 1997; IPCC, 2021). In the biosphere, the widespread availability of reactive nitrogen has caused immense biodiversity losses due to the critical role of nitrogen-availability for ecosystem structure and species composition (de Vries et al., 2011; IPBES, 2019; Vitousek et al., 1997). Moreover, high inorganic nitrogen concentrations in freshwater bodies can cause eutrophication (Schindler et al., 1985), while in our drinking water, they can cause human health disorders such as methemoglobinemia (Majumdar and Gupta, 2000).

1.2 The Nitrogen Cycle Beyond Its Natural Boundaries

To understand the role of reactive nitrogen in freshwater quality, one needs to take a detailed look at the major transformation processes in the nitrogen cycle that affect the availability and mobility of different nitrogen compounds (Figure 1; SRU, 2015).

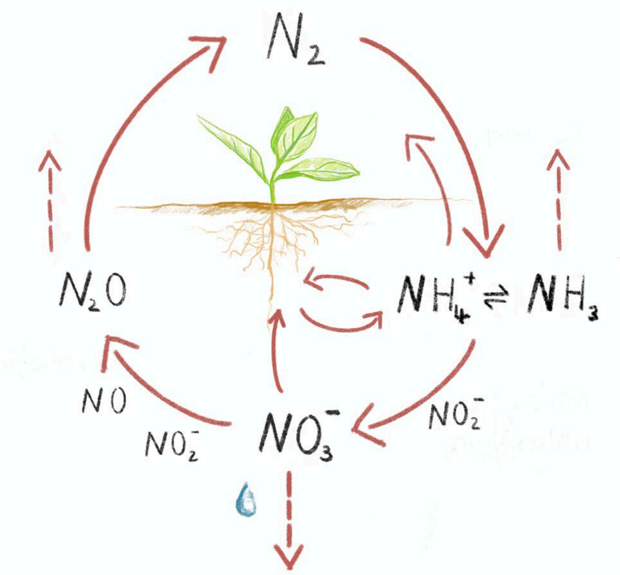


Figure 1. Biogeochemical nitrogen transformations in the soil-water-atmosphere continuum

It starts with the nitrogen flux from the atmosphere to the soil when atmospheric dinitrogen is fixed to ammonia or ammonium (NH_4^+). These two reactive nitrogen-compounds are in dissociation equilibrium, with ammonia potentially volatilizing back into the atmosphere and ammonium being available for plant uptake (i.e., assimilation). If not directly taken up by plants or other primary producers, ammonium can be further transformed into nitrite (NO_2^-) and then into nitrate (NO_3^-), which is also accessible to plants. The transformation from ammonia to nitrate is called nitrification. Organic forms of nitrogen are first transformed into inorganic ammonium (ammonification) and potentially further into nitrate (nitrification) to be accessible to plants and other primary producers. The transformation of organic nitrogen-compounds to inorganic ammonium and nitrate is called mineralization. Nitrate in the soil that primary producers have not taken up is leached into the groundwater or transferred back into the atmosphere via denitrification (Vitousek et al., 1997). While nitrogen can be temporarily stored in organic biomass, which can significantly delay nitrogen turnover, denitrification and anammox are the only known ways of transferring nitrogen back into the atmosphere as inert dinitrogen. Denitrification occurs predominantly under anaerobic conditions (Chen and Strous, 2013) when soil microbes switch from the energetically preferable electron acceptor oxygen to the less preferable nitrate, given a sufficient supply of electron donors such as organic carbon, reduced sulfur or iron(II) (Straub et al., 1996; Korom, 1992; Hayakawa et al., 2020). During denitrification, nitrate is successively transformed into nitrite, nitric oxide (NO), nitrous oxide (N_2O), and finally, dinitrogen. However, incomplete denitrification can release nitrous oxide, a greenhouse gas with an almost 300 times higher warming potential than carbon dioxide (CO_2; IPCC, 2007). The anammox process was discovered by Mulder et al. (1995), describing the transformation of ammonium and nitrite into dinitrogen under anaerobic conditions.

Due to the drastically increased availability of reactive nitrogen in the biosphere, Rockström et al. (2009) and Steffen et al. (2015) estimated that the nitrogen cycle is far beyond its planetary boundaries and a safe operating space for humanity. Hanke and Strous (2010) estimated that roughly every second nitrogen atom in the biosphere originates from fertilizers or fossil fuels. As a consequence, nitrate concentrations in many European rivers have increased ten- to fifteen-fold in the last 100 years (Fields, 2004). This human-made alteration of the nitrogen cycle further links to other environmental threats of global relevance, such as biodiversity loss and climate change (Steffen et al., 2015). Therefore, it is crucial to find a balance between carefully using nitrogen fertilization for food security and preventing its detrimental impacts on ecosystems and human health (IPBES, 2019). However, finding such balance is a delicate task given the nutritional and economic interest in nitrogen availability (IPBES, 2019; Ribaudo et al., 2011) but also due to the complexity of systems in which nitrogen is cycling (e.g., Grathwohl et al., 2013; Musolff et al., 2015; SRU, 2015). Detailed knowledge of the different nitrogen pathways and processes along these pathways is needed to understand how nitrogen is transported through and retained within heterogeneous landscapes. This includes knowledge of the spatial variability of pathways and processes, including the vulnerability of landscapes and ecosystems to different nitrogen input levels, and knowledge of the timing and duration of the transit of nitrogen-compounds through the subsurface and their exposure to biogeochemical processes.

1.3 Nitrogen Availability and Transport at Catchment Scale

Catchment characteristics and hydro-meteorological conditions play an important role in the spatiotemporal variability of nitrogen availability and its transfer from source to stream. They shape the numerous hydrological and biogeochemical processes that occur within a catchment and compose the signal of nitrate export that we can measure in the stream at the outlet of a catchment. According to the European Water Framework Directive (WFD; 2000/60/EC), catchments are the main unit of water quality management. Therefore, addressing the challenge of mitigating nitrate pollution while maintaining agricultural productivity also requires knowledge of the mechanisms behind nitrate export across a range of catchment characteristics and hydro-meteorological conditions.

As a first step, reactive nitrogen from different anthropogenic and natural sources is introduced to a catchment. While often anthropogenic nitrogen sources prevail (Elser, 2011; Vitousek et al., 1997), we can further distinguish between different types of (mainly anthropogenic) nitrogen input, which can vary with land use (Figure 2a). In agricultural areas, the diffuse input of nitrogen via fertilization is typically the dominant source (Ebeling et al., 2021a). In urban areas, the point source input from wastewater often dominates (e.g., Iverson et al., 2015). Atmospheric deposition, as another diffuse source, can be the main source of nitrogen input in relatively pristine landscapes (e.g., Knapp et al., 2020). Catchments, especially larger-scale catchments, often integrate a mix of different land use types and thus also different nitrogen sources. Overall, the most abundant source of nitrogen input is agricultural fertilization (Ebeling et al., 2021a; Elser, 2011; SRU, 2015), but this can vary locally or regionally, and different sources can change in their absolute and relative contribution over time

(Wachholz et al., 2022). Consequently, it is important to identify catchment-specific nitrate sources and their temporal dynamics.

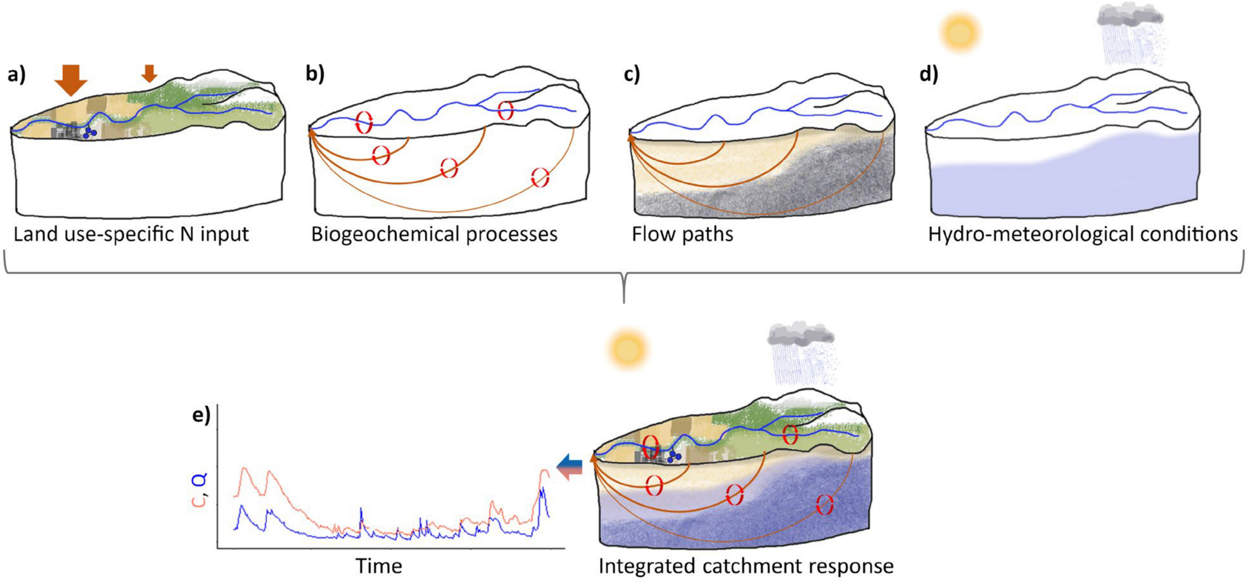


Figure 2. Catchment characteristics and hydro-meteorological conditions (a – d), which jointly shape discharge and nitrate export dynamics at the catchment outlet. Panel e) depicts an example of daily discharge (Q) and nitrate concentrations (C) over one year at the catchment outlet, which is an integrated signal of all the different processes (a – d) within the catchment.

Once entering the soils of a catchment, nitrogen can be taken up by plants or other primary producers, being temporarily stored in organic biomass or removed from a specific site via harvesting. If not taken up by primary producers, nitrogen can be removed via denitrification or anammox processes (Figure 1), or it can be leached from the soils, mainly in the form of nitrate, passing the vadose zone until reaching the groundwater (see chapter 1.2). When leached, nitrate is transported along the subsurface flow paths to the stream network or other water bodies, such as lakes (Figure 2b). These subsurface flow paths can vary between catchments and shape the nitrate transport time scale from nitrate being leached from the catchment's soils until its export at the catchment outlet. Moreover, these flow paths influence the exposure of nitrate to reactive zones that can interrupt nitrate transport via denitrification (Figure 2c; Tetzlaff et al., 2015; Nogueira et al., 2021b). When reaching the stream network, nitrate is further transported downstream along the river network. During this journey, nitrate can again be exposed to biogeochemical reactions such as nitrate uptake (temporal storage in organic biomass) and denitrification in the stream channel and within the hyporheic zone (Figure 2c; Rode et al., 2016; Nogueira et al., 2021).

Besides the internal catchment characteristics, the surrounding hydro-meteorological conditions (Figure 2d) also shape the hydrological transport of nitrate and its biogeochemical processing at catchment scale. Regarding hydrological transport, temperature and precipitation strongly control the wetness state of a catchment, which, in turn, influences the hydrological connectivity, i.e., the fraction of flow paths that actively contribute to nitrate transfer from source to stream (Jencso et al., 2009). High catchment wetness generally causes higher hydrological connectivity and leads to younger water reaching the stream network (Yang et al., 2018). Low catchment wetness, on the contrary, reduces the hydrological connectivity, with the remaining fraction of active flow paths preferentially transporting deeper and older water (Yang et al., 2018). Regarding biogeochemical processing, high temperatures generally favor high biogeochemical reaction rates, including high rates of mineralization, plant uptake, and denitrification (up to a process-specific temperature optimum; Saad and Conrad, 1993; Campbell and Biederbeck, 1982; Haynes, 1986). In contrast, low soil moisture, resulting from low precipitation but also from high temperatures, can inhibit these biogeochemical reactions (Wang et al., 2006; Miller and Johnson, 1964; Dijkstra and Cheng, 2008). Thereby, the hydro-meteorological conditions control the biogeochemical retention of nitrogen within a catchment or its provision as soluble nitrate that can be hydrologically transported to the stream network and exported at the catchment outlet.

The interplay of all these different processes, from nitrogen input to hydrological transport and biogeochemical processing, shapes nitrate export dynamics at the catchment outlet (Figure 2e). Therefore, the dynamics of discharge and nitrate concentrations measured in-stream can help to disentangle and better understand these underlying processes. Nevertheless, the great number of catchment processes and their complexity often hinder an unambiguous disentanglement, especially in larger (i.e., mesoscale or macroscale) catchments. Furthermore, all these processes are strongly controlled by individual catchment characteristics (e.g., land use, topography, and geology) and by the hydro-meteorological conditions, which vary in space and time. To address nitrate pollution in a site-specific and targeted way, we, therefore, need to identify dominant processes across spatiotemporal scales.

1.4 The Spatial Scale - Catchment Heterogeneity

Catchments often integrate different land use types, elevations, soil types, geologies, and many other characteristics, which can all be heterogeneous in space. Consequently, catchment functioning in terms of biogeochemical nitrogen processing and hydrological transport can also vary in space, and, in general, the larger the catchment, the more complex the interplay of various characteristics. A more detailed understanding of the contribution from different landscape units (i.e., sub-catchments) to nitrogen input, hydrological transport, and biogeochemical processing would allow us to better account for the complexity of catchments to develop more site-specific approaches for water quality management.

Numerous studies analyzed nitrate export in headwater catchments as the nucleus of catchment water quality (Kincaid et al., 2020; Yang et al., 2018; Knapp et al., 2020; Dupas et al., 2017). One reason is that headwater catchments are often relatively small catchments that are usually more uniform in terms of land use and other characteristics and thus provide a good test case for identifying the dominant processes that shape water quality at the headwater catchment outlet (e.g., Kincaid et al., 2020; Yang et al., 2018). Mesoscale catchments, on the contrary (10 km² - 10 000 km², Breuer et al., 2008), often cover several stream orders and can also cover a wide range of different catchment characteristics and hydro-meteorological conditions; for example, different rates of annual precipitation due to topographic differences. In large-scale catchments, such as the Elbe catchment, with approximately 148 000 km² (Wachholz et al., 2022), understanding the processes that occur at the level of headwater catchments from measurements at the catchment outlet becomes almost impossible. Nevertheless, water quality management is not restricted to first-order streams in headwater catchments but mainly has to deal with mesoscale or even larger catchments with all the complexity of hydrological and biogeochemical processes that these catchments entail.

Nested catchment studies (i.e., studies that use data measured at the catchment outlet and a minimum of one more measurement station located within the catchment) are a straightforward approach to disentangling the impact of different sub-catchments on nitrate export at the catchment outlet (e.g., Ehrhardt et al., 2019; Wollheim et al., 2017). For example, Ehrhardt et al. (2019) showed pronounced differences in nitrogen input and retention along nested sub-catchments, resulting in different export regimes of nitrate, and Wollheim et al. (2017) used a nested catchment approach to improve estimates on diffuse nitrate sources and instream biogeochemical retention at the sub-catchment level. As such, nested catchment studies allow disentangling the contribution of different sub-catchments, giving some insight into the black box of catchment processes that shape nitrate export at the catchment outlet.

Instead of zooming in to a catchment, as done in nested catchment studies, one can also zoom out and extend the scale by comparing different catchments in their nitrate export dynamics. Such multi-catchments studies allow us to compare catchments of different characteristics and draw conclusions about the impact of those characteristics on nitrate export (e.g., Ebeling et al., 2021; Van Meter et al., 2020).

1.5 The Temporal Scale – From Long-Term to High-Frequency

Nitrogen processing in catchments and nitrogen transit from source to stream can be described and analyzed at various temporal scales, which all have their relevance and specific merits. Analyses across different time scales help understand the full picture of nitrate transport and retention processes and better understand catchment functioning in terms of biogeochemical processing and hydrological transport under changing nitrogen input and hydro-meteorological conditions. Such analyses can cover, for example, long-term trends in riverine nitrate export, its divergence during climatic anomalies, its intra-annual variability (i.e., seasonality), and nitrate export during runoff events that span a few hours to days.

Long-term monitoring of nitrate concentrations in streams has a long history across industrialized countries (Vitousek et al., 1997), which allows for the analysis of trends across regions where nitrate pollution is most pressing. One prominent example is the Mississippi River basin in the United States, where increasing nitrate concentrations in the river have been associated with increasing fertilizer application rates, starting around 1950 (Turner and Rabalais, 1991). These and other long-term nitrate concentration measurements not only provide insights into how changes in nitrogen input propagate through a catchment, slowly becoming measurable at the catchment outlet, but also allow the detection of discrepancies between the total amount of nitrogen input and riverine export (Van Meter et al., 2016). Such discrepancies, often referred to as '*missing N*' (Van Meter et al., 2016), can hint at nitrogen removal via denitrification or nitrogen being retained (i.e., legacies) in the catchment (Van Meter et al., 2016). Hence, long-term analyses allow us to characterize nitrogen transit times (TTs) resulting from biogeochemical and hydrological retention and to estimate nitrogen removal via denitrification, among other things (e.g., Ehrhardt et al., 2019; Van Meter et al., 2016).

Hydro-meteorological anomalies, such as drought, may occur at inter- or intra-annual scales and can interfere with nitrogen processing and its hydrological transport. This interference can impact the timing and magnitude of nitrate export at the catchment outlet. For instance, numerous studies reported that nitrate export was significantly altered during and immediately after a drought, often degrading the overall freshwater quality (Mosley, 2015; and references therein). Consequently, hydro-meteorological anomalies, which can occur at inter- or intra-annual time scales, are another aspect to be covered for understanding the whole picture of nitrate export at catchment scale.

Seasonality of nitrate export, in general, describes the intra-annual variability in nitrate concentrations and loads. Numerous studies that analyzed nitrate export in temperate climates at intra-annual scales revealed a strong seasonality in nitrate export driven by the seasonality in the hydro-meteorological conditions, shaping nitrate availability and transport (e.g., Ebeling et al., 2021b; Wachholz et al., 2022; Van Meter et al., 2020). Therefore, for a detailed understanding of the magnitude and timing of nitrogen export at catchment scale, we also need to understand the seasonality in nitrate export and the processes behind it (Duncan et al., 2015).

Runoff events often occur within hours or days and are thus hidden if looking at low-frequency data (i.e., biweekly - monthly), typically available from long-term nitrate concentration monitoring. In contrast to nitrate concentration data, hydro-meteorological data such as precipitation and discharge at high frequency (i.e., sub-hourly to daily) have been available for decades, allowing for robust characterizations of long-term catchment hydrologic functioning (Kirchner et al., 2004). With the advent of sensors for automated high-frequency nitrate concentration measurements, we can now measure the dynamics of nitrate export at the same temporal resolution, at which we observe the hydrological processes (Kirchner et al., 2004; Rode et al., 2016b). This development was a big step towards a better understanding of water quality dynamics at the catchment scale (Kirchner et al., 2004; Rode et al., 2016b). Studies that took advantage of high-frequency nitrate concentration measurements revealed intra-annual differences in nitrate export during runoff events (Knapp et al., 2020), hysteresis patterns in discharge versus solute concentration dynamics (Musolff et al., 2021), or diurnal cycling driven by instream processing (Rode et al., 2016a; Greiwe et al., 2021). Especially runoff events, initiated by, e.g., rainfall or snowmelt, often transport a disproportionate amount of annual nitrate loads over a relatively short period (e.g., Inamdar et al., 2006; Blaen et al., 2017). Thus, analyzing nitrate export in concert with discharge dynamics at high frequency is relevant for closing the mass balance of nitrogen input and export. Overall, the analysis of high-frequency discharge and nitrate concentration data allows for a deeper insight into catchment functioning in terms of nitrogen retention and release under different hydro-meteorological conditions and bridges the gap between hydrological and biogeochemical processes that shape catchment nitrate export.

2 Research Question and Study Overview

As explained in the previous chapter, nitrate concentration and discharge dynamics at the outlet of a catchment are the integrated signal of numerous hydrological and biogeochemical processes that operate across a wide range of spatially heterogeneous catchment characteristics and at different temporal scales. Therefore, understanding the underlying mechanisms that shape nitrate export at the catchment outlet requires studies that cover different spatiotemporal scales and draw a linkage between them. Hence, the overarching research question in this thesis is:

How do hydrological and biogeochemical processes, operating across different temporal scales, shape the dynamics of nitrate concentrations and loads at the outlet of spatially heterogeneous catchments?

To disentangle the effects of catchment heterogeneity, I zoomed in on a heterogeneous mesoscale catchment by analyzing data from three nested gauges (Wollschläger et al., 2017), and I zoomed out by comparing nitrate export from this catchment with other mesoscale catchments. The temporal scales covered in this thesis are those of multi-year long-term trends, hydro-meteorological anomalies (here, a two-year drought), seasonality, and individual runoff events that span several hours to days. In the following, I briefly summarize how the three studies that form the core of this thesis contribute to answering the overall research question (Figure 3).

In study 1, I strived to understand how the different sub-catchments of a heterogeneous mesoscale catchment respond to changing nitrogen input and how these sub-catchments compose the integrated nitrate export signal at the catchment outlet. To this end, I analyzed the sub-catchment-specific long-term trends of nitrate export in response to an abrupt and strong decrease in nitrogen inputs after the German reunification. Furthermore, I studied seasonal differences in these long-term trends and their implications for nitrate export during runoff events for the period with available high-frequency data. With this comprehensive analysis across spatiotemporal scales, I aimed to better understand the catchment's functioning in terms of nitrate retention and export and the interplay of the contributions from the different sub-catchments.

In study 2, I asked if a hydro-meteorological anomaly, such as the severe, two-year drought in 2018 and 2019, can change (sub-)catchment functioning in terms of nitrate retention within the catchment and its export at the catchment outlet. In this study, I could build upon the knowledge gained from study 1, investigating (sub-)catchment functioning under severe drought compared to long-term behavior. I used data-driven analysis to detect deviations in catchment functioning, and I used process-based modeling to investigate the underlying mechanisms that may cause these deviations at the scale of three different sub-catchments. With this approach, I aimed to understand how a severe drought can change biogeochemical processes and hydrological transport of nitrogen at the level of different sub-catchments.

In Study 3, I looked at nitrate export during runoff events, striving to understand if and how different runoff generation processes affect the dynamics of nitrate export. Specifically, I asked what we can learn from an extensive hydro-meteorological event characterization about runoff event-driven nitrate mobilization and transport across contrasting mesoscale catchments and how long-term trends in these event characteristics could potentially impact future nitrate export. In this study, I extended the spatial scale from the mesoscale catchment in Studies 1 and 2 by integrating three neighboring mesoscale catchments that differed in their land use characteristics, among others. By combining runoff event characteristics with characteristic nitrate export patterns, I aimed to identify hydro-meteorological and catchment controls on nitrate export during runoff events.

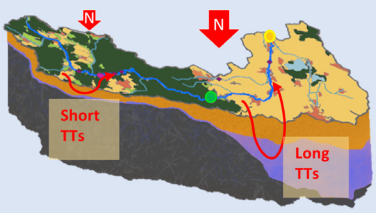
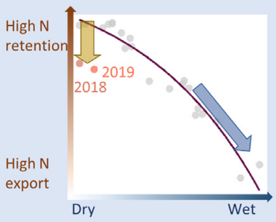
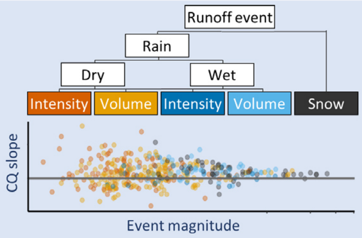
Study	**1**	**2**	**3**
Title	Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales	Droughts can Reduce the Nitrogen Retention Capacity of Catchments	Explaining the Variability in High-Frequency Nitrate Export Patterns Using Long-Term Hydrological Event Classification
Overview			
Spatial scales	Mesoscale catchment with 3 nested gauges	Mesoscale catchment with 3 nested gauges	Mesoscale catchment with 3 nested gauges + 3 neighboring catchments
Temporal scales	Long-term trends Seasonality Runoff events	Long-term trends Two-year hydro-meteorological anomaly Seasonality	Long-term trends Seasonality Runoff events
Methods	C-Q relationships WRTDS TTDs	C-Q and L-Q relationships mHM-SAS TTDs N_{ret}-Q relationship	C-Q relationships Runoff event classification

Figure 3. Overview of the three studies that form the core of this thesis. The abbreviations *TTs* and *TTDs* stand for transit times and transit time distributions, respectively. *WRTDS* stands for Weighted Regression on Time Discharge and Season (Hirsch et al., 2010). *C* stands for concentrations, *Q* for discharge, *L* for loads, N_{ret} for nitrogen retention capacity, and mHM-SAS for the mesoscale Hydrological Model with implemented StorAge Selection functions. Runoff event classes, abbreviated in Study 3, represent different runoff generation processes related to different hydro-meteorological conditions.

The three studies presented here cover different hydro-meteorological conditions and spatiotemporal scales for nitrate export. Nevertheless, there are also strong consistencies between the spatial and temporal scales covered by the three studies; for example, they all include analyses of long-term discharge and short-term, high-frequency nitrate concentration data from the Selke Catchment. The reason for these consistencies is that rather than separately naming the specific merits of different spatial and temporal scales, in this thesis, I aimed to highlight the value of bridging different scales and to point out their interlinkages, thereby providing a holistic picture of nitrate retention and export controls at the catchment scale. I am convinced that such comprehensive, cross-scale approaches are needed to account for the complexity of hydrological and biogeochemical processes and break down this complexity into a set of comparably simple dominating processes and controls. From such an assessment, we can then derive well-informed and thus more targeted solutions for water quality management. This View is mirrored by the guiding principle of the Helmholtz Research School on TRAjeCtories towards watER security (TRACER), which I am part of, originally stated by Oliver Wendell Holmes, Jr. (1841-1935): *"The only simplicity for which I would give a straw is that which is on the other side of the complex – not that which never has divined it."*

3 Materials and Methods

3.1 Study Site

The main study site for the analyses of nitrate export in this thesis is the Selke Catchment (Figure 4), a mesoscale catchment with an area of approximately 460 km² located in the Harz Mountains (Germany) and the foreland of the Harz Mountains. The Selke Catchment is one of the intensively monitored research sites within the Bode Catchment, which drains into the Elbe River and is part of the Helmholtz network of TERestrial Environmental Observatories (TERENO; Wollschläger et al., 2017).

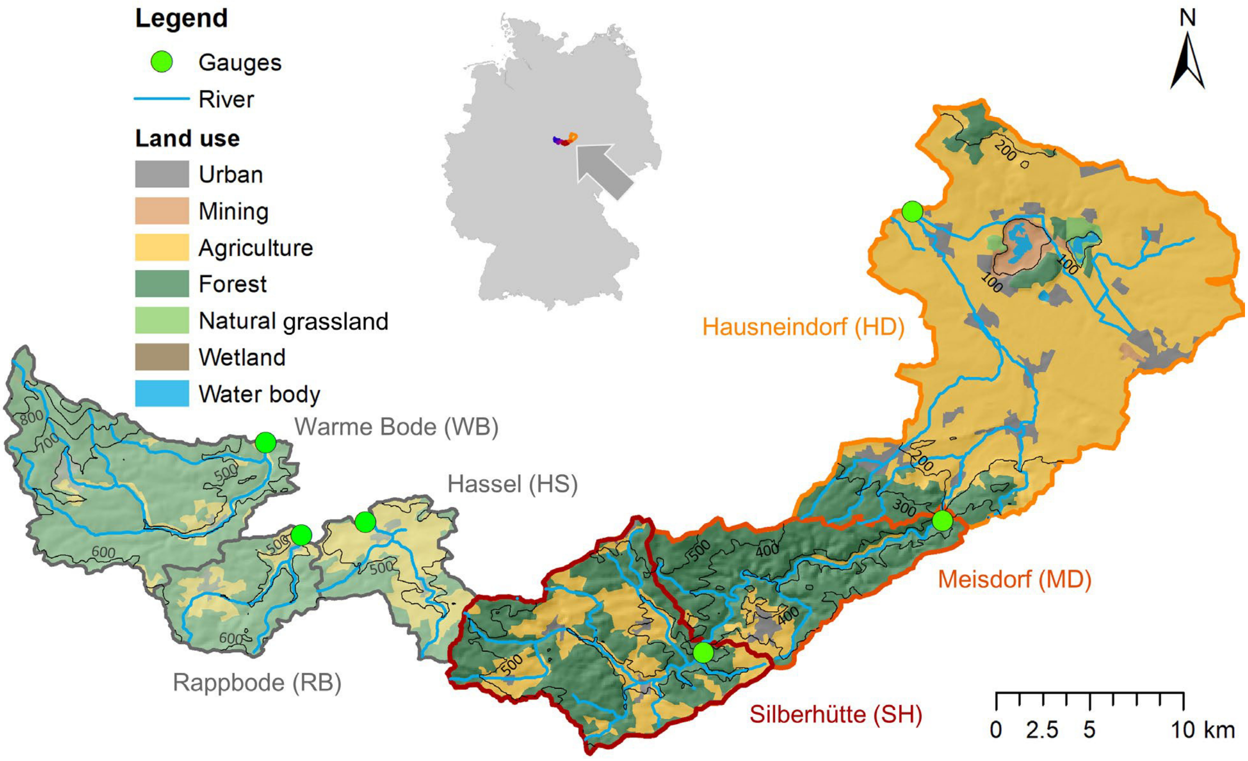


Figure 4. Land use map of the Selke Catchment with its three nested gauges and the three additional catchments analyzed in Study 3 depicted in more transparent colors. Black contour lines indicate the elevation in meters above sea level.

Three gauges and nitrate measurement stations are located in the Selke Catchment, one upstream at Silberhütte, delineating an upstream sub-catchment of around 100 km², a second one further downstream at Meisdorf, delineating a sub-catchment of around 180 km² (including the upstream area of Silberhütte) and a third one at the catchment outlet, downstream at Hausneindorf. The sub-catchments delineated at Silberhütte and Meisdorf have relatively similar characteristics. Both are located in the Harz Mountains and have higher elevations, steeper slopes, shallower soils (dominantly Cambisol), and forest as the dominant land use type, with around 20 % to 35 % agricultural land use located mainly upstream of Silberhütte. In contrast, the downstream sub-catchment, delineated at Hausneindorf, is an agricultural lowland with thick soils (dominantly Chernozem) and deep sedimentary aquifers.

In Study 3, I extended the spatial scale by including data from three neighboring mesoscale catchments (39 km² - 101 km²), namely the Hassel Catchment, the Rappbode Catchment, and the Warme Bode

Catchment (Figure 4). Like the Selke Catchment, these three catchments are sub-catchments of the Bode Catchment and part of the TERENO network. Additionally, they are part of the Rappbode Reservoir Observatory (Rinke et al., 2013), as they all drain into the Rappbode Reservoir, the largest drinking water reservoir in Germany (Rinke et al., 2013).

3.2 Data

Various studies have been conducted in the Selke Catchment, revealing, for example, spatiotemporal variations in runoff generation processes (Sinha et al., 2016) or concurrent diurnal cycling in assimilatory nitrate uptake and gross primary production in the stream (Rode et al., 2016a). One reason for this wealth of knowledge about the Selke Catchment and the knowledge gained from it is the abundance of available data for this site. Here, I give a brief overview of data related to nitrate export, with no claim for completeness (Figure 5).

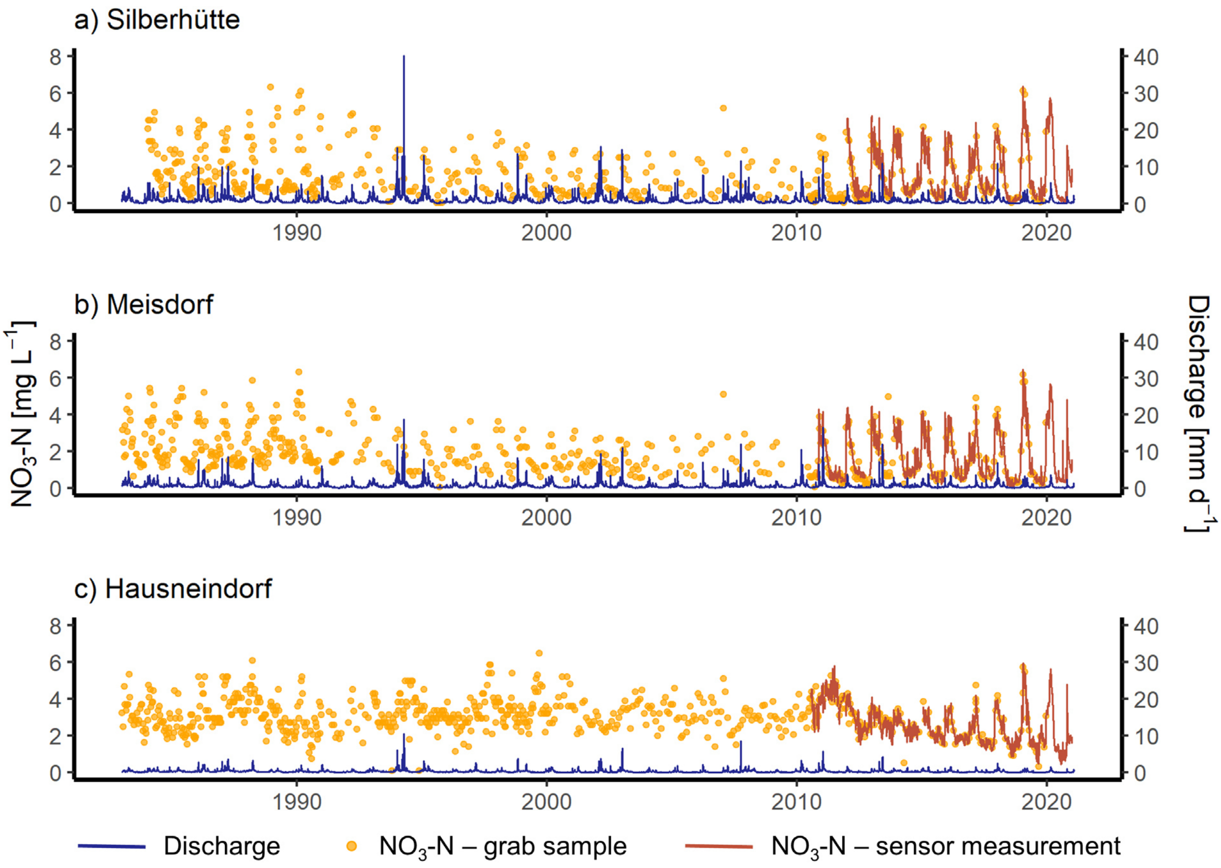


Figure 5. Nitrate concentration and discharge data from the three nested gauges in the Selke Catchment.

At all three gauges, long-term discharge data at a daily resolution has been provided by the State Office of Flood Protection and Water Quality of Saxony Anhalt (LHW) since 1955, and since around 2006, it is also available at a resolution of 15 minutes. Biweekly to bimonthly nitrate concentration measurements from the LHW started in 1983. Between 2010 and 2012, the Helmholtz Centre for Environmental Research (UFZ) started measuring high-frequency (i.e., 15-minute resolution) nitrate concentrations at all three gauges using TRIOS ProPS-UV sensors (Rode et al., 2016a). Long-term meteorological data, such as daily precipitation and temperature, were provided by the German Meteorological Service (DWD). Data on nitrogen input was gathered from different sources described in more detail in Study 1. This data includes diffuse inputs from fertilizer application, biological fixation, atmospheric deposition, and point source inputs from wastewater treatment plants.

3.3 Analysis

3.3.1 Data-Driven Analysis of Concentration-Discharge Relationships

As introduced above, nitrate export from a catchment is the integrated signal of numerous complex hydrological and biogeochemical processes within a catchment that operate at various spatiotemporal scales. Process-based models, which require a prior definition of all processes involved, allow their explicit simulation but also carry the risk of biased assumptions and, in turn, biased models that might produce the right answers for the wrong reasons (Kirchner, 2006). In contrast, data-driven top-down approaches have the advantage that they allow analyzing the integrated signal of discharge and nitrate concentrations (or other solutes) as it is without prior assumptions on the underlying mechanisms. Only in a later step, after identifying dominant patterns, these data-driven approaches allow for a deduction of the underlying processes and mechanisms. Common data-driven approaches for solute export from catchments focus on the relationship between instream solute concentrations (C) and discharge (Q), thus enabling the characterization of nitrate export dynamics under different hydrological conditions (Hirsch et al., 2010; Musolff et al., 2015). A parsimonious and straight-forward approach is the fitting of a power-law relationship in the form:

$$C = a\,Q^b \tag{1}$$

where a and b are fitted parameters representing the intercept and the slope of the C-Q relationship (Godsey et al., 2009). Of the two parameters, especially the parameter b (i.e., the C-Q slope, Figure 6) is a frequently applied measure to characterize nitrate export under different hydrological conditions (e.g., Bieroza et al., 2018; Burns et al., 2019; Musolff et al., 2015). A positive C-Q slope (i.e., positive parameter b) describes increasing nitrate concentrations with increasing discharge, for example, during runoff events. A negative C-Q slope represents decreasing nitrate concentrations with increasing discharge. These two scenarios imply a directional relationship between nitrate concentrations and discharge, often described as a chemodynamic export pattern (Figure 6). On the contrary, a C-Q slope close to zero indicates no clear directional relationship, which can be described as chemostatic behavior, under the assumption that the variability of nitrate concentrations is smaller than the variability of discharge (Godsey et al., 2009; Musolff et al., 2015; Thompson et al., 2011). To ensure compliance with this assumption, we can combine the C-Q slope with the ratio of the coefficient of variation of concentrations and discharge (CV_C/CV_Q) in an integrated framework (Musolff et al., 2015; Thompson et al., 2011). In the case of nitrate export, the C-Q slope and the CV_C/CV_Q are often positively correlated, as most variability in nitrate concentrations can be explained by discharge (Jawitz and Mitchell, 2011; Musolff et al., 2015). In this case, the CV_C/CV_Q does not add significant additional information on the C-Q relationship and can be neglected. Therefore, in the three studies of this thesis, I focused on the C-Q slope as the main measure for characterizing nitrate export patterns. Specifically, I used the C-Q slope as a measure to characterize nitrate export patterns across long-term data (Studies 1 and 2), during a two-year drought (Study 2), and between and within runoff events (i.e., inter-event and events-specific C-Q slopes in Studies 1 and 3).

The load-discharge (L-Q) relationship is closely related to the C-Q relationship. As L is the product of C and Q (i.e., a discharge-weighted concentration), the L-Q relationship can be mathematically described as:

$$L = a\,Q^{(b+1)} \tag{2}$$

Fitting the L-Q relationship to measured data gives a higher weight to high discharge values than the C-Q relationship does, where the weight is comparably higher for lower discharge values. Therefore, parameter *b* for the same data can vary between equation 1 and equation 2 (Tunqui Neira et al., 2021).

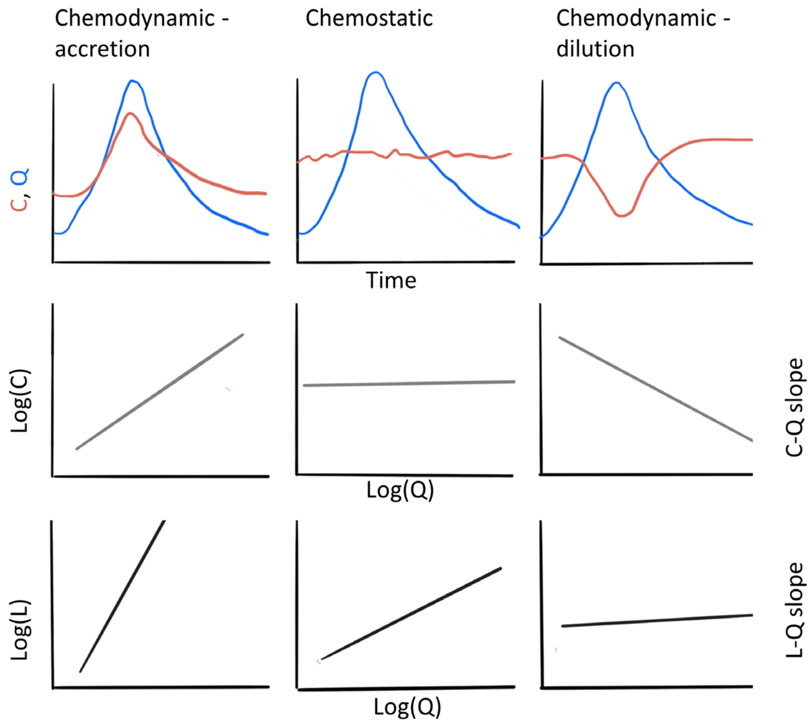


Figure 6. Conceptual framework of concentration-discharge (C-Q) relationship, showing how the C-Q slope and the load-discharge (L-Q) evolve from concentration and discharge measurements over time.

Other, more complex approaches for the characterization of the C-Q relationship exist that account, for example, for the temporal variability of C-Q relationships or hysteresis behavior. One example is the Weighted Regression on Time, Discharge, and Season (WRTDS), which allows for the calculation of seasonally distinguishable and flow-weighted long-term trends in daily nitrate concentrations, loads, and C-Q slopes (Hirsch et al., 2010; Zhang et al., 2016), with:

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

where subscript *i* stands for the specific day, *t* is the time in decimal years, $\beta_1 - \beta_4$ are fitted coefficients on time, discharge and season, and ε is an error term. Similar to parameter *b* in eq. 1, the fitted parameter β_2 can represent the weighted, temporally variable C-Q slope.

Another example is the analysis of hysteresis behavior between C and Q by including an additional fitting parameter (*c*) together with the derivative of discharge (*dQ/dt*) into equation 1 (Krueger et al., 2009; Musolff et al., 2021):

$$C = aQ^b + c\,dQ/dt \tag{4}$$

This addition allows us to distinguish between the rising and the falling limb of discharge and, thus, to account for hysteresis patterns in the C-Q relationship. A positive value of parameter *c* indicates clockwise hysteresis, a negative value counter-clockwise hysteresis, and a value close to zero indicates no or complex hysteresis patterns. Accounting for hysteresis in C-Q relationships enables the detection of time shifts between the dynamic of nitrate concentrations and discharge, for example, during runoff events, and thus allows us to deduce locations of solute sources (Musolff et al., 2021; Lloyd et al., 2016)

3.3.2 The Strength of Combining Complementary Approaches

Combining complementary methods can strongly increase the explanatory power of scientific results. As mentioned before, C-Q and L-Q relationships are data-driven approaches that allow analyzing the integrated signal of nitrate export top-down, which has the advantage of not requiring prior assumptions about the underlying mechanisms. This way, however, data-driven approaches only allow formulating hypotheses about the underlying mechanisms but do not allow directly disentangling or individually quantifying them. In contrast, other methods explicitly characterize or simulate the underlying processes bottom-up and can, thus, complement top-down approaches such as C-Q and L-Q relationships. For example, we can directly characterize underlying mechanisms for runoff generation based on the hydro-meteorological conditions and relate the resulting runoff event characteristics with nitrate export patterns from C-Q analysis. Another option is to complement top-down approaches with bottom-up, process-based models that allow us to simulate and quantify the underlying processes, analyze their sensitivity to changes in environmental conditions, and test their ability to reproduce observed patterns from C-Q relationships. This joint approach could help refine model structures and routines, while model results can also inform about additional data needs.

Large parts of this thesis are based on data-driven analyses, mainly focusing on C-Q and partly also L-Q relationships, which are powerful tools to analyze catchment water quality dynamics. Nevertheless, a combined approach with complementary methods allows for a better disentanglement of the underlying processes and can thus increase the explanatory power. While in study 1, I fully relied on a set of different data-driven methods (including equations 1, 3, and 4), in study 2, I combined the data-driven analysis of C-Q and L-Q relationships (equations 1 and 2) with process-based modeling using the mesoscale Hydrological Model with StorAge Selection functions (mHM-SAS; Nguyen et al., 2021). In study 3, I combined data-driven C-Q analysis (equation 1) with an extensive characterization and classification of runoff events linked to the dominant runoff generation processes developed by Tarasova et al. (2020). Those complementary approaches allowed me not only to analyze and characterize nitrate export under different hydro-meteorological conditions but also to shed light on the driving mechanisms and their interactions.

3.3.3 Analysis of Water and Nitrogen Transit Times

Transit times (TTs) describe the time it takes from the input of water or other substances to a catchment until their riverine export at the catchment outlet (Kirchner et al., 2010). For water, this means that TTs describe the time from the input of a water parcel to a catchment (i.e., via precipitation) until its discharge at the catchment outlet. Consequently, TTs of water describe the velocity of a water parcel, which differs from wave celerity, i.e., the response of the hydrograph to a precipitation event (Rinaldo et al., 2011). Nitrogen is transported with water in the form of soluble nitrogen compounds; thus, the TTs of water are strongly linked to the TTs of nitrogen. However, TTs of nitrogen may deviate from the TTs of water due to the occurrence of biogeochemical processes that temporally store nitrogen in organic biomass. As such, TTs of nitrogen describe the time from the input of a nitrogen atom (for example, via fertilization), followed by soil processing, leaching and hydrological transport through the subsurface until its riverine export, mainly in the form of nitrate. Generally, the longer the TTs of water (i.e., hydrological transport of nitrate), the more time there is for nitrate removal via denitrification, given anaerobic conditions and a sufficient supply of electron donors. Therefore, older water often exhibits lower nitrate concentrations compared to relatively young water (Yang et al., 2018). In summary, TTs of nitrogen reflect the integrated dynamics of hydrological transport and biogeochemical retention along the flow path; thus, understanding TTs is crucial for understanding the dynamics of nitrate export.

Due to the large variety of flow paths within a catchment, also the flow paths-specific TTs within a catchment can strongly deviate. Consequently, some water parcels (and thus also nitrogen compounds) might reach the stream within a few days, whereas others might reach the stream only decades later. The variety of flow path-specific TTs is described by transit time distributions (TTDs) with descriptive metrics such as the mean, standard deviation, skewness, or shape parameters (Heidbüchel et al., 2020). For example, defining "effective" TTDs of nitrogen that convolve the dynamics of long-term annual nitrogen input into long-term flow-weighted export allows us to estimate catchment-specific TTDs of nitrogen and catchment nitrogen retention or the so-called *"missing N"* (Ehrhardt et al., 2019; Van Meter et al., 2016). Moreover, several studies have shown that TTDs are not constant over time; instead, they can vary over time with changing hydro-meteorological conditions (e.g., Botter et al., 2010; Heidbüchel et al., 2020; Rinaldo et al., 2011; Seeger and Weiler, 2014). The concept of StorAge Selection (SAS) functions, therefore, accounts for the variability in TTDs by describing the selective discharge of water from a subsurface storage with different water ages and nitrate concentrations (Rinaldo et al., 2015). SAS functions are especially helpful in describing high-frequency (e.g., daily) nitrate transport dynamics under changing hydro-meteorological conditions (Benettin et al., 2017; Nguyen et al., 2021).

Overall, a good understanding of catchment-specific TTDs is crucial if the aim is to analyze catchment functioning in terms of nitrate retention and export across different spatiotemporal scales. In this thesis, I have relied on two different TT-modeling approaches also mentioned above, namely using long-term catchment-specific TTDs of nitrogen and daily analyses of nitrate export using SAS functions.

4 General Results and Discussion

In this thesis, I analyzed how hydrological and biogeochemical processes across different temporal scales shape nitrate export at the outlet of a heterogeneous mesoscale catchment. Results of the three studies that form the core of this thesis shed light on the dominant processes and controls behind the complex interplay of nitrate source availability and its hydrological transport. In the following chapters (4.1 and 4.2), I synthesize the results of the three studies by breaking them down into different spatial and temporal scales. In the subsequent chapter, 4.3, I discuss interlinkages between these spatiotemporal scales. Based on this, I give an outlook on emerging research questions that could benefit from the methods applied in and process understanding gained from this thesis (chapter 5). Finally, in the concluding chapter 6 of this thesis, I summarize the knowledge gained and formulate targeted suggestions for water quality management considering the complexity of catchments and processes occurring within.

4.1 Spatial Distribution of Nitrate Sources and Hydrological Transport

The spatial variability in nitrate source availability and hydrological transport is essential for understanding the integrated catchment response of nitrate export. In Study 1, I could show that sub-catchment differences in nitrogen input and TTDs strongly influence long-term trends and seasonality in nitrate concentrations and C-Q relationships at the catchment outlet. Furthermore, in Study 3, I could show that land use differences between mesoscale catchments shape the overall level of nitrate concentrations and loads during runoff events. Nitrate export patterns (i.e., C-Q slopes) during high-magnitude events were similar across catchments, indicating common biogeochemical and hydrological controls. Instead, differences in the spatial distribution of nitrate sources could explain part of the variability in export patterns between low-magnitude events.

Studies 1 and 2 showed that nitrogen input to the upstream sub-catchments of the Selke Catchment was comparably low, and TTs were predominantly short (Figure 7a). In contrast, nitrogen input in the downstream sub-catchment was significantly higher, and longer TTs prevailed (Figure 7a). These spatial differences in the nitrate source availability and the time scales of nitrate mobilization and subsequent hydrological transport resulted from different sub-catchment characteristics. Nitrogen input increased with agricultural land use as a consequence of the well-established increase in nitrogen input with increasing fertilization (Elser, 2011). Differences in the TTDs can be explained by a set of characteristics, including soil type, geology, and climatic conditions (Hrachowitz et al., 2010, 2009). Shallow soils, low-permeable geology, and higher precipitation in the upstream sub-catchments create relatively short flow paths and enable fast nitrate transport (Figure 7a). In contrast, deep sedimentary aquifers and lower precipitation in the downstream sub-catchment create longer flow paths and slow nitrate transport (Figure 7a). Such sub-catchment differences in nitrogen input and TTDs are not restricted to the Selke Catchment but can be expected in many mesoscale catchments that integrate different characteristics, such as land use, soil types, geology, and topography (e.g., Ehrhardt et al., 2019; Hrachowitz et al., 2010, 2009). Therefore, the spatial heterogeneity (here analyzed as sub-catchment differences) in nitrogen input and TTDs are important for understanding nitrate export at the catchment outlet and defining locally or regionally adapted management strategies.

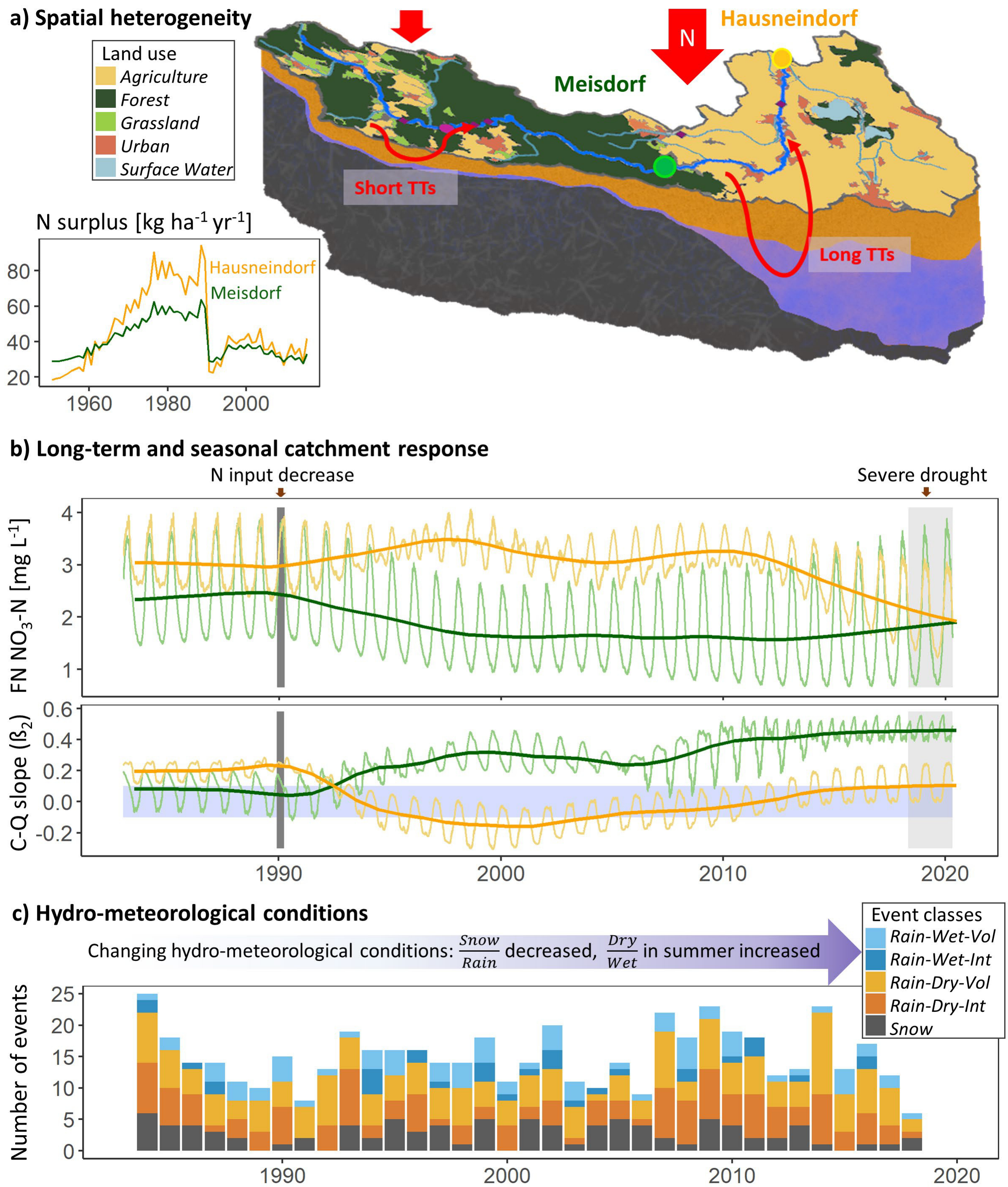


Figure 7. Summary of results, showing a) spatial differences in land use and related nitrogen surplus within the Selke Catchment and sub-catchment-specific transit times (TTs). b) Long-term daily (thin line) and annual average (bold line) flow-weighted (FN) nitrate concentrations and concentration-discharge relationships (C-Q slopes, fitted via WRTDS), separated for the upstream catchment area (measured at Meisdorf) and the entire catchment (measured at Hausneindorf). C-Q slopes in the range of chemostatic nitrate export patterns ($-0.1 < ß2 < 0.1$) are underlain in light blue. Shifts in the nitrate source availability, analyzed in this thesis, are marked in gray. These cover the decrease in fertilization due to the German reunification (dark gray) and the reduced biogeochemical nitrogen retention during the 2018-2019 drought (light gray). c) Long-term trends in hydro-meteorological conditions, here depicted as the number of different runoff event types from 1983 to 2018, indicating the inducing event type (*Rain* or *Snow*), antecedent conditions (*Wet* or *Dry*), and volume-dominated (*Vol*) versus intensity-dominated (*Int*) precipitation.

In study 3, I analyzed runoff event-driven nitrate export across different mesoscale catchments and showed that catchments with a higher proportion of agricultural land use generally exported higher nitrate concentrations and loads during runoff events. Hence, in agreement with results from Studies 1 and 2, the fraction of agricultural land use controlled the nitrate source availability and, thereby, the overall level of nitrate concentrations and loads. Furthermore, I showed that nitrate export patterns (i.e., C-Q slopes) during high-magnitude events were surprisingly homogeneous across catchments. I explain this homogeneity by the wet antecedent conditions associated with high-magnitude events across all catchments. High catchment wetness increases the fraction of flow paths that actively contribute to nitrate transfer from source to stream (i.e., hydrological connectivity). High hydrological connectivity, thus, allows for the extensive mobilization of nitrate sources across the catchment (Yang et al., 2018), overriding potentially catchment-specific characteristics and processes.

Only during low-magnitude events did some catchment differences become visible, mainly in the tendency towards more enrichment patterns (i.e., positive event-specific C-Q slopes) in the forested catchments and more dilution patterns (i.e., negative event-specific C-Q slopes) in the agricultural catchments. Enrichment patterns can be explained by relatively shallow nitrate sources that become hydrologically connected during runoff events (Musolff et al., 2015; Bowes et al., 2015). In contrast, high base flow nitrate concentrations (from high nitrogen input) and comparably lower nitrate sources in the discharge-generating areas activated during the runoff event can explain the dilution patterns observed during low-magnitude runoff events (Musolff et al., 2015; Bowes et al., 2015). In other words, nitrate export patterns during low-magnitude events can be explained by the differences in the spatial distribution of nitrate sources between catchments, while wet conditions homogenize the catchment's solute response.

In summary, the spatial variability of land use and flow paths within and between catchments shapes the spatial availability and distribution of nitrate sources and the time scales of nitrate transfer from source to stream. Both components are important to understand the integrated signal of nitrate export at the catchment outlet or differences in nitrate export between catchments. Therefore, dividing heterogeneous mesoscale catchments into characteristic landscape units and analyzing nitrate export across contrasting catchments, as done in this thesis, are important steps to disentangle the complex interplay of processes shaping nitrate export.

4.2 Temporal Variability in Nitrate Availability and Hydrological Transport

Besides the spatial variability, the temporal variability in nitrate source availability and hydrological transport is also crucial for understanding nitrate export dynamics. In this thesis, I could show that the relationship between nitrate concentrations and discharge (i.e., the C-Q relationship) can change i) in the long term (Study 1; Figure 7 b), ii) during a two-year drought (Study 2), iii) seasonally (Study 1; Figure 7 b), and iv) between different runoff events (Study 3). These changes indicate that nitrogen input and the mechanisms behind nitrate retention, mobilization, and transport are not steady over time and that different processes dominate at different time scales. In the following, I discuss nitrate export dynamics and underlying processes at the four different time scales, from (long-term) trends to (runoff) events.

4.2.1 Long-Term Trends

Long-term trends in nitrate export reflect the time between changes in the nitrate source availability and the response of stream nitrate concentrations to such changes. In Study 1, I analyzed the catchment response to an abrupt and strong decrease in nitrogen input caused by the decrease in fertilization rates in the Selke Catchment after the German reunification in 1990 (Figure 7a). I could show that sub-catchment-specific TTDs can cause diverging long-term trends in nitrate export upstream and downstream. In the upstream part of the catchment with relatively short TTs, stream nitrate concentrations at the gauges in Silberhütte and Meisdorf decreased shortly after the decrease in nitrogen input (Figure 7b). On the contrary, in the downstream part of the catchment with long TTs, it took much longer until changes in nitrogen input were transferred to stream nitrate concentrations (Figure 7b). These differences in sub-catchment-specific long-term trends of nitrate concentrations were also reflected in transitional changes in the C-Q relationship at the catchment outlet (Figure 7b, lower Selke). Shortly after the decrease in nitrogen input, low nitrate concentrations from upstream caused a dilution pattern downstream (i.e., negative C-Q slope). After a prolonged period of relatively stable nitrogen input, nitrate concentrations between the sub-catchments converged, resulting in rather chemostatic export patterns at the downstream gauge (i.e., C-Q slope close to zero). A similar dynamic in nitrate export and C-Q relationships has been reported by Ehrhardt et al. (2019) for another mesoscale catchment with a similar decrease of nitrogen input after the German reunification, indicating some generality of the observed patterns. From this, we can learn that differences in the sub-catchment-specific TTDs play an important role in understanding how nitrogen availability changes shape the integrated signal of nitrate export at the catchment outlet. Similarly, measures to improve water quality by reducing nitrogen input can show immediate success in areas where short TTs prevail, whereas the response in stream nitrate concentration might be considerably delayed where long TTs predominate.

Besides changes in nitrogen input, also long-term trends in the runoff event characteristics due to changing hydro-meteorological conditions can affect nitrate concentrations, loads, and export patterns. In study 3, I could show that between 1983 and 2018, the relative number of snowmelt-induced runoff events decreased compared to rainfall-induced events in most of the catchments (Figure 7c). Another trend, detected in half of the catchments, is an increase in the number of runoff events during summer that occurred under dry antecedent conditions compared to summer events under wet antecedent conditions. These trends align with predictions of rising temperatures, decreasing summer precipitation, and an increased risk for summer droughts, such as the drought analyzed in Study 2 (IPCC, 2021; Stahl et al., 2010; Hari et al., 2020). Regarding nitrate export, I showed that both snowmelt-induced and rainfall-induced events under wet antecedent conditions exported the highest nitrate loads, with no significant difference between the two event types. Thus I could not find any indication that a shift in the ratio of snowmelt- versus rainfall-induced events might change nitrate export patterns, but this shift might change the timing of high nitrate export peaks to times outside of the snowmelt season. Regarding the increase of summer events under dry antecedent conditions, I showed that these events were associated with higher variability in event-specific C-Q slopes compared to wet conditions. Therefore, increasingly dry summer conditions due to climate change might also increase the variability in nitrate export patterns.

While results from Study 3 provide indications for possible trajectories of runoff event-driven nitrate export patterns, an explicit simulation of future projections was beyond the scope of this work. Nevertheless, the results of rigorously assessing nitrate export during different types of runoff events provide a novel process understanding that could be incorporated into mechanistic models to improve their ability to predict scenarios of nitrate export under climate change.

4.2.2 Hydro-Meteorological Anomalies: A Two-Year Drought

The temporal variability in the hydro-meteorological conditions shapes the availability of nitrate sources by influencing biogeochemical reaction rates and hydrological transport through selective flow path activation. Consequently, anomalies in the hydro-meteorological conditions can also considerably affect nitrate export at the catchment outlet (Mosley, 2015). In Study 2, I analyzed nitrate export at the three nested gauges of the Selke Catchment under a two-year hydro-meteorological anomaly, the 2018-2019 drought, which affected large parts of Central Europe (Hari et al., 2020). This drought was unprecedented in intensity over at least the last 250 years, but severe and prolonged droughts are becoming more likely due to climate change (Hari et al., 2020).

I found that the 2018-2019 drought altered catchment functioning in terms of nitrate retention, causing a deviation from long-term catchment behavior (Figure 8). Using a combination of data-driven analysis and process-based modeling, I could show that low soil moisture during the dry summer months reduced nitrogen uptake by plants and denitrification in the catchment soils. Consequently, the biogeochemical retention capacity of the catchment was reduced, and the overall nitrate availability increased. Another effect of the low soil moisture during summer was the low hydrological connectivity of nitrate sources. Median TTs during the summer periods were between 8 and 44 years longer than the long-term median. Therefore nitrate that was not taken up nor denitrified accumulated in the catchment soils (instead of being exported). At the same time, nitrate concentrations in the stream were exceptionally low because discharge during the dry summer periods was composed of relatively old and largely denitrified water from previous years. With rewetting in late autumn of both years, TTs in the upstream sub-catchments shifted back to relatively short TTs (median < 2 months), which allowed for a fast mobilization and transport of the accumulated nitrate sources. As a consequence, nitrate concentrations measured at the gauges at Silberhütte and Meisdorf reached the highest values on record, and nitrate loads were up to 70 % higher than the long-term L-Q relationship. In the downstream sub-catchment, TTs remained relatively long (median 20 years), inhibiting a fast export of accumulated nitrate but potentially creating elevated groundwater concentrations and a hydrological nitrogen legacy for the future. Thus, high nitrate concentrations measured during the drought years at the gauge in Hausneindorf were driven by the contribution from the fast-responding upstream sub-catchments.

Overall, I found evidence that a severe and prolonged drought can considerably decrease catchment nitrogen retention and that sub-catchment-specific TTDs are essential to understand the catchment response. Additionally, the general framework developed in Study 2 indicates that years of high discharge would also increase nitrogen export relative to nitrogen input. Consequently, both scenarios, very dry and very wet conditions, potentially reduce catchment nitrogen retention (Figure 8).

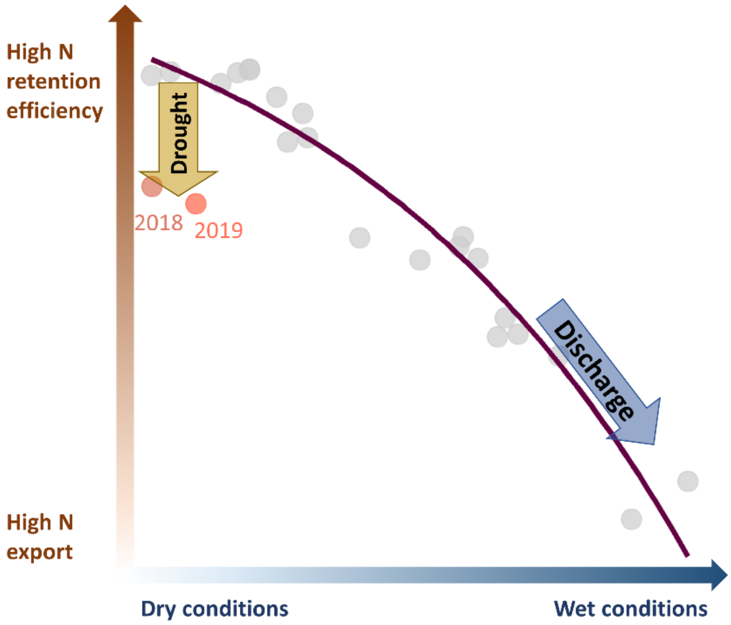


Figure 8. Conceptual framework of annual average catchment nitrogen retention under varying wetness conditions, approximated by annual average discharge, developed in Study 2. The years 2018 and 2019 of the two-year drought, analyzed in Study 2, are marked in reddish colors. The years from 1997 to 2017 are depicted in gray. Drivers for a decrease in catchment nitrogen retention capacity are indicated as arrows. Data was taken from the gauge at Meisdorf and the sub-catchment delineated at Meisdorf.

4.2.3 Seasonality

Nitrate export dynamics in temperate climates often show a strong seasonality (e.g., Wachholz et al., 2022; Ebeling et al., 2021b; Van Meter et al., 2020). Hence, we need to analyze the seasonal dynamics of nitrate export and differences within and between catchments to unravel the hydrological and biogeochemical processes shaping it.

In this thesis, I found pronounced seasonal dynamics in nitrate export in all three studies, with high discharge and nitrate concentrations in winter and spring and lower ones in summer and autumn. Seasonal differences were more pronounced in the upstream sub-catchments and less pronounced downstream (Figure 7b), leading to a disproportionate contribution of the upstream sub-catchments to elevated nitrate concentrations during high flow in winter and spring and thus also to annual loads (Studies 1 and 2). In contrast, the downstream sub-catchment showed a disproportionate contribution in elevating summer low-flow concentrations when ecosystems are most sensitive to eutrophication (Whitehead et al., 2009). Runoff events during winter and spring were mainly characterized as snowmelt-induced or rain-induced under wet antecedent conditions and exported comparably high nitrate concentrations and loads. In contrast, runoff events during summer and autumn were mainly characterized as rain-induced under dry antecedent conditions and showed a comparably low nitrate export (Study 3).

In temperate climates, the seasonality in nitrate export is generally driven by two components. One is the seasonality in temperature and light availability controlling nitrogen uptake and removal, which is highest during summer and lowest in winter (Dupas et al., 2017; Nogueira et al., 2021a; O'Connell, 1990). In other words, biogeochemical processes such as plant uptake and denitrification reduce the overall nitrate availability during summer, while more nitrate is available during winter. The other component is the seasonality in catchment wetness, which is strongly driven by evapotranspiration that is highest during summer (i.e., low catchment wetness) and lowest during winter (i.e., high catchment wetness) (Yang et al., 2018; Sinha et al., 2016), and by snowmelt in early spring. Consequently, catchment wetness is highest in winter and spring and lowest in summer and autumn. The degree of catchment wetness controls the hydrological connectivity of nitrate sources within a catchment (Jencso et al., 2009; Yang et al., 2018). Generally, higher catchment wetness causes higher hydrological connectivity, enabling more nitrate export from wider areas. In contrast, with lower catchment wetness, only a fraction of nitrate sources get mobilized and transported, mainly from deeper and older groundwater and often from areas close to the stream network (Yang et al., 2018). Due to these seasonal changes in the spatial extent of hydrological connectivity, the location of nitrate sources within a catchment (for example, in the distance to the stream, with depth and water age, or between sub-catchments) shapes the seasonal dynamics of nitrate export. Still, disentangling both components, seasonality in nitrate source availability and its hydrological connectivity, remains a challenge that is beyond the scope of this study to resolve.

Sub-catchment-specific long-term changes in nitrate availability, such as the ones described in chapter 4.2.1, can change the seasonal signal of nitrate export at the catchment outlet (Figure 7b). At times when the difference between nitrate concentrations upstream and downstream was relatively small, nitrate concentrations at the catchment outlet were highest in winter and lowest in summer. However, in years when nitrate concentrations from upstream were much lower than those downstream, seasonality in nitrate concentrations at the catchment outlet reversed, with the highest nitrate concentrations in summer and lowest in winter. These long-term changes in the seasonality of nitrate export can be explained by the seasonality in the relative contribution of the different sub-catchments to nitrate export (i.e., higher contribution of the upstream sub-catchments during winter and spring and lower contribution during summer and autumn). Hence, in addition to the seasonality in the hydro-meteorological conditions, sub-catchment differences in TTDs and nitrate availability can shape the seasonality of nitrate export at the catchment outlet.

4.2.4 Runoff Events

Runoff events are often described as *"hot moments"* (McClain et al., 2003) of nitrate export, as they can transport a disproportionate amount of annual nitrate loads within a relatively short time (e.g., Inamdar et al., 2006; Vaughan et al., 2017; Speir et al., 2021). In study 3, I could show that around 74% of event-driven nitrate loads were exported during high-magnitude events (either snowmelt-induced or rain-induced events) under wet antecedent conditions, which mainly occurred in winter and spring. In contrast, nitrate concentrations during low-magnitude events were lower and revealed high variability in the event-specific export patterns.

Across all six (sub-)catchments analyzed in Study 3, event-driven nitrate concentrations increased with event magnitude (i.e., median discharge during an event; Figure 9a). Moreover, the event-specific C-Q slopes converged from a high-variability during low-magnitude events towards more chemostatic patterns during high-magnitude events (i.e., C-Q slope close to zero and CV_C/CV_Q smaller than 0.5;

Figure 9b). These rather chemostatic export patterns during high-magnitude events indicate that there was no nitrate source limitation in none of the six catchments, not even in the Warme Bode Catchment, with 90 % forest cover (i.e., lower nitrogen input from fertilization). Other studies have shown dilution patterns (i.e., negative C-Q slopes) during high-magnitude events and related it to source limitation in relatively pristine catchments (Kincaid et al., 2020; Vaughan et al., 2017) or the dilution of high base flow concentrations (Fovet et al., 2018). However, no such dilution could be observed in the studied catchments, indicating that the available pool of nitrate sources was sufficient to sustain nitrate concentrations during high-magnitude events (Figure 9b). As discussed in chapter 4.1, high-magnitude events can be associated with high hydrological connectivity of nitrate sources, allowing extensive mobilization of nitrate sources and rapid transport to the stream network. Together with the result that the studied catchments were non-source limited, I conclude that the extensive hydrological connectivity during high-magnitude events can homogenize nitrate export over potentially heterogeneously distributed sources, making nitrate export a mainly transport-limited process.

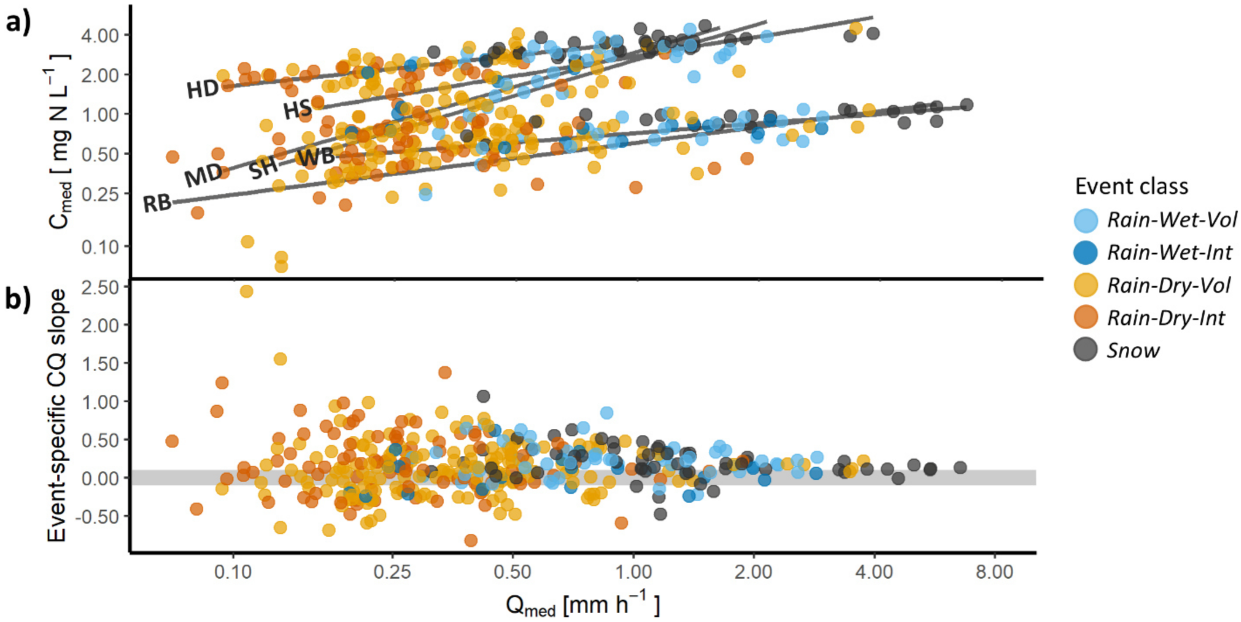


Figure 9. Runoff-event-driven nitrate export patterns across all six catchments analyzed in Study 3: Hausneindorf (HD), Hassel (HS), Meisdorf (MD), Silberhütte (SH), Warme Bode (WB), and Rappbode (RB). Runoff event classes are composed of the inducing event type, being either rainfall (*Rain*) or snowmelt (*Snow*), the antecedent conditions that are either *Wet* or *Dry,* and the temporal distribution of precipitation that is either intensity-dominated (*Int*) or volume-dominated (*Vol*). a) Runoff event-specific median nitrate concentrations and median discharge with log-transformed axes. Gray lines depict the catchment-specific inter-event C-Q relationships. b) Runoff event-specific C-Q slopes and runoff event magnitude (approximated by median discharge, shown on the log-transformed x-axis). The gray area marks the range of C-Q slopes close to zero (from -0.1 to 0.1), indicating chemostatic export patterns.

In contrast to high-magnitude runoff events, low-magnitude events exported lower nitrate concentrations (Figure 9a) and loads and showed high variability in event-specific C-Q slopes (Figure 9b). Other studies have also shown high variability in event-specific export patterns (e.g., Knapp et al., 2020; Blaen et al., 2017; Speir et al., 2021). In study 3, however, I could show that this high variability was evident mainly for low-magnitude events that were rain-induced and occurred under dry antecedent conditions in summer and autumn. Furthermore, I could explain part of this variability by i) the temporal distribution of rainfall (i.e., intensity-dominated versus volume-dominated precipitation), ii) a higher impact of biogeochemical processes during low-magnitude compared to high-magnitude events, and ii) the selective fraction of flow paths activated in combination with the nitrate source distribution. Assuming heterogeneously distributed nitrate sources within a catchment, it plays an important role where the inducing rain has fallen and which parts of a catchment become hydrologically connected. Therefore, the variability in nitrate export patterns among low-magnitude runoff events can reflect the spatial variability of nitrate sources within a catchment.

4.3 Crossing Spatiotemporal Scales – Interlinkages

In the previous chapters, I discussed nitrate export and its drivers at different spatial and temporal scales. However, those spatiotemporal scales are strongly interlinked. For example, I could show that long-term trends in nitrogen input and the spatial distribution of nitrate sources in the Selke Catchment shaped the seasonality in nitrate export. In the following, I discuss interlinkages between spatial and temporal scales, focusing on how nitrate export is shaped by the spatiotemporal variability in nitrate source availability and the hydrological connectivity of these sources to the stream network.

The availability of nitrate sources can strongly vary in both space and time, driven by nitrogen input, biogeochemical processing, and TTDs. The first driver, nitrogen input, is strongly controlled by the spatial distribution of land use, specifically by the fraction of agricultural land use. Besides spatial changes in land use, the related nitrogen input can change over time, as shown by the decrease in fertilizer application analyzed in Study 1. The second driver, biogeochemical nitrogen processing, is controlled by the temporal variability in the hydro-meteorological conditions. As shown in Study 2, a decrease in biogeochemical nitrate retention as a consequence of drought can temporarily increase the nitrate source availability within a catchment. In both cases, changing nitrogen input and its biogeochemical retention, TTDs govern how fast changes in nitrate source availability propagate through a catchment (Kirchner et al., 2010). Therefore, sub-catchments with relatively short TTs tend to predominantly store water and nitrate from recent times, with nitrate concentrations equilibrated to current nitrogen input levels and its biogeochemical retention. In contrast, sub-catchments with predominantly long TTs store water of a much larger range of different ages, which can have very different nitrate concentrations (as shown in Study 1). Therefore, sub-catchment differences in the respective TTDs, which reflect the time between nitrogen input and its riverine export, can create spatial heterogeneity in the nitrate source availability within a catchment.

The hydrological connectivity of these spatiotemporally variable nitrate sources can also vary across space and time. Like the biogeochemical processes, the hydrological connectivity varies with changing hydro-meteorological conditions, for example, with seasons, drought, or individual runoff events. As explained in previous chapters, high catchment wetness (e.g., in winter and spring or during high-magnitude runoff events) activates a large fraction of flow paths, connecting nitrate sources across the entire catchment to the stream network (Yang et al., 2018). In contrast, at times of low catchment wetness (e.g., in summer and autumn or under drought), only a small fraction of flow paths is active, typically connecting only those nitrate sources that are in close distance to the stream and stem from deeper and older groundwater (Yang et al., 2018). Therefore, the temporal variability in catchment wetness leads to spatial differences in the connectivity of nitrate sources to the stream network.

In summary, the dynamics of nitrate export that we can measure at the outlet of a heterogeneous mesoscale catchment result from a complex interplay of spatiotemporally variable hydrological and biogeochemical processes shaping nitrate source availability and its hydrological connectivity. By covering a wide range of spatiotemporal scales and bridging them, this thesis provides a more holistic perspective on the range of processes shaping riverine nitrate export and, in turn, a valuable step forward toward a better understanding of the integrated signal of nitrate export at the catchment outlet. Only after facing the complexity of catchment systems can we, in the next step, break down this complexity to identify dominant processes and controls to derive well-informed and more targeted management solutions that allow us to protect water quality and prevent nitrate pollution.

5 Outlook

Human alteration of the nitrogen cycle has improved global food security but has also led to biodiversity loss, accelerated climate change, and degradation of drinking water quality (Vitousek et al., 1997; Elser, 2011). In order to find an acceptable balance between the benefits and the detrimental impacts of reactive nitrogen use, we need to face the complexity of the systems in which nitrogen is cycling. This thesis provides new insights into dominant processes and controls for nitrogen retention and nitrate export at the scale of heterogeneous mesoscale catchments. The process understanding gained can be used to build upon in future studies, for example, to improve mechanistic models that are able to predict nitrate export at different sites and under changing climatic conditions.

With climate change, hydro-meteorological conditions are changing towards higher temperatures and more extreme conditions, including floods and droughts (IPCC, 2021). In Study 2, I showed evidence that a severe and prolonged drought can considerably decrease catchment nitrogen retention and that periods of high discharge would also increase nitrogen export relative to nitrogen input. Thereby, both scenarios would reduce the nitrogen retention of the catchment. Thus with more extreme conditions, one might expect an overall decrease in catchment nitrogen retention and, consequently, an increase in exported nitrate loads, which would further threaten freshwater quality. However, findings in Study 2 are restricted to one single catchment and are mainly focused on one specific drought event. As shown in Study 3, different catchments might respond differently to different hydro-meteorological conditions. Therefore, studies across a broader range of catchments looking at variable hydro-meteorological conditions, including droughts and floods (i.e., changing water quantity), are needed to understand the important link between changing hydro-meteorological conditions, water quantity, and water quality. These studies should consider different time scales, from short-term runoff events to long-term trends, because changes in nitrogen availability can get visible in stream water measurements at very different time scales, as demonstrated in this thesis. Therefore, I would like to make a case for increasing our efforts to combine hydrologic disciplines dealing with water quantity and water quality at different spatiotemporal scales to ensure water security under climate change.

The nitrogen cycle is only one of the global cycles beyond its boundaries for a safe operating space for humanity (Steffen et al., 2015; Rockström et al., 2009). Consequently, freshwater quality is not only affected by nitrate and other reactive nitrogen compounds but also by other nutrients, such as reactive phosphorus (P) or reactive forms of organic Carbon (C) (Ebeling et al., 2021a), and by emergent pollutants such as pharmaceuticals, microplastics, and many more (e.g., Du et al., 2014; Schmidt et al., 2017). Therefore, studies on freshwater quality in general, and especially in the face of climate change, should also look at a range of different pollutants that might vary in their sources, hydrological transport pathways, and the way they are biogeochemically retained. One way to address the lack of process understanding in this regard could be using the set of methods applied in this thesis, such as a combination of runoff event classification or process-based modeling and C-Q relationships.

Finally, macronutrients in a stream (i.e., carbon, nitrogen, and phosphorus) are not independent, as their stoichiometric ratio can influence the reaction rates of microbial processes in aquatic ecosystems (Stutter et al., 2018; Graeber et al., 2021). For example, higher availability of carbon favors the microbial processing of nitrogen and phosphorus, whereas the depletion of any of these three macronutrients can hinder the microbial processing of the respective other two (Stutter et al., 2018; Graeber et al., 2021). Therefore, for a better system understanding of the complex interplay of biogeochemical processes in catchments from the perspective of aquatic ecosystems, future studies should also look at the export of different nutrients in concert, considering their stoichiometric ratios.

6 Summary and Conclusions

In this thesis, I aimed to disentangle the underlying mechanisms that shape nitrate export and their spatiotemporal interlinkages in a heterogeneous mesoscale catchment. The Selke Catchment offered favorable conditions for this goal due to the heterogeneity in catchment characteristics and the wealth of available data at three nested gauges, covering long-term discharge, nitrogen input, riverine nitrate concentration, and meteorological data, but also high-frequency data from more recent years. The nested catchment approach further allowed me to separate the contribution from distinct landscape units to nitrate export at the catchment's outlet. In the three studies that form the core of this thesis, I covered different temporal scales of nitrate export – from trend to event – in response to changes in nitrogen input (Study 1) and changing hydro-meteorological conditions (Studies 2 and 3). Results highlighted the importance of disentangling the spatiotemporal variability in nitrate source availability and the variable connectivity of these nitrate sources to the stream network in order to understand the integrated signal of nitrate export at the scale relevant to water management (i.e., in mesoscale catchments).

Changes in the nitrate source availability can occur due to changes in land use (e.g., decrease in fertilization rates) or alterations in nitrogen retention within a catchment (e.g., reduced nitrate retention during drought). The analysis of **long-term trends** in nitrate export reveals how such changes in nitrogen availability are transferred through the catchment and result in the signal of nitrate export at the catchment outlet, thereby allowing for an estimation of TTDs. The interplay of different sub-catchments with potential differences in nitrogen input and TTDs plays an important role in understanding the integrated catchment response.

Hydro-meteorological anomalies, such as a severe drought, can decrease the capacity of catchments to retain nitrogen via biogeochemical processes, thereby changing the overall nitrate source availability. Furthermore, a drought can inhibit nitrate transport from source to stream because only a small fraction of flow paths is active during dry conditions, which can cause an accumulation of nitrate sources. Sub-catchment-specific TTDs during rewetting govern how fast the accumulated nitrate sources are transported to the stream network. If TTs are relatively long, even during wetter periods, the propagation of changes in nitrogen availability might only become visible if looking at long-term trends. In contrast, short TTs can reveal the catchment response to drought during the first runoff events with rewetting in autumn. Moreover, the drought-induced changes in nitrate availability and the timing of nitrate transport can intensify the seasonality in nitrate export.

Not only under hydro-meteorological anomalies but also generally in a temperate climate can nitrate export exhibit pronounced **seasonality**, often with higher discharge and nitrate concentrations in winter and spring compared to summer and autumn. This seasonality is driven by seasonal differences in biogeochemical processes (uptake and removal), which control the availability and spatial distribution of nitrate sources. Furthermore, the seasonality in nitrate export is driven by the seasonality in catchment wetness, controlling hydrological transport via activating or deactivating different flow paths, thereby connecting nitrate sources from different locations and age distributions. Disentangling these two components, nitrate source availability and hydrological connectivity, remains a challenge, but, most likely, a combination of both shapes the seasonality in nitrate export. Here again, sub-catchment differences in the degree of seasonality should be considered to understand the overall catchment response.

Runoff events mark relatively short periods that, nevertheless, have an important role in annual nitrate export. High-magnitude events, in particular, exported a disproportionate amount of annual nitrate loads and approximated chemostatic export patterns across all catchments, indicating no nitrate source limitation. Wet antecedent conditions during high-magnitude events allow the activation of a significant fraction of a catchment's flow paths, connecting all heterogeneously distributed nitrate sources to the stream network. In contrast, low-magnitude events can exhibit high variability in nitrate export patterns, reflecting the spatial heterogeneity of nitrate sources. Dry antecedent conditions during low-magnitude events allow activation of only a small fraction of flow paths, resulting in nitrate transport from selective areas within a catchment. Changing hydro-meteorological conditions due to climate change might alter the spatiotemporal heterogeneity in nitrate source availability and its hydrological transport, thereby likely increasing the variability of nitrate export patterns.

6.1 Implications for Management

I have drawn a complex picture of spatially heterogeneous catchments that retain and release nitrate, driven by different but interlinked processes across time scales. With this at hand, in the following, I derive some targeted suggestions for water quality management that can be drawn from the presented studies and their synthesis, and that might enable more site-specific decision-making and effective reduction of nitrate pollution:

- Results from the Selke Catchment revealed significant differences in nitrate export dynamics between sub-catchments that differ in their characteristics, such as land use, soil type, and geology. Furthermore, the contribution to nitrate export from the different sub-catchments varied with changing hydro-meteorological conditions. These sub-catchment differences underline the importance of defining meaningful land use units for nitrate export within heterogeneous mesoscale catchments and extending the density of monitoring stations accordingly. Monitoring at the sub-catchment level could help disentangle the contribution from different sub-catchments to nitrate export, allowing for more site-specific management strategies.

- Nitrate export can strongly vary with discharge, and different catchments or sub-catchments can show different dynamics and ‘hot moments’ of nitrate export. Therefore, the analysis of C-Q relationships is a simple and easy-to-apply method to identify site-specific export regimes and pinpoint site-specific problems. C-Q relationships allow us to approximate the location of nitrate sources because they reveal their connectivity to the stream network under low-flow versus high-flow conditions. Therefore, characterizing catchment or sub-catchment-specific C-Q relationships could help water quality managers to differentiate between different types and dynamics of nitrate pollution. For example, constantly high nitrate concentrations, driven by elevated nitrate concentrations in the base flow, are reflected by chemostatic or dilution patterns, whereas high peak loads mobilized and transported during relatively short periods of high discharge can be identified by chemodynamic enrichment patterns. Furthermore, C-Q relationships would allow for more targeted water quality monitoring, as catchments with chemodynamic export patterns are likely to require more frequent measurements than catchments with chemostatic export patterns.

- Catchment-specific TTDs are crucial for understanding the time scale between changes in nitrogen input (for example, due to measures to reduce nitrate pollution) and the response of nitrate concentrations in the stream. In this thesis, I could further show that TTDs can substantially differ between sub-catchments, leading to different responses that form an integrated signal of nitrate export at the catchment outlet. Therefore, it is important to consider TTDs and their spatial differences to understand nitrate export in mesoscale and heterogeneous catchments. Precise and site-specific knowledge of TTDs could help water quality managers to set priority on short- or long-term strategies and to have realistic estimates on the time scale of conducted measures to show an effect on stream water quality.

These suggestions may help to leverage our understanding of catchment functioning for a more efficient reduction of nitrate pollution. However, I want to stress that, in the end, it is still the overall nitrogen input brought by human interference with the nitrogen cycle, which is the main reason for nitrate pollution. Improving the efficiency of catchment nitrogen retention is important. However, it either contributes to storing nitrate temporarily, thus postponing the problem to later generations, or it may cause higher denitrification, which is good in terms of water quality but also releases greenhouse gases. Therefore reducing nitrogen input, especially fertilizer application, is the first crucial step to addressing the problem of nitrate pollution.

Nevertheless, the societal and economic benefits of nitrogen fixation and fertilization are huge. Therefore, finding an acceptable balance between the benefits and the detrimental impacts of high nitrogen loads – for example, on water quality – is a delicate but crucial task. Moreover, besides preventing new pollution, we also need to cope with biogeochemical and hydrological nitrogen legacies from the past (e.g., Ehrhardt et al., 2019; Van Meter et al., 2016; Dupas et al., 2020). Both challenges, reducing nitrogen input (prevention) and coping with legacies (mitigation), require management strategies and decision-making based on site-specific knowledge. Specifically, addressing these challenges should take into account the spatial heterogeneity in nitrate source availability and hydrological connectivity and the many different temporal scales relevant to nitrogen retention and transfer from source to stream. With this thesis, I contributed new knowledge to address these challenges by elucidating nitrate retention and export processes in heterogeneous mesoscale catchments and highlighting the important role of spatiotemporal variability in nitrate source availability and nitrate transport from source to stream.

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Study 1:

Disentangling the Impact of Catchment Heterogeneity on Nitrate Export Dynamics From Event to Long-Term Time Scales

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- Concept and study design 70%
- Data acquisition 10%
- Data analyses 100%
- Figures 100%
- Discussion of results 80%
- Manuscript writing 85%

The study was designed by CW, SL, AM, and JF. High-frequency data was provided by Michael Rode (MR), and long-term data was measured by the LHW and compiled by AM and CW. Nitrogen input data was provided by MW and RK. CW performed all analyses and created all figures and tables. CW wrote the manuscript. All co-authors revised the manuscript.

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RESEARCH ARTICLE
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Key Points:

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

Supporting Information:

- Supporting Information S1

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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 when based on concentration measurements at the outlet only. One reason for this is our limited understanding of the subcatchment contributions to nitrate export and their importance at different time scales. While upstream subcatchments 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 of nitrate pollution. To examine the interplay of different subcatchments, 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 subcatchments (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 subcatchments dominated nitrate export during high flow and disproportionally contributed to overall annual nitrate loads at the outlet (64.2%). The downstream subcatchment 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 subcatchments for temporally elevated nitrate concentrations and net annual loads can lead to an overestimation of the role of agricultural lowlands. Nonetheless, constantly high concentrations from nitrate legacies pose a long-term threat to water quality in agricultural lowlands. 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. Previous studies have shown that upstream catchments often have a disproportional impact on nutrient export, while agriculture (a major nitrate source) is often located in 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 needed 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 subcatchments, their impact poses a long-term threat to water quality.

1. Introduction

High nitrate concentrations in ground water and surface water are a well-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 transformation is needed. While much is known about these processes for rather uniform headwater catchments, our understanding of those in spatially more heterogeneous and complex mesoscale catchments (10^1–10^4 km^2, Breuer et al., 2008) is yet an open challenge but vital for identifying management options. On the one hand, upstream subcatchments often have a disproportional contribution to runoff 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). On the other hand, agricultural areas are known to be a major source of nitrate pollution (e.g., Padilla et al., 2018; Strebel et al., 1989). A typical setting for mesoscale catchments located in the transition zone between uplands and lowlands is, however, an elevated upstream area with no or only 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 subcatchments can have quite different nitrate export dynamics. Both subcatchments are relevant for nitrate export from the entire catchment and may operate at very different times and time scales. Their specific contributions, however, remain widely unknown when measuring only the integrated signal of nitrate export at the catchment outlet, making it difficult to localize important source zones of nitrate and to identify important driving forces for their mobilization. Nested catchment studies are a promising approach to shedding light on the contribution of subcatchments to nitrate export (e.g., Dupas et al., 2017; Ehrhardt et al., 2019). They enable us to analyze changes in nitrate transport along the river, to connect these changes to the specific characteristics of upstream and downstream subcatchments and to interpret the integrated observations of concentration, discharge (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 for assessing trends in water quality over time and for assessing transit times (TTs) and legacy stores, both of 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 the introduction of a solute into the catchment and its riverine export, leading to a temporal storage of N in the catchment. Legacy stores refer to the mass of solute that has been retained and accumulated in the catchment. In the case of N, legacy stores are separated into organic N retained in the soil (biogeochemical legacy) and inorganic N that is moving in the groundwater (hydrological legacy) with TTs that strongly depend on catchment-specific characteristics such as recharge and the storage capacity (Haitjema, 1995). A precise understanding of the contribution of TTs and legacy stores to nitrate export dynamics and the long-term persistence of nitrate is still missing (Van Meter et al., 2016). However, this knowledge is crucial for understanding 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), as methods to continuously measure high-frequency nitrate concentrations have only recently been developed (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 when only long-term trends are looked at (Duncan et al., 2017; Rose et al., 2018). For example, Dupas et al. (2016) found chemostasis (i.e., the 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 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 in order to be able 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 and other solutes on 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 differentiation 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 to 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 becoming 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, i.e., where nitrate sources are not ubiquitously available (Basu et al., 2010; Goodridge & Melack, 2012). On the contrary, chemostasis indicates constant nutrient concentrations instream 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 and Mitchell (2011) and Musolff et al. (2015) combined the two 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 the need for research on how the role of internal organization of catchments (i.e., nested subcatchments) shapes the outlet observation seasonally and under varying flow conditions in terms of nitrate inputs, reactive transport in the subsurface, and the stream network. 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) that 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 subcatchment. Furthermore, we (iii) calculated subcatchment-specific transit time distributions (TTDs) from N inputs and riverine nitrate outputs to address the potential extent and effect of legacy stores and their impact on nitrate export dynamics and long-term trends. Using this comprehensive approach, our aim was to obtain a better understanding of how nested subcatchments (i) contribute to the integrated signal of nitrate concentrations, loads, and *CQ* relationships observed at the catchment outlet at different times scales (long term, seasonal, and event scale), and how they (ii) affect the response of nitrate concentrations, loads, and *CQ* relationships to changes in N input.

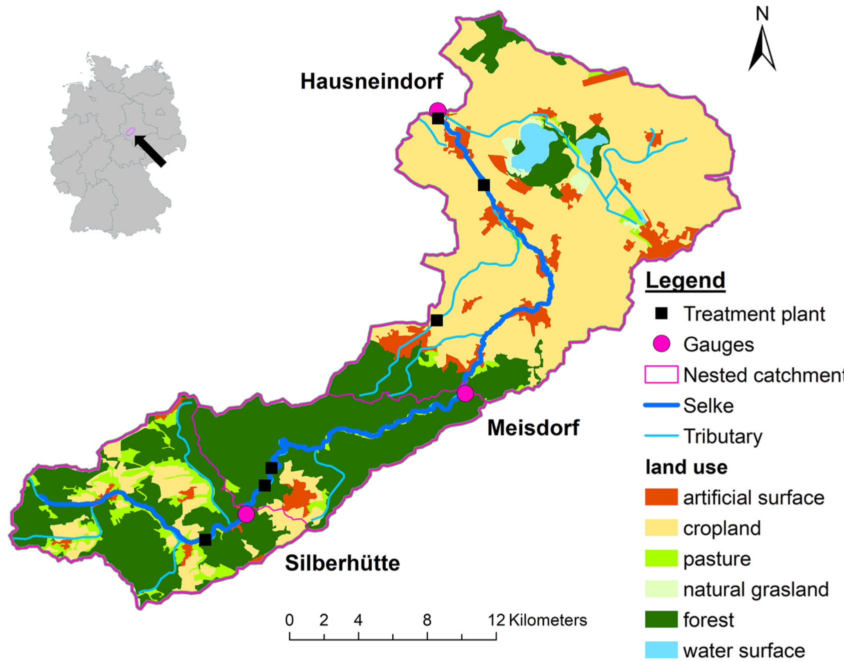

Figure 1. Land use map of the Selke catchment with gauging stations (pink dots) and wastewater treatment plants (black squares).

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 (Figure 1). It is a subcatchment of the Bode catchment, which is an intensively monitored catchment within the network of TERrestrial ENvironmental Observatories (TERENO, Wollschläger et al., 2017). We considered three nested subcatchments in the Selke catchment (Figure 1 and Table 1), delineated by the following gauging stations: (i) Silberhütte, (ii) Meisdorf, and (iii) Hausneindorf. Characteristics of the subcatchments are summarized in Table 1.

Silberhütte and Meisdorf are located in the Harz Mountains and drain the upper part of the catchment. In the following, these two nested subcatchments are summarized as the *upper Selke*. The upper Selke is dominated by forests, followed by agriculture, which is mainly located upstream of Silberhütte (Table 1). Soils are dominated by Cambisols overlaying low permeable schist and claystone, resulting in relatively shallow groundwater systems (Jiang et al., 2014). Due to the higher elevation (Table 1), a considerable amount of snowmelt contributes to stream discharge during late winter and spring (X. Yang et al., 2018). 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.

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 (Table 1) mainly in the form of arable crops. Soils are dominated by Chernozems above quaternary sediments and mesozoic sedimentary rocks (sandstone and limestone) that allow for considerably deeper groundwater systems than those found in 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 (Figure 1). Furthermore, there was an opencast mine (closed in 1991) located in the northeastern part of the lower Selke. Selke water has been abstracted from 1998 on to fill the open pit with an average annual abstraction rate

Table 1
Characteristics of the Three Nested Subcatchments Within the Selke Catchment

Catchment characteristic		Unit	Upper Selke		Lower Selke		Data source
					Hausneindorf		
			Silberhütte	Meisdorf	Nested[a]	Separate[a]	
Area		(km^2)	105	184	456	272	LHW[b]
MAP[c]		(mm $year^{-1}$)	739.1	694.3	588.9	519.0	DWD[d], Zink et al. (2017)
Elevation range		(m.a.s.l.)	335–597	196–597	68–597	68–396	EEA (2013)[e]
Mean slope		(%)	6.9	8.4	4.9	2.7	EEA (2013)
Specific discharge		(mm day^{-1})	0.90	0.65	0.32		LHW
Land use	Agriculture	(%)	30.5	20.9	47.8	65.0	EEA (2012)
	Forest		65.0	75.3	39.8	17.1	
	Urban		3.3	3.1	5.9	7.7	
	Others		1.2	0.7	6.5	10.2	

Note. [a]Nested catchment characteristics for Hausneindorf (left column) integrate the upper Selke while the separate characteristics exclude the upper Selke (right column). Analysis and results in this study are based on the nested version. [b]State Office of Flood Protection and Water Management of Saxony-Anhalt. [c]Mean annual precipitation. [d]German Weather Service. [e]Digital elevation model of the European Environment Agency downscaled to a resolution of 100 m.

of 3.1 million m^3. In 2009, a landslide occurred on the banks of the pit-lake, so that water from the filling pit has been pumped (annual rate of 10.4 million m^3) into the Selke in order to stabilize the banks since 2010.

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 and high-frequency Q data (15 min) are available since 2010. All data are provided by the State Office of Flood Protection and Water Management of Saxony-Anhalt (LHW; Figure 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 biweekly to bimonthly intervals and published previously by X. 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). Sensor performance was reported to be high, with an R^2 of 0.93 for the regression of grab samples and sensor-derived concentrations ($y = 1.001x$, $n = 122$) and a bias of 0.01 mg NO_3^-N (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):

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

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 $m^3\ s^{-1}$, β_1–β_4 are fitted coefficients with β_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 weighting 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, Equation 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 β_2 from Equation 1 (which was developed by Zhang et al., 2016). The parameter β_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 ($\beta_2 > 0.1$), (ii) chemodynamic with a dilution pattern ($\beta_2 < -0.1$), and (iii) chemostatic ($-0.1 < \beta_2 < 0.1$). We chose the threshold for chemostatic at −0.1 and 0.1 as according to Zhang et al. (2016) and Bieroza et al. (2018), although we are aware that this somewhat arbitrary threshold only indicates chemostatic patterns if $CV_C/CV_Q << 1$ (Musolff et al., 2015). The CQ slope and the CV_C/CV_Q were found to be positively correlated for nitrate (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. The methods and results of this study are therefore restricted to the CQ slope.

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. Spring was defined as lasting from March to May, summer from June to August, autumn from September to November, and winter 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 β_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

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 represent 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; Behrendt et al., 2000; Häußermann et al., 2019). Our study area covers three 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 as according to Bach et al. (2006, personal communication), 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, the data were provided by the Meteorological Synthesizing Centre – West of the European Monitoring and Evaluation Programme (e.g., Bartnicky & Benedictow, 2017; Bartnicky & Fagerli, 2004). From 1950 to 1980, the county-based input is assumed to be constant (25.03 kg ha^{-1} $year^{-1}$ in Silberhütte, 28.75 kg ha^{-1} $year^{-1}$ in Meisdorf and 16.15 kg ha^{-1} $year^{-1}$ in Hausneindorf) due to a lack of further data for that time. We considered N deposition data only for nonagricultural land cover classes (e.g., forest, water bodies, wetlands, and grassland) because the agricultural N surplus data already account for atmospheric deposition and biological fixation (see above). We added biological N fixation to nonagricultural land cover classes according to Cleveland et al. (1999) and Van Meter et al. (2017). Cities were neglected (except urban grassland such as parks) under the assumption that nitrogen from sealed surfaces is directly discharged into the WWTPs. We acknowledge that sealed-surfaces runoff which enters directly into the stream can have a considerable impact (Decina et al., 2018; Hope et al., 2004). However, due to the small percentage of urban areas in the Selke catchment (5.9%, Table 1), we believe that this simplification is acceptable.

Data on the 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. We calculated nitrate input from WWTPs with the provided nitrate concentrations and an additional maximum estimate for the contribution of WWTPs to nitrate export during high-flow seasons (HFSs) and low-flow seasons (LFSs) under the assumption of a complete nitrification of wastewater-borne ammonium. Nitrate concentration values from 2010 were assigned to all years previous to 2010. As their contribution to N input in the Selke catchment is relatively small, compared to agricultural N input, we believe 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 data set for each of the three different input types was created on county level (average area of 887 km^2) for the period of 1950–2015 and combined to one single N input data set that was clipped for all three nested subcatchments. To this end, we used the weighted average, taking into account the areal fractions of involved counties and the respective (sub)catchment boundaries. To compare N input with nitrate export, we assume that entire N input is eventually mineralized and that nitrate concentration patterns (with nitrate as the most abundant species of inorganic N, Meybeck, 1982) reflect the main processes of riverine N export and subcatchment-specific differences in N export dynamics. To account for this simplification, we discuss other important processes that play a role in reactive N transport, such as instream assimilation or denitrification in riparian zones.

2.5. Transit Time Distributions

Apparent TTDs for nitrate were calculated by 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 us 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 (mean and standard deviation of the natural logarithm of the target variable, defining the tailing and mode) 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 subcatchment 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 that it is still in the catchment as hydrological legacy (delayed by long TTs of subsurface water i.e., hydrological TTs) or as biogeochemical legacy (stored as organic N in the catchment soils). Determining which form of legacy the *missing N* can be contributed to is challenging (Van Meter & Basu, 2015; Van Meter et al., 2016) and beyond the scope of this study. Nevertheless, long-term trends in *CQ* relationships together with pronounced changes in N input can give first indications on their contribution (Ehrhardt et al., 2019). In respect to hydrological legacies, a decline in N input can cause a temporal increase in the concentration heterogeneity belowground (e.g., between younger and older water fractions), which can go along with a shift in *CQ* relationships from chemostasis toward more chemodynamic patterns. In contrast, *CQ* relationships under the dominance of biogeochemical legacies are likely to be more buffered and less affected by changes in N input (Ehrhardt et al., 2019). Hence, we used long-term trends in the *CQ* slope to discuss indications toward either hydrological or biogeochemical legacies. Additionally, we 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 nonoverlapping 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 permits 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 h. 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 criteria that (i) the event included a minimum of 20 data points, (ii) peak Q reached at least the 5% percentile of all Q measurements, (iii) fast flow contribution at the peak of the event was at least 30% of total flow, and (iv) Q decreased at least to one third of its former increase. Events with data gaps larger than 5 h 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 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:

$$C = a * Q^b + c * \frac{dQ}{dt} \tag{2}$$

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 (Equation 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 Equation 2 was larger than 0.5.

3. Results

3.1. Nitrogen Budget

Since the start of the N input 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} $year^{-1}$ in the upper Selke and 79.4 kg ha^{-1} $year^{-1}$ in the lower Selke. Maximum N input was reached in 1988. In 1990, after the reunification of Germany and the associated breakdown of the intensive agriculture in East Germany (Gross, 1996), N input decreased markedly within 1 year and then stabilized again at a lower level (around 33.9 ± 3.3 kg ha^{-1} $year^{-1}$ in the upper Selke and 37.7 ± 5.2 kg ha^{-1} $year^{-1}$ in the lower Selke) from 1995 onwards (Figure 2 and Table 2).

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

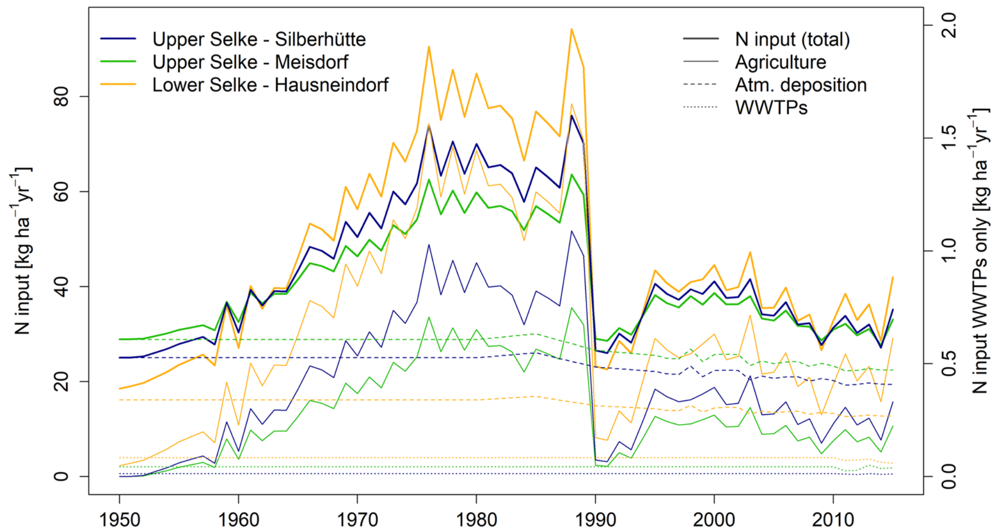

Figure 2. Total N input per hectare and year for all three nested subcatchments of the Selke catchment and N input divided into its components: (i) from agricultural areas, (ii) atmospheric deposition and biological fixation on nonagricultural areas, and (iii) outflow from wastewater treatment plants (WWTPs, second *y* axis).

to the gauge at Hausneindorf; Figure 2 and Table 2). The only exceptions were found during years when the total N input was especially low (e.g., 1990/1991). In these years, the scenario was reversed, with the highest N input in the upper Selke and the 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 (Figure 2 and Table 2). 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 2). 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 N input mainly stemmed from natural areas (mainly forests and grasslands), while the contribution of WWTPs was small. When assuming constant N input from WWTPs over the year, they contributed an average of 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 of WWTPs to nitrate export was an average of 3.4%–7.4% and 6.2%–9.5% for the upper and lower Selke, respectively.

3.2. 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 LFSs (summer and autumn) and higher concentrations during 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 (Figure 3), 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 and 1.8 mg L^{-1} in the upper Selke and between 2.0 and 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 and 3.4 mg L^{-1} in the upper Selke and between 2.4 and 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.

Besides general differences in nitrate concentrations and their different seasonalities, long-term trends also showed varying behavior between upper and lower Selke, again most pronounced during LFSs. Here, a marginal decrease beginning in 1990 occurred in the upper Selke, while FN nitrate concentrations increased substantially in the lower Selke, 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 (Figures 3c and 3d).

Table 2
Balance Between Nitrogen (N) Input and Its Riverine Export as Nitrate Loads and Transit Time Distributions (TTDs)

			Upper Selke		Lower Selke
		Unit	Silberhütte	Meisdorf	Hausneindorf
N input vs. export (1983–2015)	Cumulative N input	(t)	14,078.7	23,195.4	67,146.9
	N $export_{conv}$ (conservative)	(kg ha^{-1} $year^{-1}$)	44.3	41.2	50.3
	Cumulative N $export_{conv}$ (conservative)	(t)	15,352.9	25,045.3	75,753.0
	Cumulative N export, (measured)	(t)	3,052.1	3,912.0	6,094.3
	Missing N (conservative – measured)	(kg ha^{-1} $year^{-1}$)	35.5	34.8	46.3
		(t)	12,300.7	21,133.3	69,658.6
		(%)	80.1	84.4	92.0
TTDs	μ	(year)	2.12	1.59	2.91
	σ	(year)	1.15	1.10	0.73
	R^2	(–)	0.57	0.92	0.40
	Mode (year of peak travel time)	(year)	3	3	12

Note. 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. TTDs follow a log-normal distribution with fitted parameters μ and σ and the R^2 as the coefficient of determination.

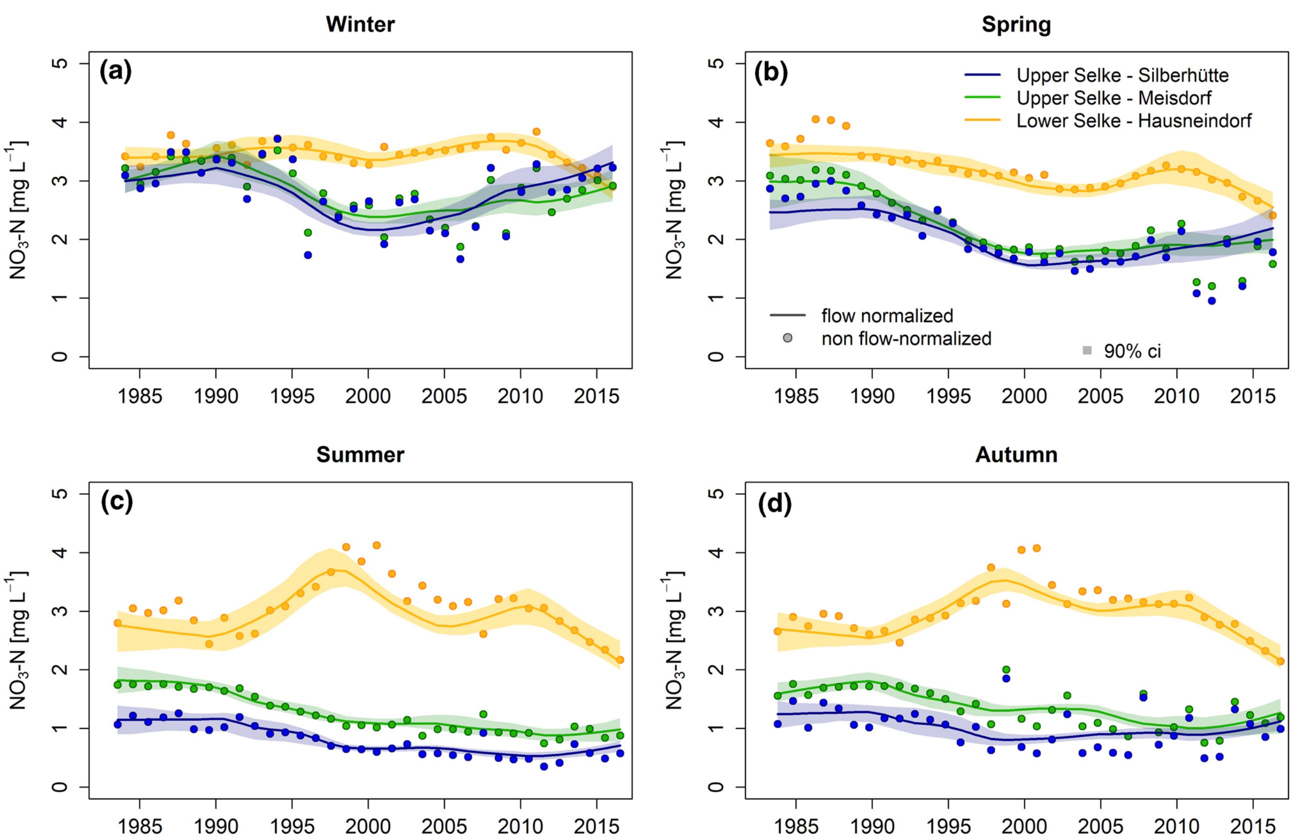

Figure 3. Long-term trends of annual flow normalized (FN, lines) and annual non-FN (dots) nitrate concentrations from three nested subcatchments of the Selke catchment, separated by season (a–d). Uncertainty bands in the subcatchment-specific color indicate the 90% confidence intervals from bootstrapping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

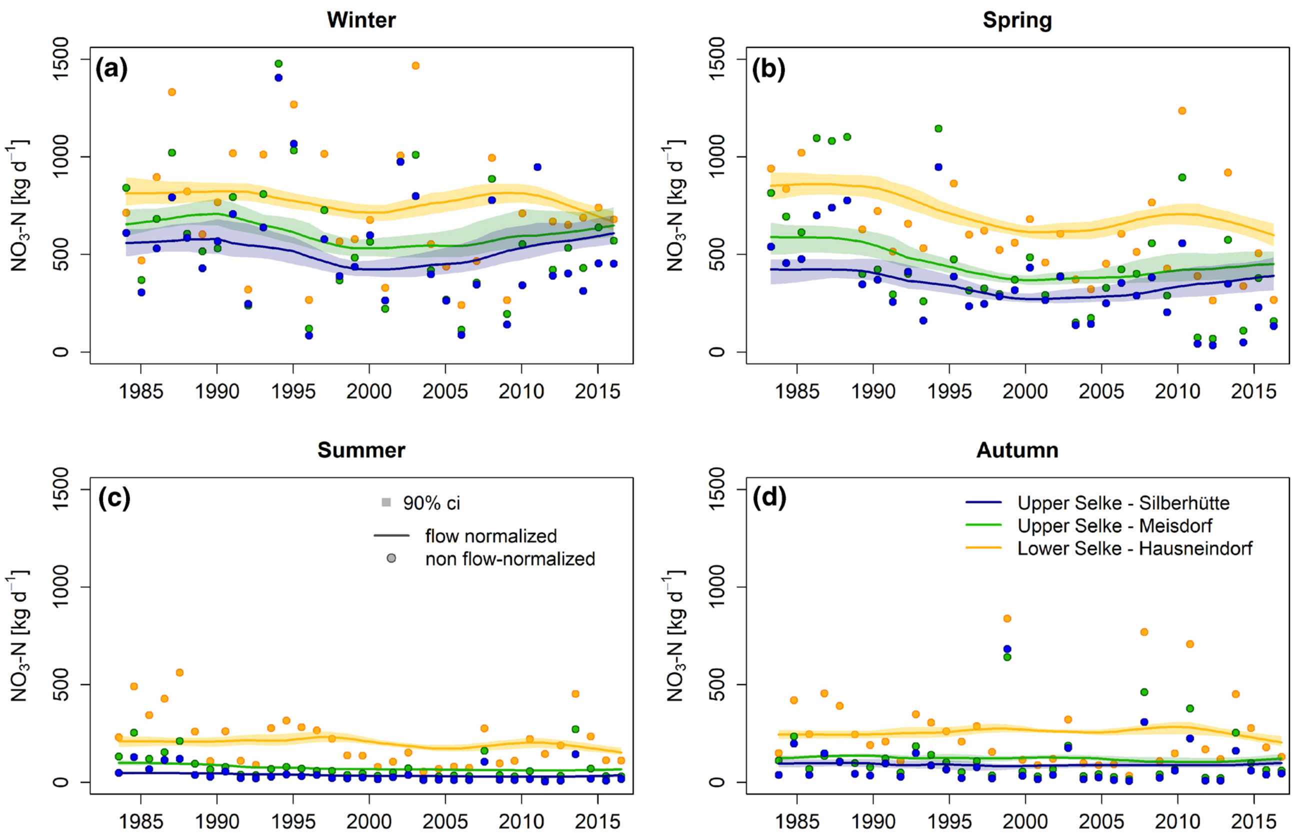

Figure 4. Long-term trends in annual flow normalized (FN, lines) and annual non-FN (dots) nitrate loads from three nested subcatchments of the Selke catchment, separated by season (a–d). Uncertainty bands in the subcatchment-specific color indicate the 90% confidence intervals from bootstrapping FN values.

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 staring in 2000. 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 (Figures 3a and 3b).

3.3. Seasonal and Long-Term Behavior of Nitrate Loads

Nitrate loads generally showed similar long-term trends than nitrate concentrations did (Figure 4). The main difference was in the pronunciation of seasonality, with much higher loads during HFSs compared to LFSs (Figure 4). This seasonality was even more pronounced in the upper Selke than in the lower Selke, and the relative contribution from subcatchments to nitrate loads varied seasonally in consequence. Overall, highest loads occurred during winter, with an average of 515.5 kg day^{-1} in Silberhütte, 607.8 kg day^{-1} in Meisdorf, and 774.8 kg day^{-1} in Hausneindorf (average from non-FN values). When neglecting in-stream losses of nitrate, this implies that the upper Selke transported 78.4% of the total catchment's nitrate loads which are exported from the lower Selke during winter (1983–2016). Lowest loads occurred during summer with 39.5 kg day^{-1}, 77.4 kg day^{-1}, and 207.6 kg day^{-1} for Silberhütte, Meisdorf, and Hausneindorf, respectively. Contrary to the situation in 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. When taking the subcatchment area into account, the average of annual loads was highest in Silberhütte with 8.6 kg ha^{-1} $year^{-1}$, followed by Meisdorf with 6.3 kg ha^{-1} $year^{-1}$ and smallest in Hausneindorf with 3.9 kg ha^{-1} $year^{-1}$.

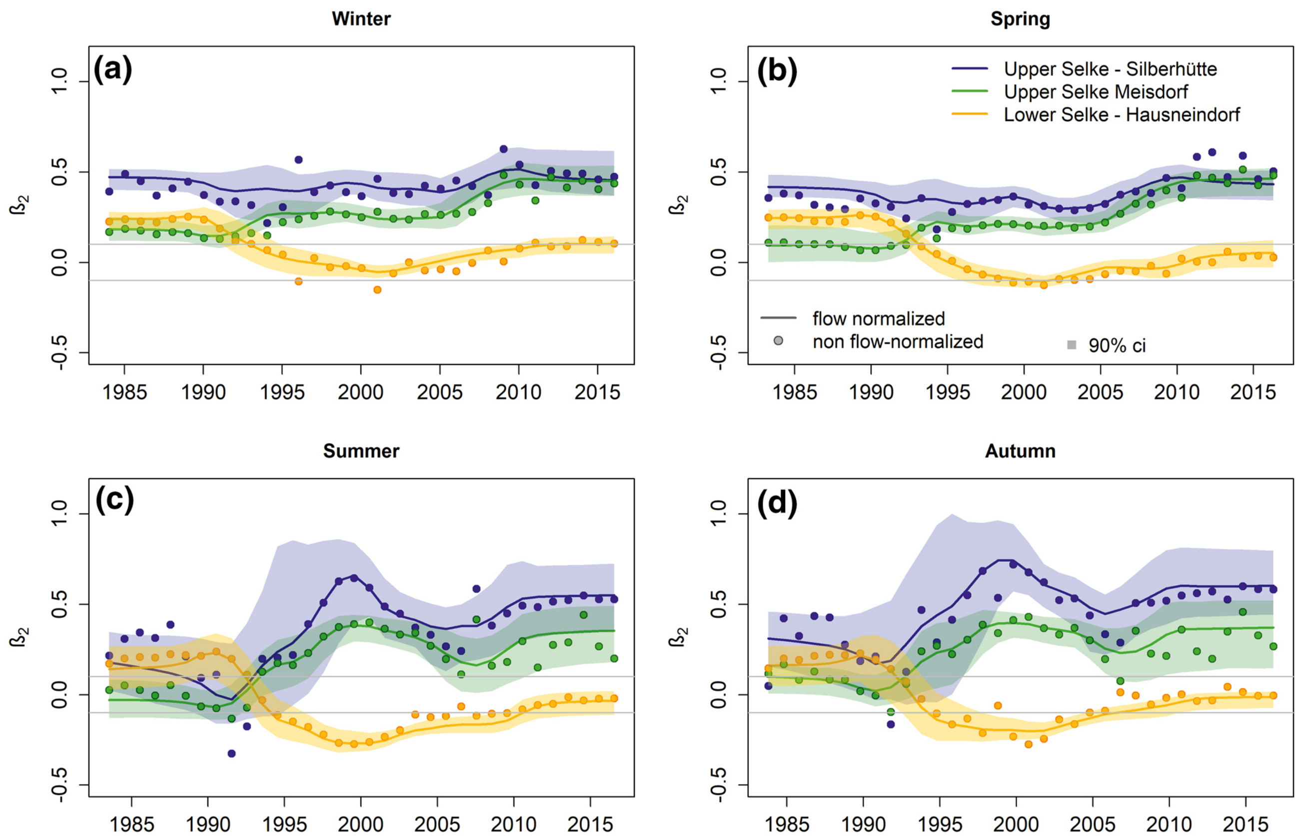

Figure 5. Long-term trends of the fitted parameter β_2, indicating the annual flow normalized (FN) and annual non-FN ln(concentration)–ln(discharge) relationship (*CQ* slope) from three nested subcatchments in the Selke catchment, separated for each season (a–d). Uncertainty bands in the subcatchment-specific color indicate the 90% confidence intervals from bootstrapping FN values. Horizontal gray lines delineate the border between chemostatic and chemodynamic nitrate transport.

3.4. Nitrate Retention and TTDs

Fitted TTDs 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 2 and Figure. S3). Smaller modes and μ-values together with larger σ-values ($\sigma > 1$) in the upper Selke indicate a dominance of short TTs, whereas the higher mode and μ-value together with a lower σ-value ($\sigma < 1$) of the TTD in the lower Selke indicates a dominance of longer TTs and a considerably longer tailing. 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 2).

TTD-derived conservative N export over the period from 1983 to 2015 was higher than N input for this period (Table 2), 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 the form of measured annual nitrate loads as the *missing N* (Van Meter et al., 2016; Table 2), which is either still in the catchments as legacy or removed via denitrification. All subcatchments of the Selke catchment showed a considerable 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} year^{-1} more N being missing than in the upper Selke.

3.5. 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), as was observed in seasonal (Figure 5) as well as in annual *CQ* slopes

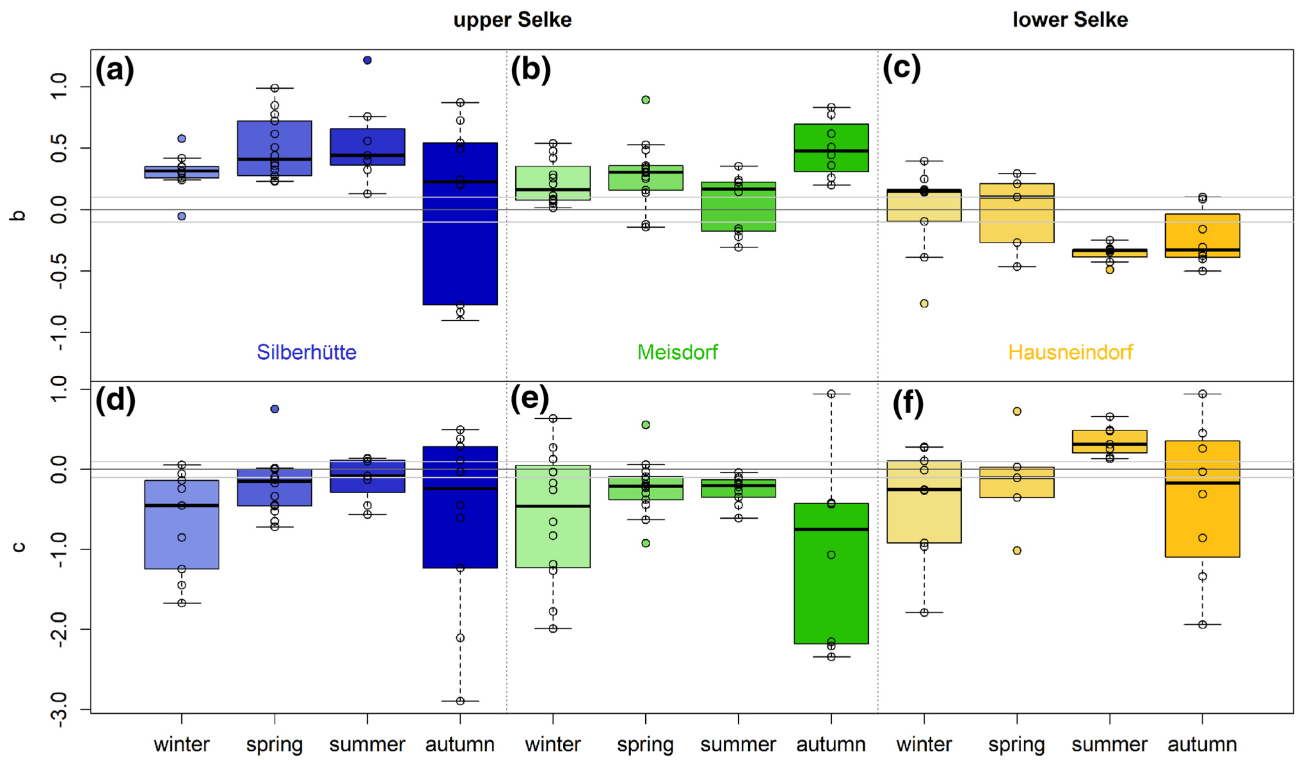

Figure 6. Boxplots of the event-specific fitted parameters *b* (*CQ* slope) and *c* (hysteresis) in Equation 2 with $R^2 > 0.5$. Parameters were separated by seasons and gauging stations within the Selke catchment, displayed from upstream (left) to downstream (right).

(Figure S2c). The only exception was for Meisdorf during LFSs between 1983 and 1990, where nitrate export was chemostatic with a *CQ* slope close to zero (Figures 5c and 5d). *CQ* slopes in Silberhütte were higher than the ones in Meisdorf, except for HFSs from 2010 on, for which *CQ* slopes were both around 0.45 (Figures 5a and 5b). During LFSs, *CQ* slopes in the upper Selke peaked in 1999 and, following a minimum around 2005, leveled out afterward. Uncertainty from sample estimates assessed via bootstrapping was highest for LFSs, but the generally positive *CQ* slopes beginning in 1990 were still evident (Figures 5c and 5d).

In contrast to the upper Selke, the export regime in the lower Selke changed significantly over time (Figure 5 and Figure S2c). *CQ* slopes in the lower Selke were positive between 1983 and 1990 for all seasons, indicating chemodynamic nitrate transport with accretion patterns. After 1990, *CQ* slopes decreased toward values around zero during HFSs (Figures 5a and 5b), which indicates chemostatic transport, and toward negative *CQ* slopes during LFSs (Figures 5c and 5d), which indicates chemodynamic nitrate export with a dilution pattern. Beginning around 2010, nitrate transport in the lower Selke was chemostatic during all seasons, with a tendency toward slightly higher *CQ* slopes during HFSs compared to during LFSs.

3.6. Storm Events

We identified a total of 200 storm events: 59 for Silberhütte (from 2013 to 2016), 72 for Meisdorf, and 69 for Hausneindorf (both from 2010 to 2016). Of all these events, 56% could be described adequately with the empirical formula which defines the hysteresis loop (Equation 2) with $R^2 > 0.5$. This is true for 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 Figure 6 and Figures S4 and S5. Upper Selke *CQ* slopes were dominantly positive, indicating chemodynamic nitrate export during storm events with an accretion pattern (Figures 6a and 6b). Some exceptions were found during November in Silberhütte, when some small events 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* (Figures 6d and 6e). 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 (Figure 6c). During HFSs however, event-specific *CQ* slopes were dominantly positive, indicating an accretion pattern, similar to that found for the upper Selke. Hysteresis was clockwise during summer and dominantly counterclockwise during all other seasons, again similar to the situation in the upper Selke. For all three subcatchments, variability in hysteresis behavior was most pronounced during autumn. When looking at all identified events—regardless of their R^2 (Figures S4 and S5)—the described patterns in *CQ* slopes and hysteresis stayed evident, with the only exception being that *CQ* slopes in the lower Selke during spring were dominantly around zero or negative.

4. Discussion

4.1. Long-Term Trends in Nitrate Export

The nested catchment structure provided an ideal setting for analyzing the contribution of different subcatchments to nitrate export measured at the catchment outlet. This structure enabled us to calculate subcatchment-specific TTDs which revealed distinct time scales in the response of riverine nitrate export to N input within one mesoscale catchment. In the mountainous upper Selke, TTDs had their mode after 3 years, indicating a dominance of short TTs, while in the agriculturally dominated lower Selke, the TTD showed a peak after 12 years and a considerably longer tailing (Table 2). This difference can be explained mainly by a difference in hydrological TTs caused by a lower storage capacity (shallow soils and relatively impermeable geology) in the upper Selke, compared to the lower Selke (Haitjema, 1995). Consequently, N input in the upper Selke is transported rapidly to the stream network, and instream nitrate concentrations respond quickly to changes in N input, 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 more an issue in the lower Selke than in the upper Selke.

The subcatchment-specific differences in TTDs, furthermore, help to explain the different long-term trends in nitrate concentrations, loads, and *CQ* slopes (Figures 3–5). The rapid response of instream nitrate concentrations to changes in N input explains the decrease of nitrate concentrations and loads after 1990 in the upper Selke as an immediate consequence of the drastic decrease in N inputs (Figure 2) due to the German reunification and the associated break down of intensive agriculture. Our finding of short TTs in the upper Selke is in agreement with reported TTs from a small headwater catchment in the upper Selke (J. Yang et al., 2018) and with studies in other responsive headwater catchments for which comparably short TTs were reported (e.g., Hrachowitz et al., 2009; Soulsby et al., 2015). However, the increase in nitrate concentrations and loads during HFSs beginning in 2000 cannot be explained by TTDs and N input, because no pronounced increase of N input occurred around that time. One possible explanation could be an increase of distant nitrate sources that become connected to the stream with higher soil moisture content during HFSs and consequently more active flow path. Reasons for this might be local changes in agricultural practices, forest management, or land use arrangement, which were not accounted for in the county-based N input data. For example, spruce forests of the Harz Mountains were subjected to increased bark beetle attacks as a likely consequence of increasing temperatures (Lindner et al., 2010; Overbeck & Schmidt, 2012). The consequent die-back of trees could have caused changes in the N-balance of forest ecosystems in the upper Selke (Huber, 2005; Mikkelson et al., 2013).

In view of the large TTs in the lower Selke, we argue that the increase in N input before 1976 caused the increase in nitrate concentrations around 1990, while the decrease in N input that occurred in 1990 impacted riverine nitrate concentrations about a decade later (Figures 3 and 4, Figure S3). However, there is considerable uncertainty in the comparison between N input and export dynamics in the lower Selke, as suggested by the lower R^2 of the TTD (Table 2). Larger catchments with different land use types such as agriculture and urban areas are often exposed to multiple nitrate sources (Caraco & Cole, 1999; Silva et al., 2002). Hence, the observed dynamics in the lower Selke, especially the two emerging peaks during LFSs around 1997 and 2010, are likely a mixture of delayed N input and additional direct influences from other nitrate sources. Two possible direct influences are (i) the activities around the mining pit close to the catchment outlet and (ii) the starting operation of WWTPs around 1996/1997. Water was pumped from the mining pit into the Selke River before 1991 and after 2009, while water was diverted from the river into the pit between 1998 and 2009. The few available grab samples of nitrate concentration at the outlet of the filled mining pit (mainly after 2009, Figure S6) suggest a temporal dilution of riverine nitrate concentrations and it remains unclear how these activities changed groundwater gaining or losing conditions in the Selke River itself (Figure S6). We showed not only that WWTPs generally have a small impact on nitrate concentrations (Figure 2) but also that their impact is highest during LFSs. Hence, it is possible that temporal changes that cannot be accounted for by the resolution of our WWTP data contributed to the decrease in nitrate concentrations around 1997.

In summary, although the decline in nitrate concentrations in the lower Selke is generally a good sign for improved water quality, its driving forces are related to considerable uncertainty. Nitrate concentrations might have decreased as a delayed response to the decrease in N input in 1990 or due to other more direct influences such as the nearby mining pit. We suggest that a combination of all these processes was responsible for the observed concentration dynamics.

4.2. Long-Term Trends in Concentration–Discharge Relationships

CQ slopes in the upper Selke showed an overall consistent picture of chemodynamic accretion patterns in nitrate export (Figure 5). Low *CQ* slopes during LFSs before 1990 might indicate N saturation of the catchments due to the high agricultural N input during this time (Figure 2). *CQ* slopes increased toward chemodynamic accretion patterns after the decrease of N inputs in 1990, suggesting that the landscape is becoming less saturated and that there is more heterogeneity in nitrate sources and pathways; however, nitrate export was still transport limited. In 2000, *CQ* slopes during LFSs decreased but maintained chemodynamic accretion patterns as an indication of transport limitation. We argue that the more dynamic *CQ* slopes during LFSs (compared to HFSs) are likely linked to seasonal conditions such as decreased hydrologic connectivity and a greater biological N demand.

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 toward (iii) chemostatic nitrate export during all seasons in recent years (Figure 5). 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 originating from deeper groundwater, whereas shallower subsurface flow paths which access a younger fraction of groundwater are activated during HFSs (Ehrhardt et al., 2019; Musolff et al., 2016). As N input gradually increased until 1976, deeper groundwater in the lower Selke still showed lower nitrate concentrations than shallow groundwater in the first years of our time series. 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 (Figure 2). 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 and the consequently faster transport of N 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. These diverging long-term trends were especially pronounced during LFSs (Figures 3c and 3d). Lower nitrate concentrations from the upper Selke during LFSs could therefore have diluted the higher nitrate concentrations downstream, leading to the observed dilution pattern in *CQ* slopes in the lower Selke (Figures 5c, 5d, and S2c). 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 (Figure 2; 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 subcatchments (Figure 3).

Similarly to Ehrhardt et al. (2019), we were able to 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 an indication not exclusively for intensive agriculture but also for homogenously distributed N stores, both vertically in the subsurface and between different subcatchments. 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 subcatchments due to different subcatchment-specific TTDs. Defining one unique *CQ* slope for nitrate concentrations at the catchment outlet across longer time series and seasons can be misleading, as it may integrates input and mobilization patterns as well as transport times that are not necessarily the same over space and time (Figure S7). For example, a temporal transition from accretion patterns toward dilution—as observed in the lower Selke during LFSs from 1990 to 2000—might be interpreted as constantly chemostatic if these long-term temporal changes and for seasonal differences are not taken into account.

4.3. N Legacies and Potential Denitrification

The largest proportion of N export that should have been exported according to TTDs is "missing." Only 15.4% and 8.0% of the estimated N export derived from conservative TTDs were actually exported as measured nitrate loads, which translates into 34.8 kg N ha^{-1} year^{-1} and 46.3 kg N ha^{-1} year^{-1} of *missing N* (Table 2). This is likely evidence of considerable N retention in both subcatchments, especially in the lower Selke.

The relatively constant *CQ* slopes in the upper Selke indicate biogeochemical legacies, while short TTs suggest a fast turnover of hydrological legacies that prevent a similar vertical stratification and associated heterogeneity in the belowground N storage as discussed for the lower Selke. The observed chemodynamic accretion pattern and the pronounced seasonality also indicate that N sources are stored either in the shallower zones of the subsurface 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 discharge generating zones during high-flow conditions in a small headwater catchment in the upper Selke enables the mobilization of additional N sources. In contrast, long TTs and the shifts in *CQ* relationships in the lower Selke indicate the presence of considerable hydrological legacies, 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 within 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) calculated average denitrification rates for soils in Saxony-Anhalt using the process-based DENUZ transport model (Köhne & Wendland, 1992; Kunkel & 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} year^{-1}), which is considerably lower than the rates of *missing N* for the Selke catchment mentioned above (Table 2). Even assuming the upper range denitrification rate, *missing N* would still be >20 kg N ha^{-1} year^{-1} in the upper and >30 kg N ha^{-1} year^{-1} in the lower Selke.

According to a recent study from Hannappel et al. (2018), the potential for denitrification in the groundwater is largely depleted in Saxony-Anhalt. Hannappel et al. compared N input with nitrate concentrations in the groundwater and searched for hydrogeochemical evidence of ongoing denitrification (redox status, increase in hydrogencarbonate or sulfate). Of the seven observation wells within the Selke catchment, only one (located in the upper Selke) showed evidence of ongoing denitrification. Hence, denitrification in the groundwater likely removed a part of N input in the upper Selke. However, of all observation wells in Saxony-Anhalt located in a similar geologic setting as the upper Selke (Palaeozoic), fewer than 5% showed evidence of 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 become depleted in the near future. None of the observation wells showed a potential for denitrification in groundwater in the lower Selke (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, an assumption which is in line with findings from Ehrhardt et al. (2019) made 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 by Mueller et al. (2016) in the Bode catchment (which includes the Selke catchment) found evidence for significant denitrification in the stream beds during LFSs, whereas denitrification in the groundwater was not evident, findings which are in line with those of 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 in nitrate export dynamics: it could, according to Rode et al. (2016), have removed around 5% of nitrate in the upper Selke and 13% in the lower Selke. Nevertheless, only a small percentage of nitrate uptake is the permanent removal via denitrification. Hence, we suggest that N uptake in the stream only accounts 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 (Figures 3c and 3d) indicate that assimilatory uptake was not a key process in causing the observed nitrate export patterns at longer time scales, as this would imply a more steady seasonality.

In summary, a large proportion 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 part of it was stored as biogeochemical and hydrological legacies in both parts of the catchment. We see an indication for biogeochemical legacies in the upper Selke, whereas long TTs and deeper aquifers indicated an important contribution 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.

4.4. Seasonality in Nitrate Export

The contribution of different subcatchments 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 subcatchment for nitrate export was driven by the seasonally different dynamics of mobilization and transport in the different subcatchments.

Nitrate concentrations in the upper Selke showed a pronounced seasonality, with high concentrations during HFSs and low concentrations during LFSs. This dynamic might have several reasons, such as an increased N demand of the ecosystems during warmer temperatures (Rode et al., 2016), a flushing of limited surficial N sources with peak snowmelt (Pellerin et al., 2012), and a higher hydrological connectivity due to an increased soil moisture content during HFSs (J. Yang et al., 2018). Especially, the last point is also reflected by the positive *CQ* slopes in the upper Selke, which indicate *CQ* a chemodynamic-accretion pattern (Figure 5). 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 in a chemodynamic-accretion pattern are not uniformly distributed. Instead, 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 and forest-dominated upstream catchments which include only patches of agriculture or other relevant N sources. The consequent increase in nitrate concentrations during high flows and HFSs can cause high nitrate loads, as observed in the upper Selke and other forest-dominated catchments (Seybold et al., 2019). 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% annually 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 (i) the high nitrate concentrations during HFSs which indicate an additional activation of N sources with higher Q as reflected by the described accretion pattern and by (ii) a disproportional contribution to Q from the upper Selke, which is typical for upstream catchments (Alexander et al., 2007; Dupas et al., 2019) and might be enhanced by snowmelt during HFSs due to the higher elevations in the upper Selke (Table 1).

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 (Figure 5). Chemostatic export was often found for catchments like the lower Selke which 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 nondecreasing 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 subcatchment-specific signals but reflects a seasonal dominance of different subcatchments. 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.

4.5. Event Dynamics and Their Seasonality

To examine the integrated signal of nitrate export across time scales, we analyzed not only long-term trends and seasonal patterns but also the CQ slopes and hysteresis behavior 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 (Figures 6a and 6b). Large storm events can therefore mobilize and transport large amounts of nitrate and contribute disproportionally to annual nitrate loads. The counterclockwise hysteresis found for most events (Figures 6d and 6e) 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, whereas event-specific CQ slopes were more dynamic (Figure 5; Figure 6c). 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 (Figures 3c and 3d) that diluted lower Selke nitrate concentrations. Additionally, they might be caused by a direct dilution from shallow flow paths with reduced nitrate concentrations due to an elevated N demand by agricultural crops during summer and early fall that were activated during events and diluted the more highly concentrated base flow. During winter, event-specific CQ slopes in the lower Selke became dominantly positive (Figure 6c), indicating a chemodynamic export with the same accretion pattern as in the upper Selke. It is also during recent winters that nitrate concentrations from the upper Selke were similarly high as the nitrate concentrations in the lower Selke (Figure 3a). It is therefore reasonable to assume that higher nitrate concentrations from the upper Selke during storm events also caused an increase in concentrations 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% agriculture, 27% grassland, and 23% woodland). Similarly to the findings in 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 from the upper Selke. Furthermore, they argued that diffuse N sources become depleted throughout large storm events in winter and spring, which might also be the case (to a lesser extend) in the upper Selke catchment and could explain its lower export levels of nitrate during spring compared to winter (Figures 3a, 3b, 4a, and 4b). Moreover, Dupas et al. (2016) found a similar dilution pattern during most storm events at the outlet of a mesoscale catchment in Thuringia (Germany), whereas 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 us to identify subcatchment-specific contributions, we suggest that the contrast between long-term and event-specific *CQ* slopes in the lower Selke reflects the upstream subcatchment export patterns and therefore serves as an indicator to disentangle subcatchment-specific contributions to nitrate export and its dynamics.

4.6. Conceptual Framework and Implications for Management

A key objective of this study was to analyze how different nested subcatchments contribute to the integrated signal of nitrate concentrations, loads, and *CQ* relationships at the outlet of a mesoscale catchment. While upstream subcatchments 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 of nitrate pollution (e.g., Padilla et al., 2018; Strebel et al., 1989). The available long-term and high-frequency data for three nested catchments within the Selke catchment enabled us to disentangle these contrasting drivers of nitrate export and allowed a detailed analysis of the relative impact of more mountainous upstream subcatchments (upper Selke) versus more intensively cultivated downstream lowlands (lower Selke) across time scales. The general findings, summarized in Figure 7, illustrate that TTs for nitrate in the upper Selke were relatively short (Figure 7a) and that transport patterns were quite dynamic, with nitrate concentration increasing with *Q* (Figures 7b and 7c). These dynamics led to temporally elevated nitrate concentrations during HFSs and events and a disproportional contribution to annual nitrate loads, which are both relatively short-term impacts. In contrast, the lower Selke showed long TTs (Figure 7a) and a less dynamic export behavior with relatively constant nitrate concentrations (Figures 7b and 7c). 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 will likely impact nitrate exports for years to come, dominantly during LFSs and base flow conditions. This differentiation between a more mountainous upper part of a catchment and an agriculturally dominated lowland part is very common for 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.

Water quality managers should be aware of these potential differences between subcatchments. If the aim is to reduce high nitrate loads, the focus must be on the upstream subcatchments with short TTDs and dynamic transport patterns. As nitrate concentrations are especially high during winter and spring, an application of catch crops during these seasons is a promising measure to reduce nitrate leaching (Askegaard et al., 2005; Constantin et al., 2010; McLenaghen et al., 1996). Furthermore, large buffer strips (>50 m) can decrease connectivity between agricultural fields and the stream network (Mayer et al., 2005). Unfortunately, high N loading via atmospheric deposition, as apparently occurs in the Harz Mountains (Kuhr et al., 2014), cannot be addressed locally but requires 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 to significantly and relatively quickly reduce nitrate export to the streams, as the riverine concentration decrease after 1990 suggests.

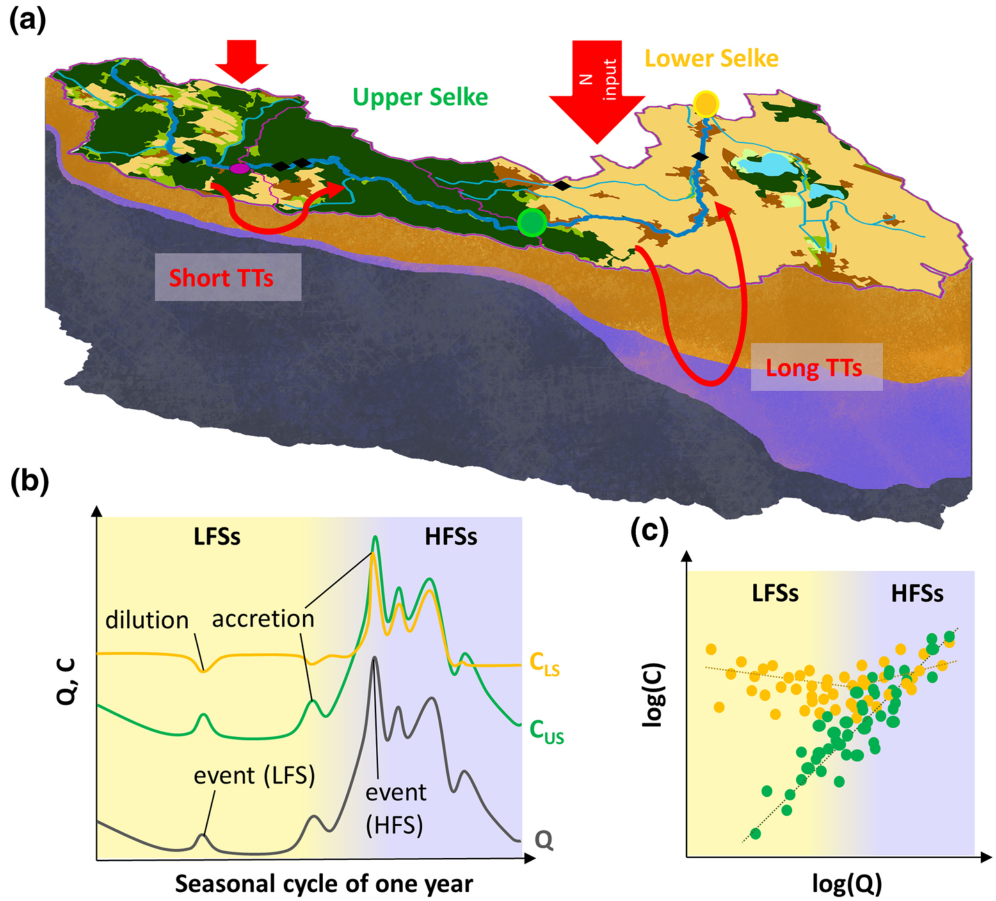

Figure 7. Conceptual framework explaining the subcatchment-specific contribution of the upper Selke (green) and the lower Selke (yellow) to nitrate export from the Selke catchment during low-flow seasons (LFSs, yellow background in (b) and (c)) and high-flow seasons (HFSs, blue background in (b) and (c)). Note that nitrate export from the lower Selke is always an integrated signal from the entire catchment. (a) The Selke catchment divided into the upper Selke (green circle) and the lower Selke (yellow circle) with its land use, its relative N input (not true to scale), and apparent travel times of nitrate (TTs). (b) Seasonal and event dynamics of nitrate concentrations (*C* with indexed US and LS representing the upper and lower Selke) 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.

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 quick 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 on 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 focus neither solely 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 subcatchments and to disentangle their respective contributions to the integrated signal of nitrate export at the catchment outlet. Taking advantage of a comprehensive data set that includes long-

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term and high-frequency data from three nested subcatchments in the Selke catchment, we were able to show that subcatchments can have very different nitrate export dynamics that lead to seasonally different subcatchment 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 therefore has a disproportionally high contribution to nitrate loads. This imbalance underlines the important role of upstream subcatchments when considering 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 subcatchments with long TTs and a dominance of agricultural land use (here the lower Selke) pose a long-term and persistent problem in terms of nitrate pollution; the quality of drinking water can be threatened for decades. Nitrate export from these subcatchments 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 the impact from upstream subcatchments is not taken into consideration. We do not aim at prioritizing individual measures to reduce nitrate pollution between subcatchments, but we emphasize the importance of subcatchment-specific characteristics in order to place nitrate reduction measures most effectively and to assume realistic time scales for their success.

We could further show that *CQ* relationships for nitrate concentrations can change as a reaction to changes in N input. Whereas chemodynamic patterns can indicate "not equilibrated systems" that are still in transition toward a new equilibrium, chemostasis can indicate homogenously distributed N sources (both vertically in the subsurface and between subcatchments) 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 analysis of long-term trends and event-scale *CQ* slopes is a promising approach to disentangle the impact from subcatchments on nitrate export at the catchment outlet, as it can reveal short-term impacts from the more dynamic upstream catchment export which 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 in order to be able to assess the full range of subcatchment impacts on nitrate export, as the times and time scales relevant for nitrate export can vary substantially between subcatchments.

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 subcatchment 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.

Data Availability Statement

Supplementary figures and tables are available as Supplementary Information. Data sets on (i) FN and non-FN nitrate concentrations, loads, and *CQ* slopes; (ii) N input; and (iii) event characteristics are available under: https://doi.org/10.4211/hs.c3ea08faa88a46a4a3ce596a09686198

Raw data on discharge and water quality are 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 archived in the TERENO data base and are 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 Programme (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 data sets can be freely obtained from the 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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AGU PUBLICATIONS

Water Resources Research

Supporting Information for

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

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Datasets S1. Annual and seasonal averaged nitrate concentration data (1983 – 2016)
Datasets S2. N input data (1950 – 2015)
Tables S1. Event characteristics for all identified events (2010 – 2016)

Introduction

In the following, we provide additional figures and datasets to support the analysis and results. Fig. S1 gives an overview on all data available for discharge (Q) and nitrate concentrations (C) in the Selke catchment. Fig. S2 depicts the annual long-term trends of flow-normalized (FN) and non-flow normalized nitrate concentrations, loads and the CQ slopes, calculated via *Weighted Regression on Time Discharge and Season* (WRTDS). Fig. S3 depicts the fitted transit time distributions (TTDs) and the dynamics of the TTD derived conservative nitrogen (N) export, N input and measured FN nitrate export. Fig. S4 and S5 show event specific CQ slopes and hysteresis patterns for all identified events (200 in total) and table S1 includes the characteristics of all these events. Fig. S6 depicts nitrate concentrations from the outflow of the mining lake into the Selke River. Dataset S1 provides annual and seasonal averages of flow-normalized and non-FN nitrate concentrations, loads and CQ slopes and dataset S2 provides annual N input data between 1950 and 2015 for the Selke catchment and its sub-catchments. Datasets and tables are available in an open repository in Hydroshare (https://www.hydroshare.org).

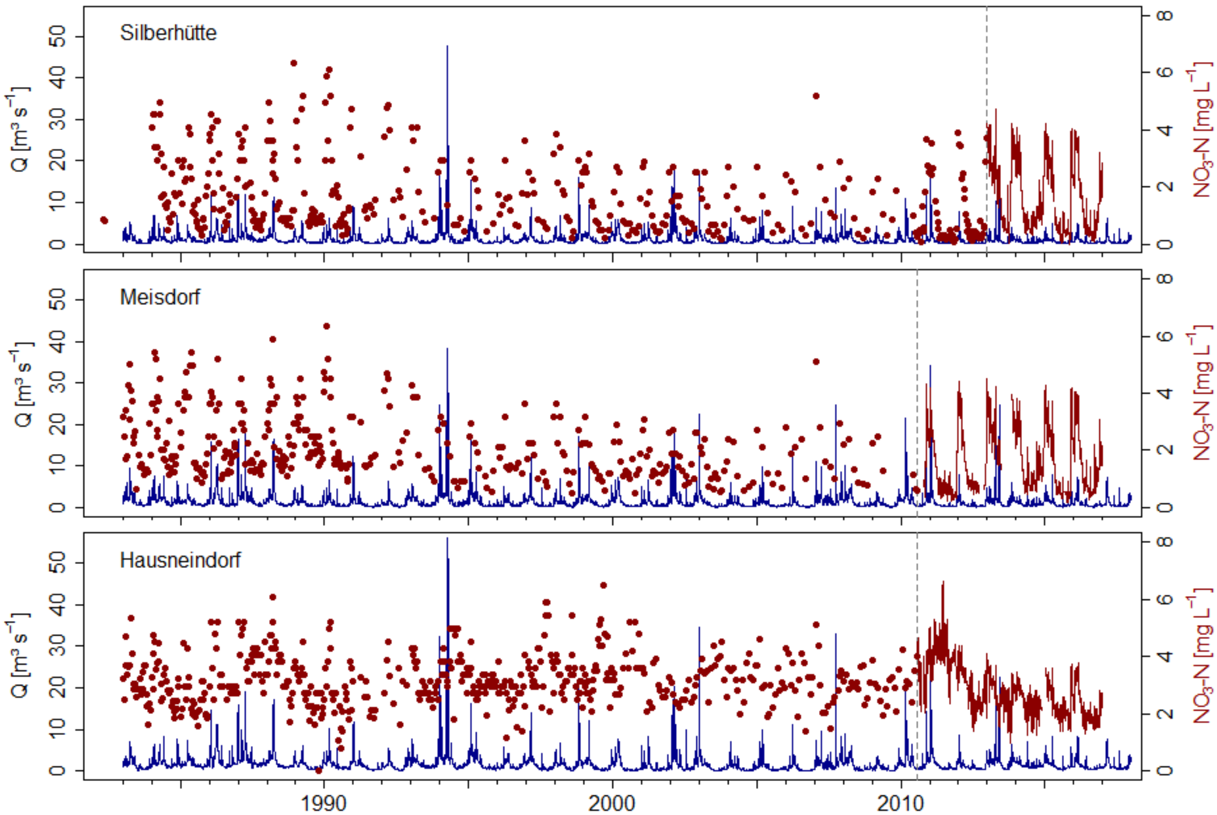

Figure S1. Long-term (red dots) and high-frequency (red lines) data of nitrate concentrations and daily discharge data (blue lines) between 1983 and 2016, measured at all three gauging stations in the Selke catchment, where Silberhütte and Meisdorf are considered as the *upper Selke* and Hausneindorf is considered as the *lower Selke*.

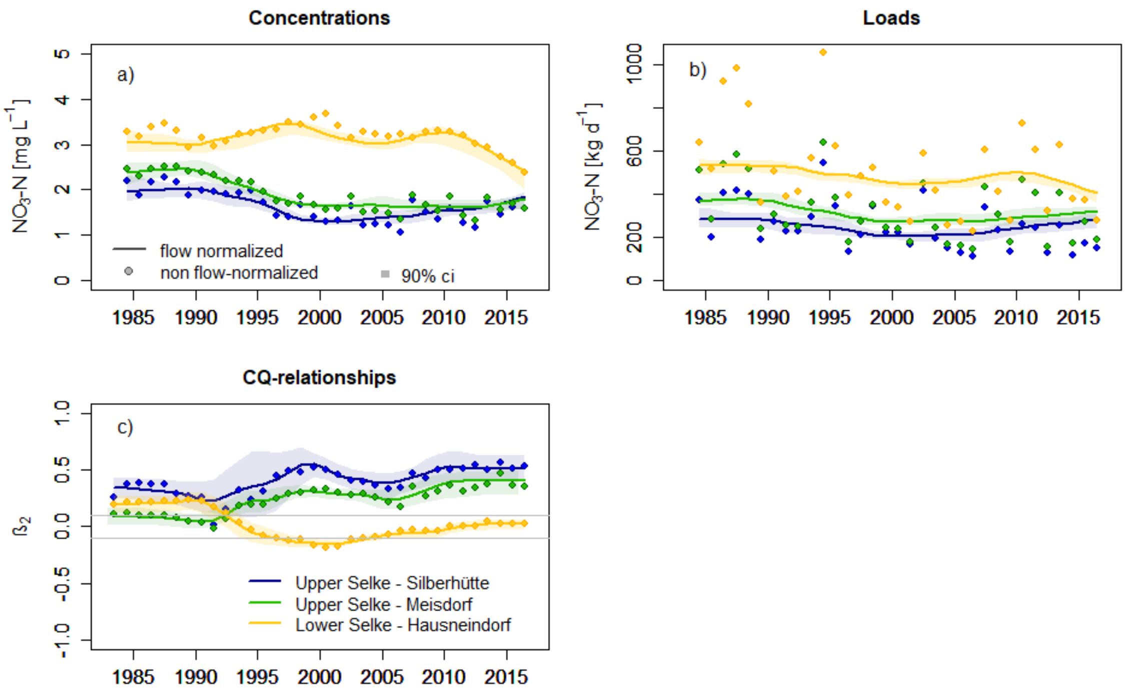

Figure S2. Long-term trends of annual flow normalized and non-flow normalized a) nitrate concentrations, b) loads and c) CQ-relationships (fitted parameter $ß_2$ from WRTDS) from three nested sub-catchments in the Selke catchment. Uncertainty bands in the sub-catchment specific color indicate the 90% confidence intervals from bootstrapping flow-normalized values.

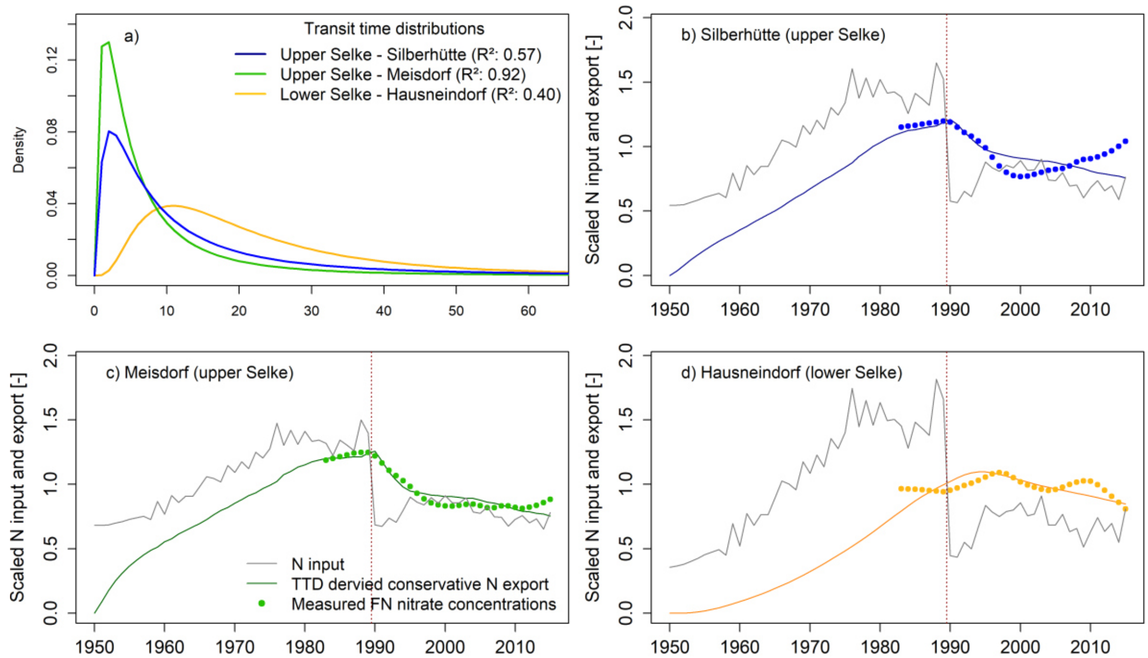

Figure S3. a) Transit time distributions (TTDs) for all three nested sub-catchments of the Selke catchment and b – d) N input, TTDs derived conservative N export and measured flow-normalized (FN) nitrate concentrations, all scaled divided into subplots of the three nested sub-catchments. The dotted dark red line indicates the German reunification which was followed by a marked decrease in N input.

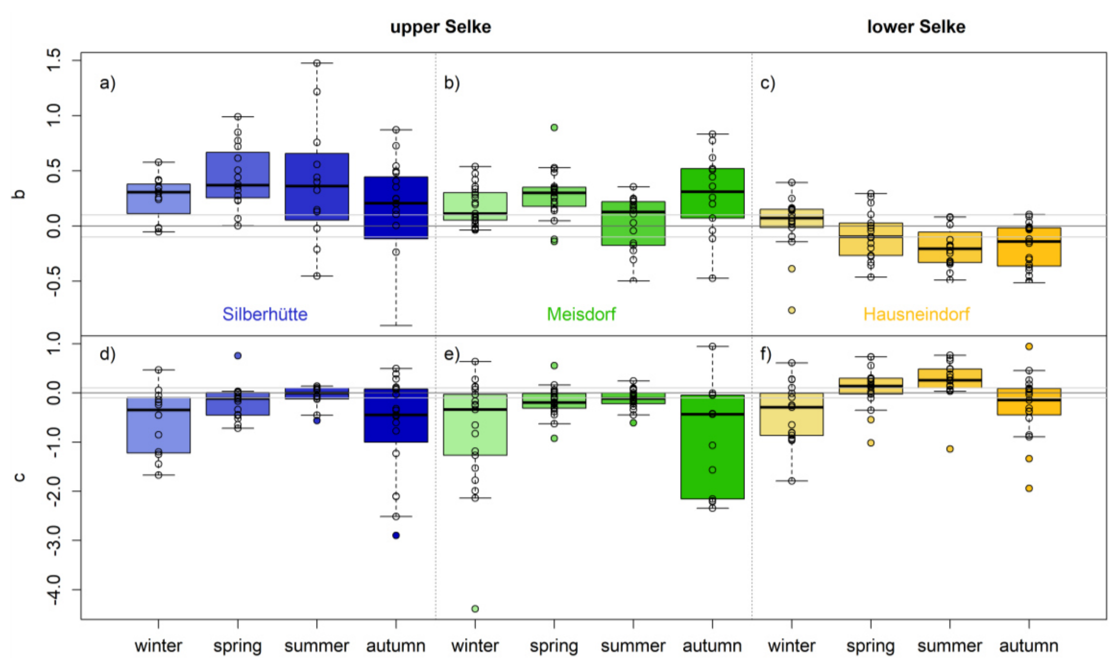

Figure S4. Boxplots of all event-specific fitted parameters b (CQ-slope) and c (hysteresis) in eq. 2. Parameters are separated by seasons and gauging stations within the Selke catchment, displayed from upstream (left) to downstream (right).

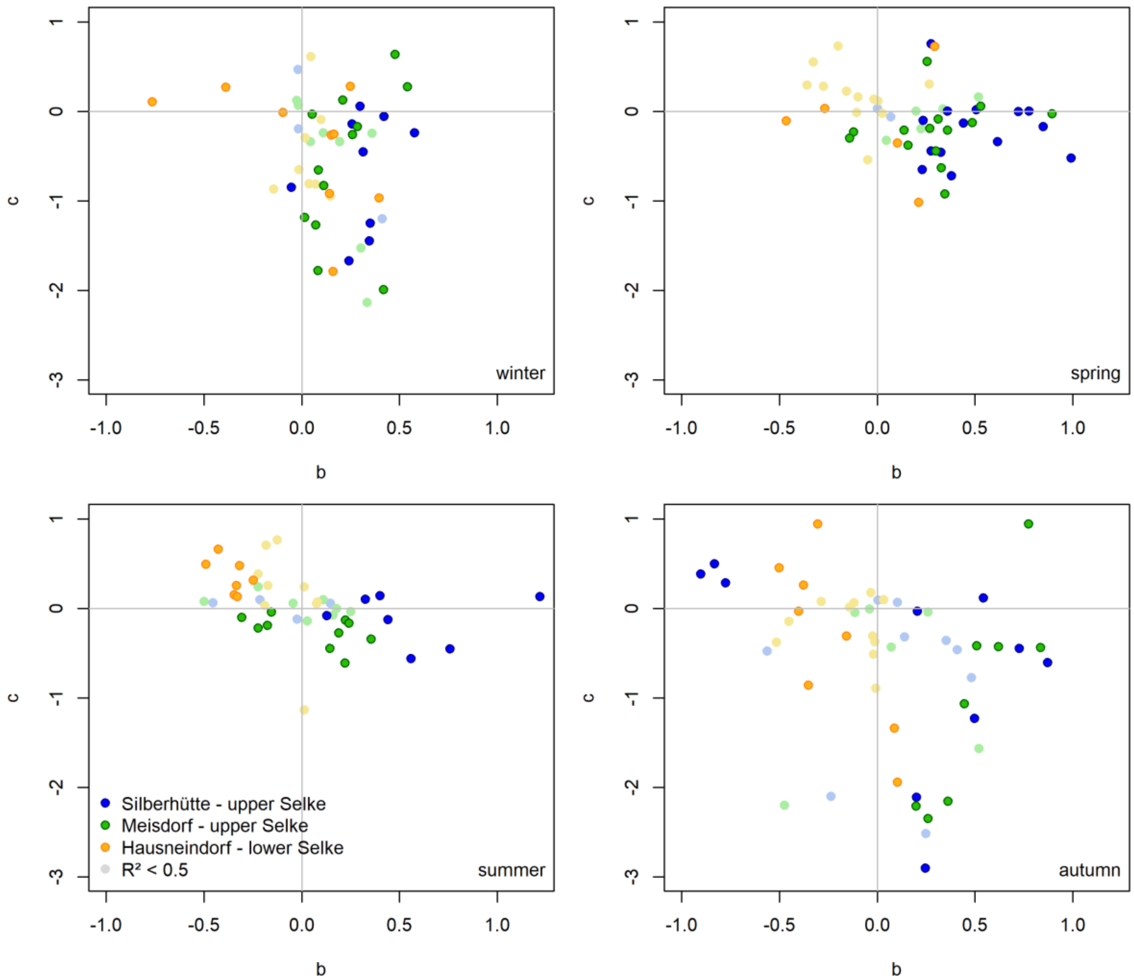

Figure S5. Relationship between the event-specific fitted parameters b (CQ-slope) and c (hysteresis) in eq. 2, separated by seasons.

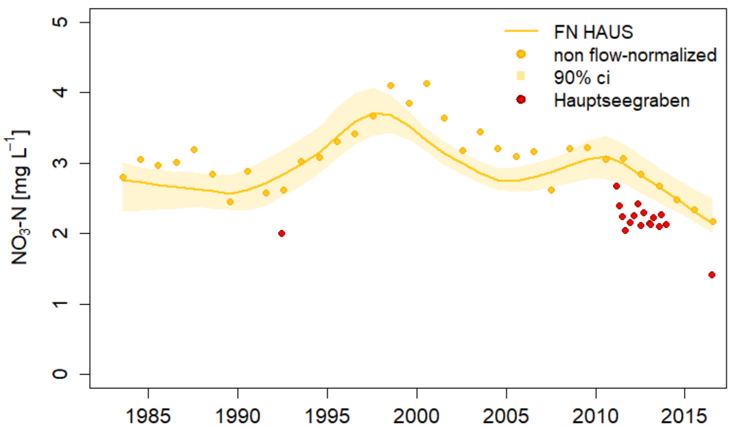

Figure S6. Flow-normalized (FN) and non-FN summer nitrate concentrations (yellow) from the Selke catchment at Hausneindorf (HAUS) and additional grab samples of nitrate concentrations from the outflow of the filled open-cast mine (red dots).

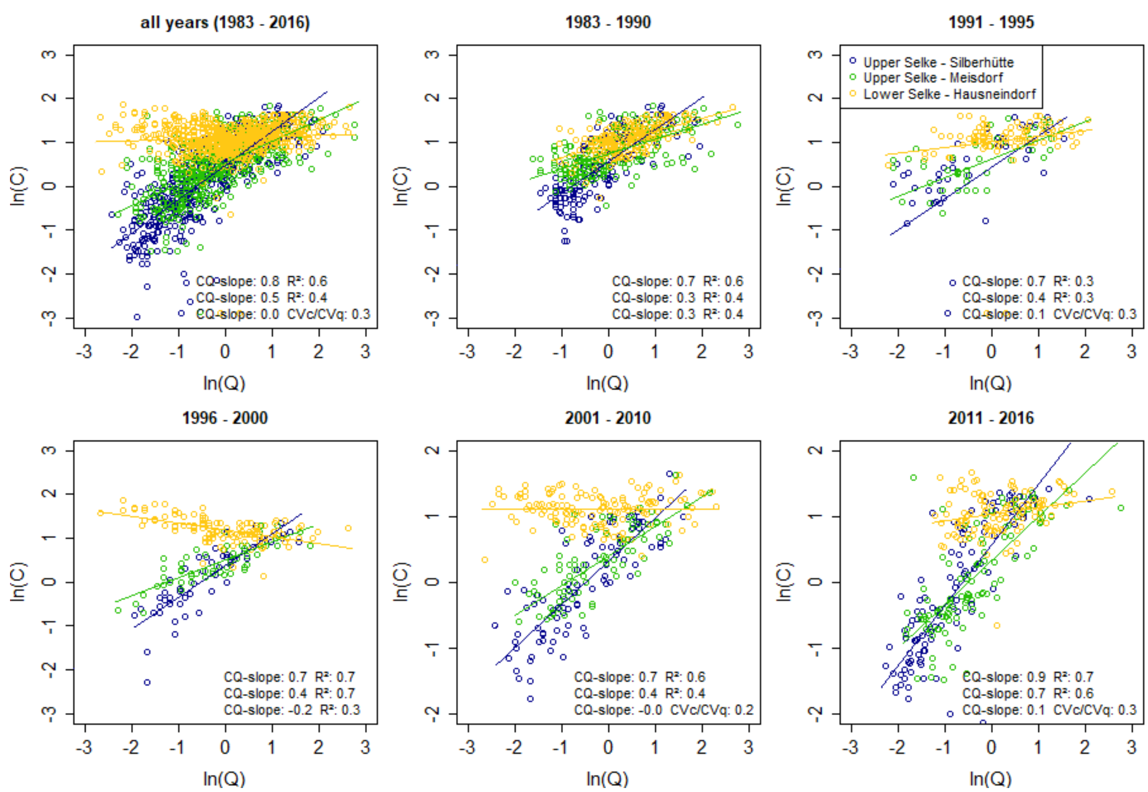

Figure S7. Relationship between nitrate concentrations (C) and discharge (Q) from long-term grab samples for all three nested catchments within the Selke catchment, as the slope between ln(C) and ln(Q) (CQ-slope). The CQ-slope is depicted a) for the given time period from 1983 to 2016 and b-f) divided into 5 smaller time periods. The coefficient of determination (R^2) is displayed for all CQ-slopes ≤ 0.1 and ≥ -0.1. For CQ-slopes around zero that are accounted for as chemostatic, the CV_C/CV_Q is displayed, with CV being the coefficient of variation.

Data Set S1. Annual and seasonal nitrate concentrations data (1983 – 2016). Average flow-normalized (FN) and non-FN values calculated with Weighted Regression on Time, Discharge and Season (WTRDS, Hirsch et al. 2010). Available under https://doi.org/10.4211/hs.c3ea08faa88a46a4a3ce596a09686198

Data Set S2. Nitrogen (N) input as the sum of N surplus from agricultural areas, N surplus from non-agricultural areas in form of atmospheric deposition and biological fixation and nitrate outflow from wastewater treatment plants (WWTPs). Available under https://doi.org/10.4211/hs.c3ea08faa88a46a4a3ce596a09686198

Table S1. Event characteristics of all events, including start and endpoint of events, maximum discharge (Q_{max}), maximum nitrate concentration (C_{max}), fitted parameters b and c and the coefficient of determination (R^2) for the fitted eq. 2. Available under https://doi.org/10.4211/hs.c3ea08faa88a46a4a3ce596a09686198

Study 2:

Droughts Can Reduce the Nitrogen Retention Capacity of Catchments

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Own contribution:

- Concept and study design 100%
- Data acquisition 5%
- Data analyses 70%
- Figures 100%
- Discussion of results 85%
- Manuscript writing 85%

CW designed the study. MR provided high-frequency data, and the LHW and the DWD provided hydrological and meteorological data. TN and RK provided model products. CW and TN performed the analyses, and CW created all figures and tables. CW wrote the manuscript. All co-authors revised the manuscript.

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Droughts can reduce the nitrogen retention capacity of catchments

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Abstract. In 2018–2019, Central Europe experienced an unprecedented 2-year drought with severe impacts on society and ecosystems. In this study, we analyzed the impact of this drought on water quality by comparing long-term (1997–2017) nitrate export with 2018–2019 export in a heterogeneous mesoscale catchment. We combined data-driven analysis with process-based modeling to analyze nitrogen retention and the underlying mechanisms in the soils and during subsurface transport. We found a drought-induced shift in concentration–discharge relationships, reflecting exceptionally low riverine nitrate concentrations during dry periods and exceptionally high concentrations during subsequent wet periods. Nitrate loads were up to 73 % higher compared to the long-term load–discharge relationship. Model simulations confirmed that this increase was driven by decreased denitrification and plant uptake and subsequent flushing of accumulated nitrogen during rewetting. Fast transit times (< 2 months) during wet periods in the upstream sub-catchments enabled a fast water quality response to drought. In contrast, longer transit times downstream (> 20 years) inhibited a fast response but potentially contribute to a long-term drought legacy. Overall, our study reveals that severe droughts, which are predicted to become more frequent across Europe, can reduce the nitrogen retention capacity of catchments, thereby intensifying nitrate pollution and threatening water quality.

1 Introduction

In 2018–2019, large parts of Europe experienced a severe 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 freshwater quality in regard to nitrate concentrations. The Nitrate Report 2020 of the Netherlands (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 and Basu, 2015). The extent of delays and removal strongly depends on the catchment characteristics and boundary conditions (e.g.,

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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, 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 and 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 paths (Górski et al., 2019; Loecke et al., 2017; 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 and Biederbeck, 1982; Haynes, 1986; Loecke et al., 2017). 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 of giving 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 and Basu, 2015; Winter et al., 2021). Tools 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 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, lateral N transport at the sub-catchment scale, and time-variant transit time distributions (TTDs). 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 modeling has several advantages: The data-driven analysis allows for robust identification of drought impacts on nitrate export and a discussion on the underlying processes, while the process-based modeling allows testing if these processes can actually explain the observed behavior.

In this study, we used data-driven analysis and process-based modeling to analyze the impact of the 2018–2019 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 relevant to 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 (ii) quantify changes in N cycling in the catchment soils and in the timescales of lateral N transport from the soil leachates to the stream network via process-based modeling (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 drought was an unprecedented event, but with accelerating climate change, such prolonged 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

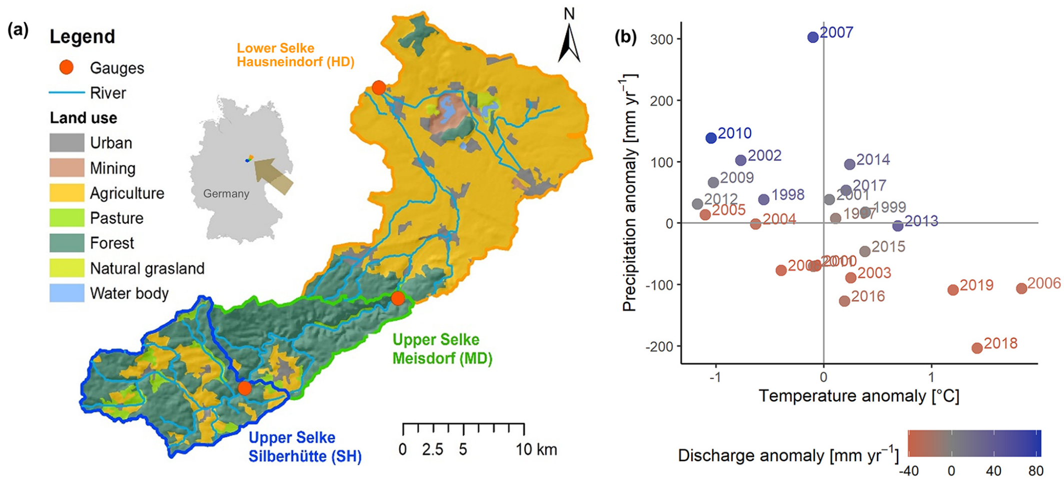

Figure 1. Study site and long-term hydro-meteorological conditions. **(a)** Land use map of the Selke catchment with its three gauging stations (SH (Silberhütte), MD (Meisdorf), and HD (Hausneindorf)). **(b)** Climatic anomalies in the Selke catchment in terms of precipitation, temperature, and discharge for the years (starting in May) 1990 to 2019.

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 (Fig. 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, Fig. 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 transit times (TTs) and comparable nitrate export dynamics (Nguyen et al., 2022; 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; Winter et al., 2021).

2.2 Characterization of different hydro-meteorological 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 starting in January, we calculated annual 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, considering the seasonality in climatic conditions in central Germany. Throughout the paper, we therefore defined years by drying–wetting cycles starting in May, with the consecutive numbering being based on the starting date. For example, the year 2018 started on 1 May 2018 and ended on 30 April 2019. In the same manner, we refer to the 2-year drought as 2018–2019, spanning a period from May 2018 until the end of April 2020.

To compare the hydro-meteorological conditions during the drought years (2018 and 2019) with the ones during previous years (1990–2017), we calculated their hydro-meteorological anomalies compared to the long-term average. To this end, we calculated the annual averages in observed temperature, precipitation, and discharge and modeled soil moisture (see Sect. 2.5) for the study catchment. We then calculated the long-term average over all years and subtracted the single annual averages from those long-term averages. The divergence of annual hydro-meteorological conditions from the long-term average is considered the hydro-meteorological anomaly. In the Selke catchment for the 2018–2019 drought, the years starting in May 2018 and May 2019 are characterized by exceptionally low pre-

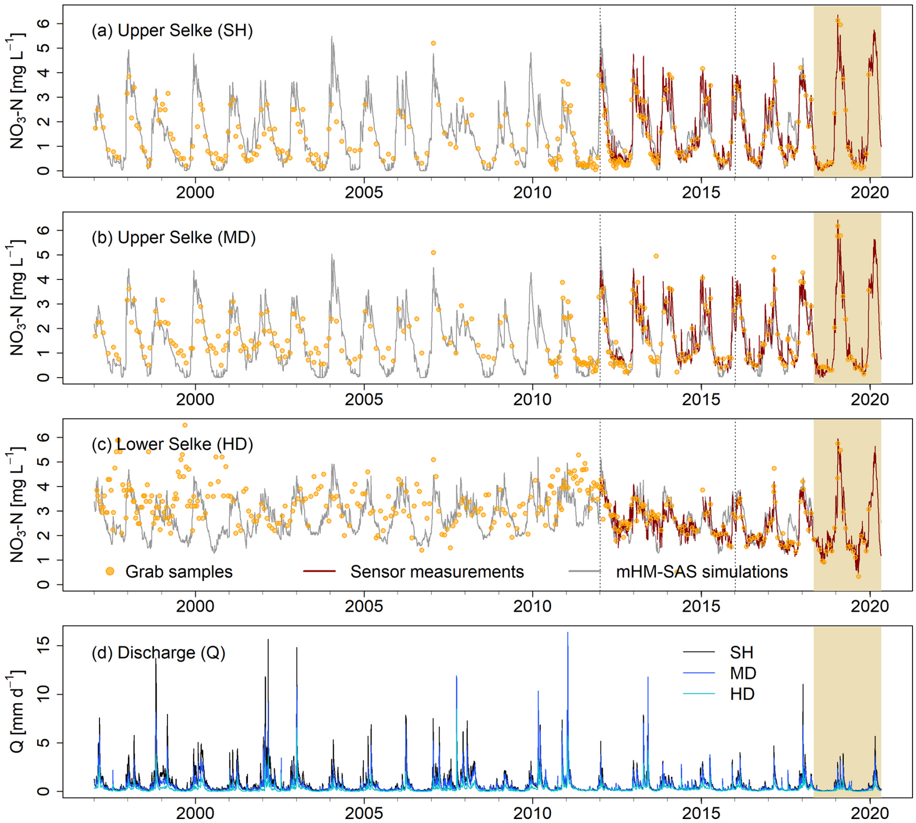

Figure 2. Nitrate as nitrogen concentrations and discharge at the gauging stations of the three Selke sub-catchments (1997–2020) with low-frequency grab samples (orange dots), simulated concentrations via mHM-SAS (grey line), daily averages of high-frequency sensor measurements from 2012 (red line), and daily discharge (bluish lines). 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.

cipitation (anomaly of -205 and $-110\,\mathrm{mm\,yr^{-1}}$ in 2018 and 2019, respectively, compared to the long-term average of $602\,\mathrm{mm\,yr^{-1}}$ over the period 1997–2020), high temperatures (+1.6 and +1.4 °C in 2018 and 2019, compared to the long-term average of 9.0 °C), and low discharge (-37.0 and $-39.2\,\mathrm{mm\,yr^{-1}}$ compared to the long-term average of $98.5\,\mathrm{mm\,yr^{-1}}$) (Fig. 1b). In terms of soil moisture, these 2 years were the driest in the Selke catchment since the start of our time series in May 1997, with 2018 being even drier than 2019 (Fig. S1 in the Supplement). Consequently, the 2-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) and gridded via external drift kriging following Zink et al. (2017). N input data (i.e., fertilizer, manure, and plant residues), 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 2- or 3-year crop rotation, as is 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; Fig. 2a–c). Sensor measurements (using TriOS Pro-UV sensors (Rode et al., 2016) of nitrate concentrations at a 15 min 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 (Fig. 2a–c). Part of this data was previously used by Musolff et al. (2021), Rode et al. (2016), Winter et al. (2021, 2022), and 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.

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 annual averages (starting in May). A simple but efficient way to describe the C–Q relationship is a power–law relationship of the following 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 are 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 $\beta+1$, 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 2-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 2 consecutive years and compared the resulting pre-drought C–Q slopes with the one from the 2-year drought.

Instead of restricting our analysis to observed daily data, as done for C–Q relationships, we calculated L–Q relationships with the annual sums of daily load and discharge data 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 % (Fig. 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 2-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; Nguyen, 2022). The mHM-SAS model is a deterministic model with a strong physical basis, explained in detail in Nguyen et al. (2022) and in the Supplement (Sect. S1). Briefly, mHM-SAS provides a spatially distributed ($1 \times 1\,\mathrm{km}^2$) 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 subcatchment using the nitrate transport model with StorAge Selection (SAS) functions (Van Der Velde et al., 2012, Nguyen et al., 2022). SAS functions describe the selective removal of water from a subsurface storage with different water ages and nitrate concentrations, which allows for a nitrate transport formulation based on time-variant TTDs. The SAS function in mHM-SAS is described using a beta function ($\beta(a,b)$), with a and b being two fitted parameters that vary in time (see Supplement, Eq. 6). The derived a/b ratio represents the selection schemes for discharge, e.g., preference for young water (a/b ratio < 1) or old water (a/b ratio > 1) (Nguyen et al., 2022).

Nguyen et al. (2022) calibrated the model in the Selke subcatchments for the years 2012–2015 with a Nash–Sutcliffe efficiency (NSE) of 0.68, 0.66, and −0.13 over the calibration, and 0.81, 0.81, and 0.57 for SH, MD, and HD over the validation period (2016–2019), which includes parts of the 2-year drought. The lower NSE in HD can be explained by the lower seasonality in nitrate concentrations (Nguyen et al., 2022; Schaefli and Gupta, 2007). Using the same setup, here we extended the model simulations to the 1997–2020 time period (Fig. 2a–c). To create an initial age distribution in the storage before 1997 and to minimize the effect of initial conditions, we replicated model input data between 1993 and 1996 10 times as a warm-up period to obtain initial conditions for our actual model runs (1997–2020). 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 distinctly different climatic conditions during the 2018–2019 drought period, nitrate concentrations simulated with mHM-SAS showed an even better fit to the measured sensor data (NSE of 0.89, 0.88, and 0.79 in SH, MD, and HD, respectively) than for the calibration period.(Fig. 2a–c). This good fit over the drought years indicates that the model is also applicable under very dry hydro-meteorological conditions. 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 (TTs).

2.6 Catchment retention capacity

We estimated the capacity of a catchment to retain N (N_{ret}) during 1 year (starting in May) by the ratio of average nitrate-N load export (N_{OUT}) against annual average atmospheric deposition and long-term average N inputs from fertilizer and manure (N_{IN}),

$$N_{ret} = 1 - \frac{N_{OUT}}{N_{IN}}. \quad (2)$$

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. This approach is justified by the fact that N input data did not show any trends and no significant deviation during the 2-year drought. Additionally, we assessed the sensitivity of our results to uncertainty in N input through crop rotation by varying N inputs by ± 20 %, which confirmed the overall robustness of our results (Fig. S3).

To estimate changes in N_{ret} relative to the hydrological conditions, we fitted a non-linear regression between N_{ret} and observed discharge (Q) for the years previous to the 2-year drought (1997–2017). To this end, we assume that Q is log-normally distributed and related to nitrate loads (i.e., N_{OUT}) in the form of a power–law relationship ($\alpha Q^{\beta+1}$), with $\beta+1$ being the L–Q slope. Consequently, N_{ret} can be described as a function of $Q^{\beta+1}$, which would be linear if the L–Q slope equals 1. The result is an N_{ret}–Q relationship that asymptotically approaches 1 (i.e., 100 % retention) at zero discharge, and that is zero if N_{OUT} equals N_{IN}. N_{ret} is a combined measure of biogeochemical N retention in the catchment soils and its consecutive transport via hydrological flow paths to the stream network, which is affected by TTs and denitrification along the flow paths. To acquire a more direct estimate of soil N retention, we additionally fitted the N_{ret}–Q relationship for simulated nitrate leachates (Fig. S4).

3 Results

3.1 Nitrate concentrations

Daily nitrate-N concentrations (i.e., sensor measurements) differed between the upper (SH and MD) and the lower Selke (HD) and between normal (i.e., 2012–2017) and drought years (2018–2019; Fig. 2a-c). Median concentrations in the upper Selke measured before the 2-year drought ranged from 0.6 and 0.7 mg L^{-1} during dry periods in SH and MD, respectively, and 2.6 and 2.4 mg L^{-1} during wet periods. Median nitrate-N concentrations measured at HD were higher and less variable, with a median of 2.2 mg L^{-1} during dry periods and 3.1 mg L^{-1} during wet periods. During the 2-year drought, nitrate-N concentrations generally showed a higher seasonal variability (Fig. 2a–c). During dry periods in 2018 and 2019, nitrate-N concentrations were lower than during previous dry periods, with a median of 0.2, 0.4, and 1.4 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, 3.8, 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. 2c).

3.2 Concentration–discharge and load–discharge relationship

Nitrate concentrations during the 2-year drought show an accelerated seasonality (see Sect. 2.3) that is reflected in a more chemodynamic C–Q relationship (Fig. 3a–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 2-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 (Fig. 3a–c), but also for block sampled C–Q slopes that account for the smaller samples size of the drought period (Fig. S5).

Median nitrate-N loads per area over the years 1997–2017 were 6.6, 5.7, and 3.2 kg yr^{-1} ha^{-1} in SH, MD, and HD, respectively. During the 2-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}) (Fig. 3d–f). They were clearly lower in HD with a load of 2.1 kg yr^{-1} ha^{-1} in both years (Fig. 3d–f).

L–Q relationships showed a good fit (R^2 0.9–0.96) with an L–Q slope close to 1 in all sub-catchments, reflecting that nitrate-N loads increased with increasing discharge (Fig. 3d–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 of 57–73 %, 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 2-year drought (0.2 kg ha^{-1} yr^{-1} in both

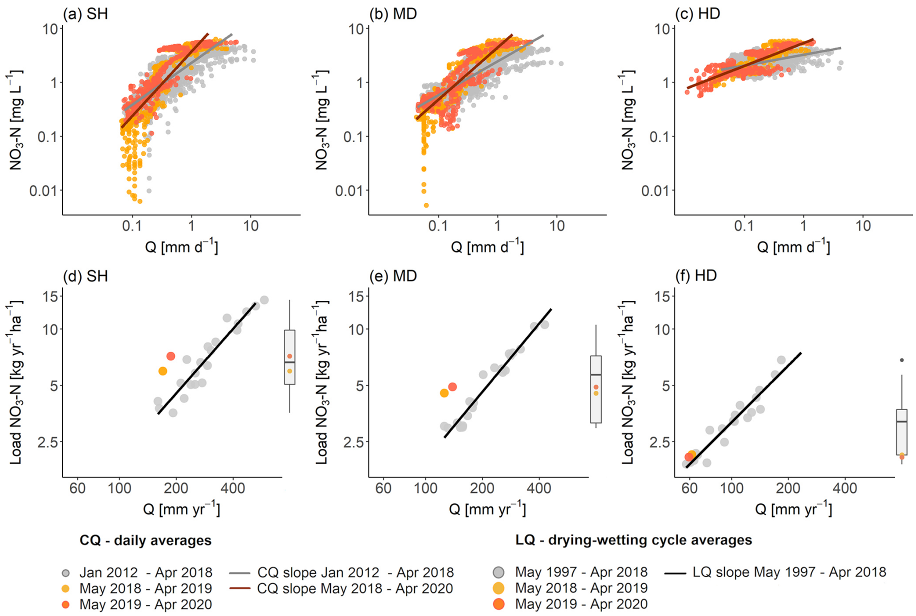

Figure 3. Concentration–discharge (C–Q) and load–discharge (L–Q) relationships for the three sub-catchments of the Selke catchment (SH, MD, and HD). **(a–c)** Daily averaged nitrate concentration and discharge data with log-transformed axes. The lines show the C–Q slope for daily averages before the 2-year drought (grey) and since the start of the 2-year drought (dark red). **(d–f)** Annual averages for loads and discharge in the log–log space since 1997 (years starting in May). Black lines show the L–Q slope previous to the 2-year drought. Box plots 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.

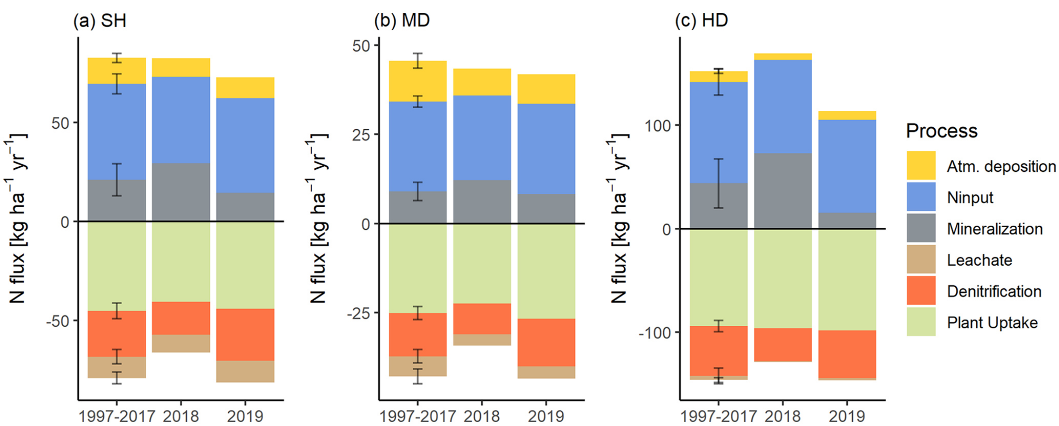

Figure 4. N input and N fluxes simulated via mHM-SAS separately for the three Selke sub-catchments (SH, MD, and HD). N entering the catchment soils are shown as positive values, N fluxes leaving the catchment soils are shown as negative values. Error bars represent the standard deviation between annual averages from 1997 to 2017.

years, equivalent to an increase of 10 %). However, exported nitrate loads in the lower Selke have generally decreased since 2011 (Winter et al., 2021). Therefore, 2013–2017 loads are the ones plotting clearly below the long-term L–Q slope (Fig. 3f); as such, the L–Q relationships from the 2-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 2-year drought are around 0.5 kg ha^{-1} yr^{-1} higher than expected from the 2013–2017 L–Q relationship.

3.3 Simulated internal nitrogen fluxes

The sub-catchment-specific N fluxes, simulated via mHM-SAS (with a good model fit for in-stream nitrate concentrations) and averaged over the years starting in May, are depicted in Fig. 4. They show that particularly in 2018, which was the driest year of the 2-year drought (Fig. 1b), N fluxes clearly differed from the long-term average (1997–2017). Notably, mineralization rates in 2018 increased by 39 %, 36 %, and 66 % in SH, MD, and HD, respectively. In the same

Table 1. Sub-catchment specific characteristics of the Selke catchment.

Sub-catchment characteristic	Unit	Upper Selke Silberhütte (SH)	Upper Selke Meisdorf (MD)	Lower Selke Hausneindorf (HD)
Area	(km^2)	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

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

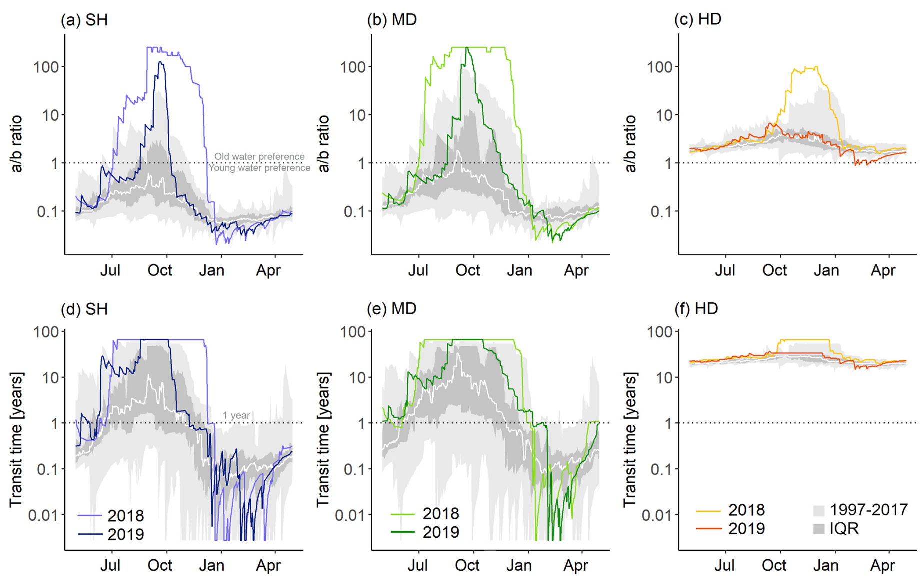

Figure 5. Simulated sub-catchment-specific water age selection preference **(a–c)** as the ratio of the fitted parameters a and b, and **(d–f)** median transit times are given in years. Grey areas indicate the range of all years previous to the drought (1997–2017, with a year starting in May), and their interquartile range and white lines are the median of all pre-drought years. Colored lines indicate the 2-year drought, with the 2 years starting in May 2018 and 2019.

year, 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 was relatively low in both cycles (2018 and 2019), especially in MD and HD, due to the dry soil moisture content (Fig. S1).

3.4 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 2-year drought compared to previous years, with clear contrasts between upper (SH and MD) and lower Selke (HD; Fig. 5). 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 42 and 56 d in SH and MD, previous to the drought and median of 23 and 39 d 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 7.0 years in SH and MD, respectively (Fig. 5d and e). Nevertheless, more than half of all years still showed a young water preference, even during

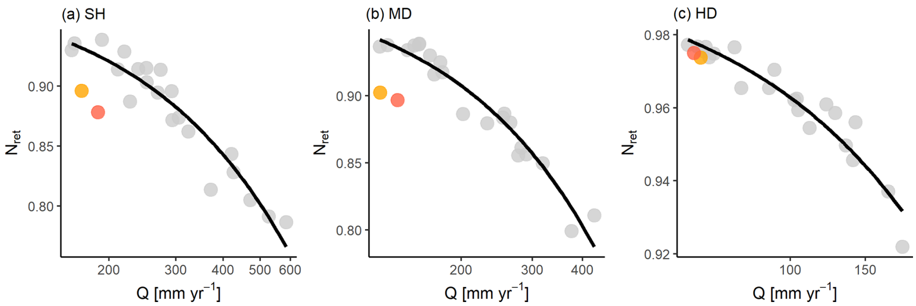

Figure 6. Relationship between the N retention capacity of catchments (N_{ret}) and log-scaled discharge (Q) at the nested catchment scale, given as annual averages (12-month period starting in May). Black lines represent the non-linear relationship between Nret and discharge (Q) prior to the 2-year drought (1997–2017), with log-transformed x axes.

dry periods (Fig. 5a and b). However, during the dry periods of the 2-year drought, median TTs were very long (median of median TTs was 66 years in both sub-catchments) with a pronounced old water preference, particularly in 2018. Note that the maximum TTs in the simulations are restricted to the number of years since the start of simulations plus the warm-up period, which explains the July–December plateau (Fig. 5). Long median TTs during the dry season can therefore be interpreted as >66 years. 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 years (1997–2017).

In the lower Selke sub-catchment (HD), there is a clear selection preference for old water throughout all years and periods (Fig. 3c). Even during wet periods, median TTs were relatively long (median 20 years) compared to the upper Selke sub-catchments (SH and MD; Fig. 5d–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 30 years compared to 24 years in previous years.

3.5 Catchment retention capacity

In all cases, the sub-catchments retained the largest part of N input (≥ 0.79). This was most pronounced in HD, where retention capacity was always ≥ 0.89 (note that these values account for the nested catchment). The fit of the N_{ret}–Q relationship (1997–2017) was high, with an R^2 of 0.90, 0.94, and 0.91 in SH, MD, and HD, respectively. In all sub-catchments, N_{ret} shows a clear decrease with decreasing annual discharge in all sub-catchments, which is steepest and most sensitive at low N_{ret} and high discharge (Fig. S3) and flattening towards low discharge conditions (Fig. 6). Similar patterns could also be observed for the N_{ret}–Q relationship with simulated nitrate leachates from the catchment soils. However, uncertainty for the simulated soil N retention is larger, due to uncertainty in the model parametrization (Fig. S4).

In the upper Selke (SH and MD), the N_{ret}–Q relationship during the 2-year drought (2018–2019) was clearly lower than that of previous cycles (1997–2017). N_{ret} dropped by around 0.04–0.05 compared to the long-term regression line, which can be translated into 1.8–2.8 $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ that are not retained but exported. In the lower part of the catchment (HD), N_{ret} was very close to the long-term regression line (difference of 0.002).

4 Discussion

4.1 Intra-annual variability of nitrate concentrations

The presented results show that the 2-year drought spanning the years 2018 and 2019 and across Central Europe had strong impacts on catchment water quality in terms of nitrate export. We found an increased intra-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). This shows that the drought did not only affect nitrate fluxes in the soil leachates, as discussed in the 2020 Nitrate Report from the Netherlands (RIVM, 2021), but it can also propagate through catchments affecting in-stream nitrate concentrations at the catchment outlet within a relatively short time. These results are in close agreement with previous studies that similarly reported low nitrate concentrations during a drought and high concentrations during subsequent rewetting (Górski et al., 2019; Loecke et al., 2017; Morecroft et al., 2000; Mosley, 2015). For example, Loecke et al. (2017) reported that the shift from very dry to wet conditions resulted in an increase in flow-weighted nitrate export compared to previous years, and Davis et al. (2014) suggested that the antecedent soil moisture conditions play an important role in the response of nitrate export during runoff events.

The shift in the C–Q relationship towards a steeper C–Q slope (Fig. 3a–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 intra-annual variability compared to that of discharge. This increased concentration variability indicates that biogeochemical and hydrological processes (e.g., runoff generation processes; Lange and Haensler, 2012) within the catchment changed during the drought, affecting the availability and transport of nitrate. The exceptionally low nitrate concentrations during the dry periods of the 2-year drought can be explained by the strong old water preference during these periods (Fig. 5a–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 relatively low nitrate concentrations. The pronounced old water preference in the upstream catchment during the 2-year drought is in agreement with a study by X. Yang et al. (2021). Using stable water 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 and 46 years) can be explained by the difference in the catchment area of around 2 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 and Weiler, 2014).

In the downstream sub-catchment, the potential for denitrification in groundwater is very low (Damköhler number < 1; Nguyen et al., 2022). Hannappel et al. (2018) looked at evidence for groundwater denitrification in the area of our study site and found such evidence only in the upstream but not in the downstream area, which can be explained by differences in the geology (Table 1) and a lack of electron donors in the aquifer which are needed for denitrification (Rivett et al., 2008). Therefore nitrate concentrations in the downstream sub-catchment do not significantly decrease with water ages and could, instead, still show signs of historically higher N inputs (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 instream uptake efficiency, mainly downstream, are responsible for the low nitrate concentrations during the dry periods of 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 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 higher accumulation of organic material during summer and the rewetting of dry soils in autumn can cause a peak in mineralization that transforms organic material into mobile inorganic N (Campbell and Biederbeck, 1982; Haynes, 1986), in agreement with the simulated high mineralization rates for 2018 (Fig. 4). 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 (Fig. 2). In contrast, in the downstream sub-catchment, old water fractions dominate all year round (Fig. 5f), 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 2-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 hydrometeorological seasonality over the study region (Sinha et al., 2016; J. Yang et al., 2018).

The changes in N cycling were only evident for the year starting in May 2018, not for the one starting in May 2019, which was dry but not as dry as in 2018 (Figs. 1b and 4). This indicates that the described perturbation in N cycling does only occur under severe drought conditions. In a small (0.6 km^2) 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 impacted nitrate export in subsequent years. One indication for this is that although the year 2018 was drier and had a stronger impact on soil N fluxes (Fig. 4), nitrate export dynamics for the year 2019 were comparable to the ones observed in 2018 (Fig. 3).

In comparison to other regions of the world, irrigation is not a common practice in the study area (EEA, 2018), but this might change in the future (Riediger et al., 2014). Crop irrigation would increase the soil moisture content and might therefore buffer drought impacts, such as the decrease in plant uptake and denitrification, and might lead to mobilization of nitrate, which would otherwise be retained in the upper soil until rewetting in autumn. As such, crop irrigation might counterbalance the reduction of N retention in the catchment soils and the accumulation of N during summer. However, irrigation would also increase the pressure on the available water resources and might enhance greenhouse gas emissions from agricultural soils (Sapkota et al., 2020)

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

The spatial configuration of land use and other characteristics within a catchment can play an important role in nitrate export from the entire catchment and its temporal variability (Casquin et al., 2021; Dupas et al., 2019; Winter et al., 2021). In the Selke catchment, considering the pronounced differences between the upstream and the downstream area is crucial to understand the integrated signal of nitrate export at the catchment outlet (Winter et al., 2021). Previous studies showed that the forested 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 2-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 comparably 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 $> 1\,\mathrm{mg\,L^{-1}}$ 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 (Figs. 1c and 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). In contrast, thick sedimentary aquifers, flat topography, and very sparse tile drainage in the downstream area favor long TTs and a preference for old water (Winter et al., 2021).

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 2-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. (2022) could show in a German floodplain forest that the drought impact on trees was even stronger in 2019 due to an accumulated drought effect. 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). Therefore, forest dieback should be considered as an additional drought-induced threat to stream water quality that might impact nitrate concentrations in the future.

4.3 Exported nitrate loads and catchment retention capacity

The overall discharge during the 2-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 73 % 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 2-year drought (November–April, Fig. 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. The long-term L–Q relationship and the N_{ret}–Q relationship showed good fits for the pre-drought year, indicating a strong discharge control. Scatter in these relationships might have been induced by other factors, such as temperature, controlling biogeochemical processes, and N availability (Nogueira et al., 2021) or specific runoff event characteristics (Winter et al., 2022). With climate change, temperature and other associated factors as well as runoff event characteristics were not stable between 1997 and 2017 (Fig. 1b; IPCC, 2018; Winter et al., 2022). Nevertheless, none of these years has shown a deviation from the L–Q relationship comparable to that in 2018 and 2019. This indicates that the 2-year drought considerably altered catchment functioning, whereas the overall L–Q relationship can be considered relatively stable over previous years.

We identified two drivers of a decrease in N_{ret}, i.e., an increase in discharge and the 2-year drought (Fig. 7). The discharge-driven decrease in the N_{ret} 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 hydro-meteorological events, such as the 2018–2019 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, also for other years with very low discharge (Figs. 6 and 7). Until the end of the data record available for this study, no recovery from this loss in N_{ret} in

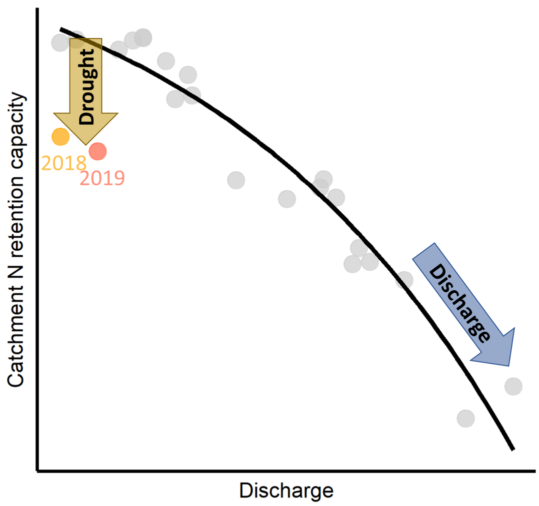

Figure 7. Conceptual framework of the capacity of a catchment to retain N in relation to average discharge. The framework illustrates two potential drivers that cause a reduction in the catchment retention capacity. Those are either an increase in discharge (blue arrow) or a drought event (yellow arrow). Data were 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.

the upstream catchment area could be observed, but 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 a loss in catchment N retention capacity after the 2-year drought, remains uncertain.

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 retention capacity can be explained by different sub-catchment-specific TTs. Whereas predominantly short 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 and Basu, 2015), especially under the assumption of low denitrification potential in groundwater (Nguyen et al., 2022). One indication is high nitrate concentrations in 2019 and 2020 in a groundwater observation well in the lower Selke catchment (Fig. S6). Moreover, Jutglar et al. (2021) reported immediate and delayed drought responses in the form of increasing nitrate concentrations in the groundwater in Southwest Germany after the drought in 2003. Besides such first evidence, estimating the potential biogeochemical and hydrological nitrogen legacies induced by severe drought will be a task for future research.

5 Conclusion

The presented study is among the first to assess the impact of the 2018–2019 drought in Central Europe on nitrate concentrations in a heterogeneous 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 intra-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 increased intra-annual variability was not only driven by a stronger temporal shift in N transport but also by a decrease in N uptake by plants and removal via denitrification 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 loads expected from the long-term L–Q relationship. We identified two drivers for a decrease in the catchment 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 TTs 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.

Code and data availability. The source code and input data for mHM-SAS are available at https://doi.org/10.5281/zenodo.7228149 (Nguyen, 2022). The source code for mHM-nitrate (X. Yang et al., 2018), on which mHM-SAS is built up upon, is available at https://git.ufz.de/yangx/mHM-Nitrate (Yang, 2023). The raw discharge data can be downloaded from the State Office of Flood Protection and Water Quality of Saxony Anhalt (LH) at https://gld.lhw-sachsen-anhalt.de/ (LHW, 2021). The raw meteorological data can be downloaded from Germany's National Meteorological Service (DWD) at https://opendata.dwd.de/climate_environment/CDC/grids_germany/daily/ (DWD, 2021), and gridded products based on Zink et al. (2017). Raw nitrate-N concentration data are archived in the TERENO database, available upon request through the TERENO-Portal (https://ddp.tereno.net/ddp; TERENO, 2021).

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Competing interests. At least one of the (co-)authors is a member of the editorial board of *Hydrology and Earth System Sciences*. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

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Supplement of

Droughts can reduce the nitrogen retention capacity of catchments

Carolin Winter et al.

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Text S1

Mechanistic process-based modeling with Storage Selection Functions

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

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

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

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

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

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

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

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

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

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

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

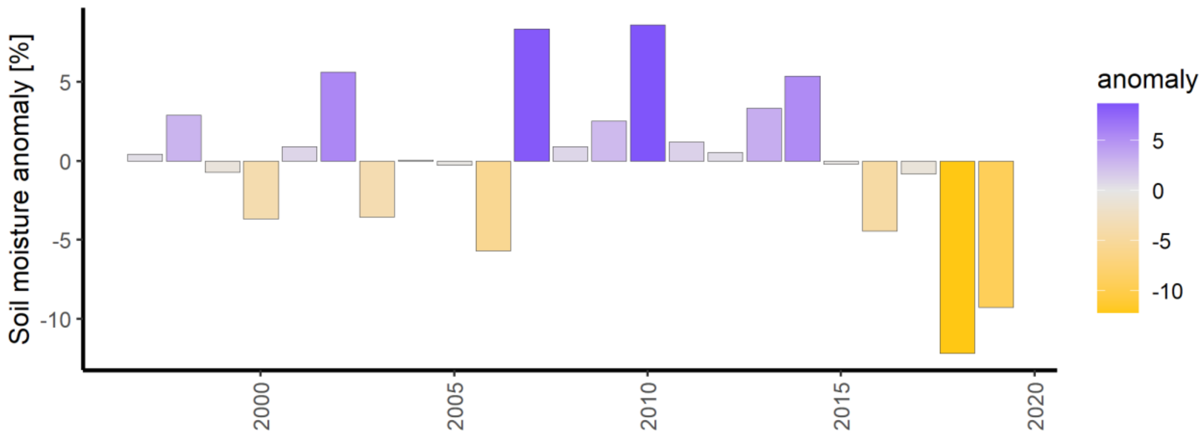

Figure S1 Soil moisture anomalies for the years (12-month period starting in May) from 1997 to 2019. Anomaly is shown as the difference between average soil saturation [%] for a specific year to the long-term mean.

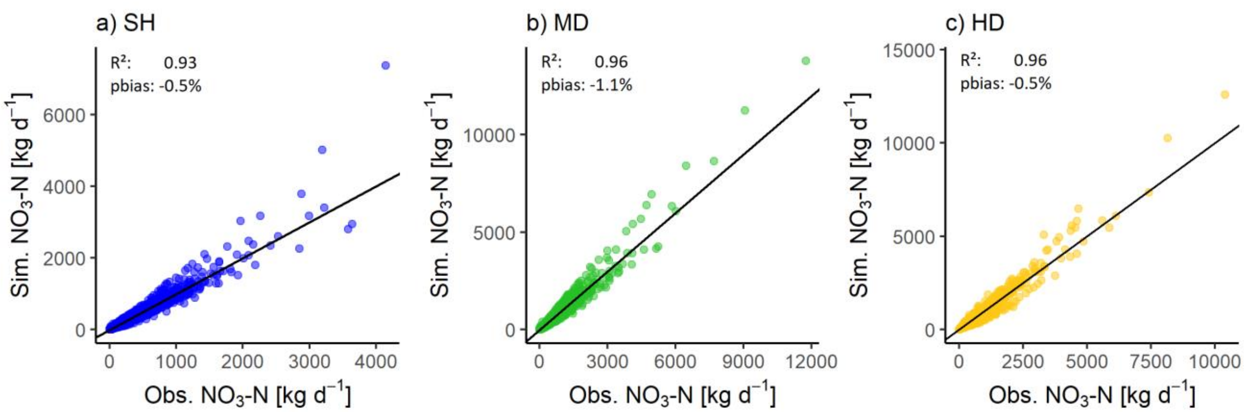

Figure S2 Observed versus simulated daily nitrate-N loads for the three sub-catchments of the Selke catchment (a-c). Observed nitrate-N loads refer to loads that were calculated from observed nitrate-N concentrations (daily averages of sensor measurements) and daily averages of observed discharge. Simulated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

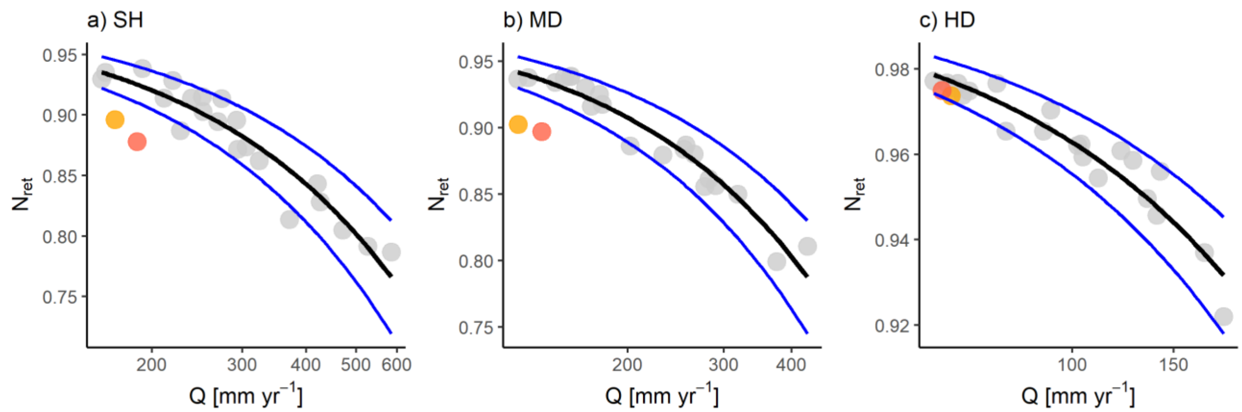

Figure S3 Relationship between the N retention capacity of catchments (N_{ret}) and log-scaled discharge (Q) at the nested catchment scale, given as annual averages (12-month period starting in May). Grey dots show the annual averages prior to the two-year drought (1997-2017); yellow and red dots show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

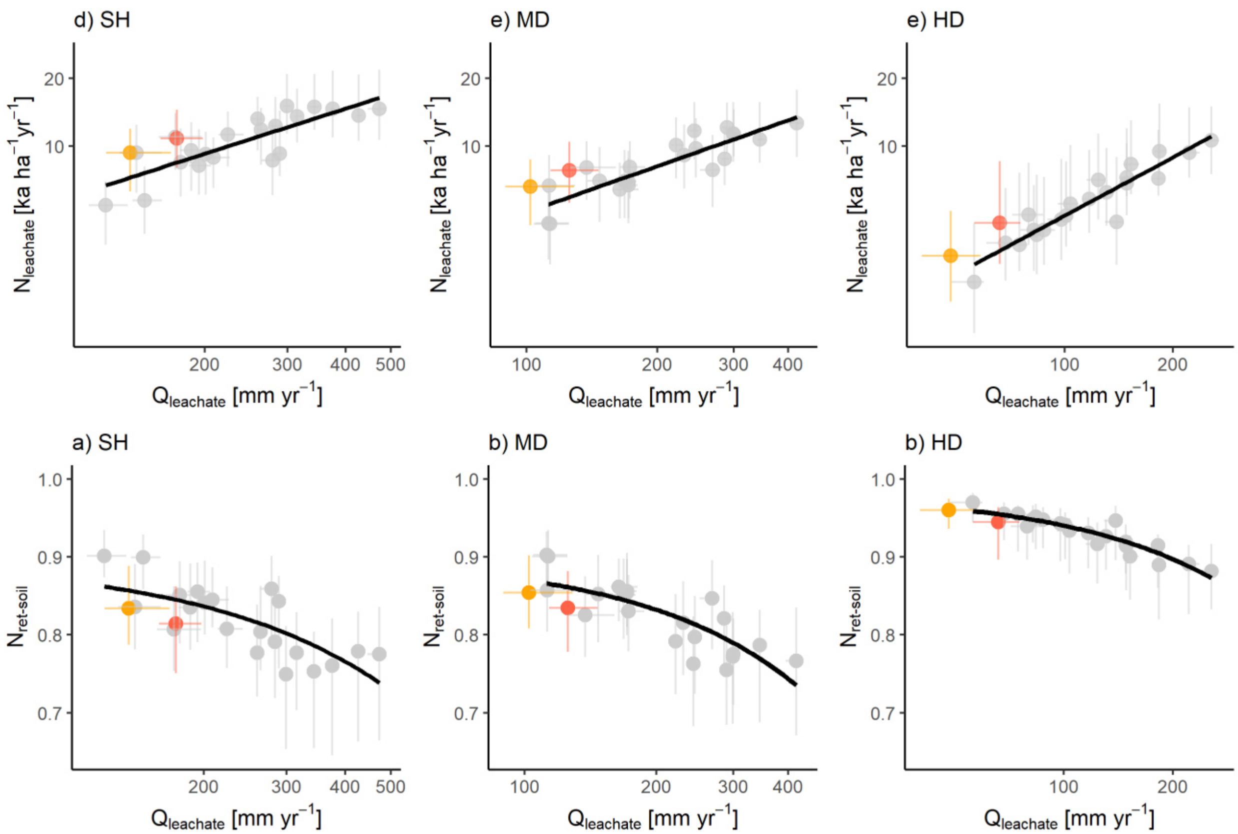

Figure S4 Long-term load-discharge (L-Q) relationship and the N retention capacity ($N_{ret\text{-}soil}$) calculated from annual (12-month period starting in May) averages of simulated soil leachate ($Q_{leachate}$) and nitrate-N loads in the soil leachates ($N_{leachate}$). Grey dots depict the annual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

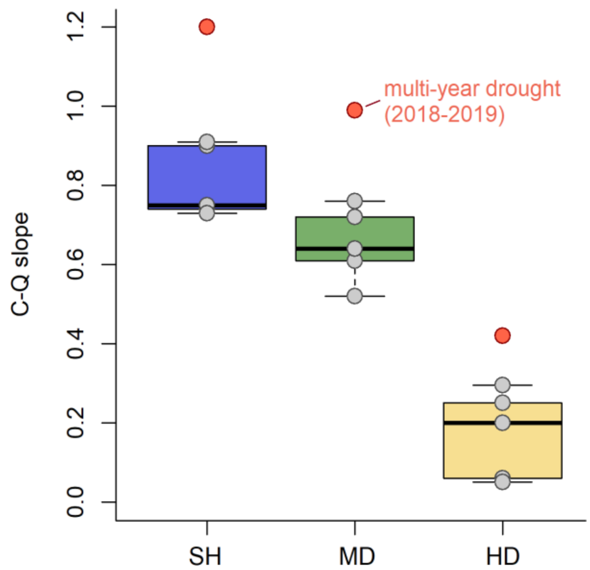

Figure S5 Block sampled concentration-discharge (C-Q) slopes (exponent of the power law relationship between C and Q) across all possible combinations of two consecutive years (12-month period starting in May) between 2012 and 2017 for the three sub-catchment of the Selke catchment (SH, MD, and HD from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

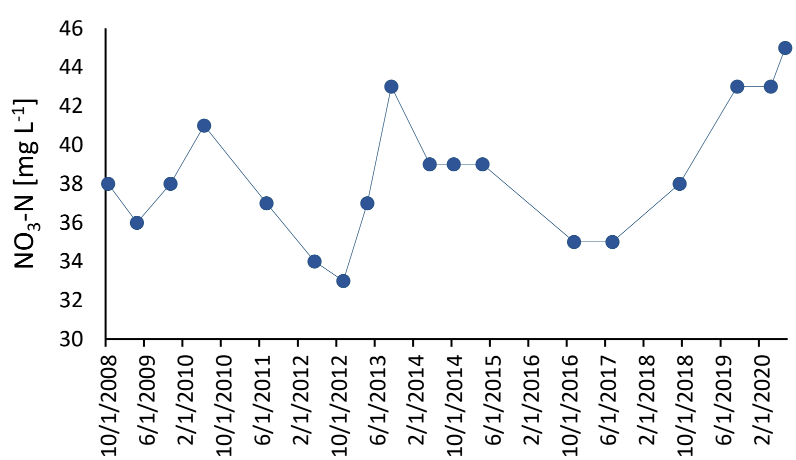

Figure S6 Groundwater observation well in Wilsleben (lower Selke catchment). Data provided by the State Office of Flood Protection and Water Quality of Saxony-Anhalt (LHW).

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Study 3:

Explaining the Variability in High-Frequency Nitrate Export Patterns Using Long-Term Hydrological Event Classification

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- Data acquisition 10%
- Data analyses 75%
- Figures 100%
- Discussion of results 85%
- Manuscript writing 85%

The study was designed by CW, LT, SL, and AM. High-frequency data was provided by MR, Karsten Rinke (KR), Xiangzhen Kong (XK), and Kurt Friese (KF). The LHW and the DWD provided long-term hydro-meteorological data. LT and RK provided model products. CW and LT performed the analyses, and CW created all figures and tables. CW wrote the manuscript. All co-authors revised the manuscript.

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Key Points:

- Runoff event classification allowed us to identify dominant drivers of event-scale nitrate export that are transferable to other catchments
- Low-magnitude events with low antecedent wetness exported low nitrate concentrations with highly variable concentration-discharge relationships
- High-magnitude events with high antecedent wetness exported high nitrate concentrations with chemostatic patterns across all catchments

Supporting Information:

Supporting Information may be found in the online version of this article.

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Explaining the Variability in High-Frequency Nitrate Export Patterns Using Long-Term Hydrological Event Classification

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Abstract Runoff events play an important role in nitrate export from catchments, but the variability of export patterns between events and catchments is high and the dominant drivers remain difficult to disentangle. Here, we rigorously asses if detailed knowledge on runoff event characteristics can help to explain this variability. To this end, we conducted a long-term (1955–2018) event classification using hydro-meteorological data, including rainfall characteristics, soil moisture and snowmelt, in six neighboring mesoscale catchments with contrasting land use. We related these event characteristics to nitrate export patterns from high-frequency nitrate concentration monitoring (2013–2017) using concentration-discharge (CQ) relationships. Our results show that low-magnitude rainfall-induced events with dry antecedent conditions exported lowest nitrate concentrations and loads but exhibited highly variable CQ relationships. We explain this by a low fraction of active flow paths, revealing the spatial heterogeneity of nitrate sources within the catchments and by an increased impact of biogeochemical retention processes. In contrast, high-magnitude rainfall or snowmelt-induced events exported highest nitrate concentrations and loads and converged to similar chemostatic export patterns across all catchments, without exhibiting source limitation. We explain these homogeneous export patterns by high catchment wetness that activated a high number of flow paths and by higher nitrate availability during high-flow seasons. Long-term hydro-meteorological data indicated an increased number of events with dry antecedent conditions in summer and a decreased number of snow-influenced events. These trends will likely continue and cause increased nitrate concentration variability during low-flow seasons and changes in the timing of nitrate export peaks during high-flow seasons.

Plain Language Summary Runoff events play an important role in nitrate export from catchments. However, the response of nitrate export to runoff events is highly variable and therefore difficult to understand. Here, we classified runoff events according to their inducing precipitation and antecedent soil moisture and related those event characteristics to nitrate export patterns. Our results show that small summer and autumn events exported lowest nitrate concentrations and loads with highly variable patterns, such as increasing or decreasing nitrate concentrations. We explain this variability with nitrate mobilization being restricted to near-stream areas with variable nitrate availability and by an increased impact of biogeochemical nitrate retention. In contrast, larger winter and spring events exported highest nitrate concentrations and loads. These events showed only a small increase of nitrate concentrations compared to discharge, so that discharge dominated overall nitrate loads. This was similar in all catchments, which we explain by high catchment wetness connecting all nitrate sources within a catchment to the stream and higher nitrate availability. Long-term trends indicate a decrease of summer soil moisture and a decrease of snow-influenced events. These trends might cause increasing variability in nitrate concentrations during summer and change the timing of nitrate export peaks during winter and spring.

1. Introduction

High riverine nitrate concentrations and loads from diffuse agricultural sources threaten drinking water quality and the health of freshwater as well as marine ecosystems (Carpenter et al., 1998; Elser, 2011; Mekonnen & Hoekstra, 2020). In this context, runoff events play a dominant role for the mobilization and transport of nitrate from catchments to the downstream receiving water resources (Blaen et al., 2017; Inamdar et al., 2006; Ockenden et al., 2016). Climate change is predicted to change the frequency and characteristics of such runoff events, and

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these changes are in turn predicted to significantly alter water quality and nutrient export (IPCC, 2018; Marshall & Randhir, 2008; Sebestyen et al., 2009; Trang et al., 2017; Wagena et al., 2018). Therefore, an in-depth understanding of nitrate mobilization and transport during runoff events under different hydro-meteorological conditions is needed to better predict and mitigate water quality deteriorations.

Hydro-meteorological data at a high temporal resolution (i.e., daily) has been readily available for many decades and allows for a robust characterization of catchment hydrologic functioning during runoff events on the long term (Kirchner et al., 2004; Tarasova et al., 2020). Those characterizations showed that with different antecedent wetness conditions, different flow paths within a catchment can become activated that connect different catchment areas with the stream network (Jencso et al., 2009). For dry antecedent conditions, typically only a smaller fraction of the catchment area is connected to the stream network, often via deeper subsurface flow paths, which deliver older water with longer transit times. In contrast, during wet antecedent conditions, additional shallower and faster flow paths become activated and transport younger water (i.e., with shorter transit times) also from more distant locations to the stream (Jencso et al., 2009; Kumar et al., 2020; J. Yang, Heidbüchel, et al., 2018). Moreover, in a temperate climate, runoff events can be generated by precipitation events of different nature, such as rainfall or snowmelt (Tarasova et al., 2020). In such climates, rain-on-snow events (i.e., snowmelt in concurrence with rainfall and high antecedent soil moisture) often form the largest runoff events of the year and can activate all or most of the available flow paths within a catchment (Berghuijs et al., 2019; Jencso et al., 2009; Stieglitz et al., 2003).

It is most likely that the spatiotemporal variability in the hydrological land-to-stream connectivity causes different responses in nutrient mobilization and transport as well (Stieglitz et al., 2003). With the advent of high-frequency measurements for nitrate and other nutrient concentrations (Kirchner et al., 2004; Rode, Wade, et al., 2016), we can now measure water quality at the same temporal resolution as water quantity to analyze in detail the connection of runoff event characteristics with nitrate export patterns. More specifically, we refer to runoff event characteristics as all related hydro-meteorological characteristics including antecedent conditions, the characteristics of the inducing precipitation event and the characteristics of the runoff event hydrograph (for example peak discharge). This also includes the proposed different runoff formation processes (Tarasova et al., 2020) that can potentially connect different sources of nitrate to the stream network. For example, from available hydroclimatic data, we can now distinguish events that are induced by rain-on-snow under wet antecedent conditions and low-magnitude rain-induced events with dry antecedent conditions (Tarasova et al., 2020). Note, that for the sake of consistency in the use of terms with previous studies (i.e., Musolff et al., 2015, 2021; Tarasova et al., 2020), we use the terms "discharge" and "runoff" synonymously, referring to the total volumetric water flow rate in the stream at a gauging point.

Several studies took advantage of high-frequency measurements and conducted a detailed analysis on nutrient mobilization and transport during runoff events and generally confirmed the importance of runoff events for nutrient export (e.g., Blaen et al., 2017; Burns et al., 2019; Fovet et al., 2018; Knapp et al., 2020; Rose et al., 2018). For example, Casson et al. (2010) and Pellerin et al. (2012) showed that high-magnitude rain-on-snow events can account for a disproportional amount of annually exported nitrate loads. These studies also revealed large inter-event and inter-catchment variability of nutrient export dynamics. For example, Blaen et al. (2017) found a positive correlation between antecedent wetness and event nitrate concentrations in a catchment with mixed agricultural and forested land use. On the contrary, Knapp et al. (2020) found a negative correlation between antecedent wetness and event nitrate concentrations in a small mountainous catchment that is covered by forest and meadows. While both studies could explain parts of their findings by changes in the hydrological catchment connectivity, their differences might mainly be caused by different nitrate source availabilities, induced by different catchment characteristics such as land use. Knapp et al. (2020) summarized that the variability of event responses was driven by changes in source availability, hydrological connectivity, and biogeochemical reaction rates. The role of temperature- and soil-moisture-driven differences in biogeochemical reaction rates for nitrate export was also stressed by Lutz et al. (2020) and Rode, Angelstein et al. (2016). Both, hydrological connectivity and biogeochemical removal (or retention) are driven by environmental conditions and thus often have a similar seasonal timing in temperate climates. In consequence, connectivity and removal can be difficult to disentangle. For example, rain-on-snow events with a high hydrological connectivity typically occur in colder periods of lower ecosystem nitrate uptake and hence a higher nitrate availability. All these examples show that nitrate export patterns can be potentially related to hydrological event characteristics, such as the contribution of meltwater or antecedent conditions as well as to biogeochemically controlled source availability. The response of nitrate export to runoff events is obviously highly variable between catchments of different configurations for example, with regard to land use and nitrate availability. Therefore, we see a need for larger-scale studies that analyze the connection of event characteristics and nitrate export patterns across the entire annual cycle and in contrasting catchments.

A common tool to reveal the relevant sources and flow paths for nitrate transport under changing hydrological conditions are concentration-discharge (CQ) relationships, which represent the directional relationship between concentrations and discharge (e.g., Bieroza et al., 2018; Bowes et al., 2015; Musolff et al., 2021; Vaughan et al., 2017). A negative slope of the CQ relationship can indicate high base flow concentrations that are diluted by water from newly activated flow paths (Bowes et al., 2015) or a depletion of nutrient sources (Vaughan et al., 2017). A positive CQ slope can indicate the additional activation of more shallow and younger (Musolff et al., 2015) or more distant nutrient source zones (Bowes et al., 2015). A chemostatic pattern is instead described by a CQ slope close to zero (Godsey et al., 2009; Musolff et al., 2015; Thompson et al., 2011) and is mainly attributed to ubiquitous and uniformly distributed N sources in agricultural catchments (Basu et al., 2010). The CQ slope is not necessarily consistent across time scales and can thus reveal complementary information on nutrient export during single runoff events compared to CQ relationships across seasons that integrate several events (e.g., Godsey et al., 2019; Knapp et al., 2020; Minaudo et al., 2019; Musolff et al., 2021).

Yet, a rigorous assessment of how much of the inter-event variability of nutrient export patterns can be explained by a more thorough understanding of runoff event characteristics and classifications of runoff formation processes is still missing and has not yet been applied across a range of hydro-climatic conditions and land use settings (Knapp et al., 2020; Tarasova et al., 2020). Studies that relate hydrological runoff events with nutrient transport are typically limited to single catchments and/or to relatively short time periods, which is often not more than one or two years, frequently excluding the cold seasons (e.g., Blaen et al., 2017; Carey et al., 2014; Knapp et al., 2020). Therefore, the full range of runoff event characteristics is not always covered and it remains unclear if analyzed event characteristics are representative across catchments and for the long-term catchment behavior. Moreover, it is largely unknown if runoff event characteristics are changing over longer time scales. In this study, we conduct an extensive assessment across catchments and time scales to explore to what extent runoff event characteristics and runoff formation processes govern nitrate export during and across runoff events. To this end, we related event characteristics such as the wetness state of a catchment, the nature of an inducing precipitation event and the temporal distribution of rainfall to nitrate concentrations and loads. For this, we used a 5-yr period of high-frequency water quality and hydro-meteorological data from six mesoscale Central European catchments with different land use settings. We classified runoff events according to their different hydro-meteorological conditions (Tarasova et al., 2020) and utilized CQ relationships to infer the relevant flow paths and source areas for nitrate transport and mobilization. We then combined the findings from such analysis with the changes in event characteristics and catchment state conditions over past decades obtained from long-term daily hydro-meteorological time-series to identify possible trends in the long-term runoff event characteristics that could impact nitrate export dynamics in the future.

2. Materials and Methods

2.1. Study Area

Event characteristics and nitrate export patterns were analyzed in six sub-catchments of the Bode River catchment (Figure 1), which is an intensively monitored catchment within the network of the TERrestrial Environmental Observatories (TERENO, Wollschläger et al., 2017). Warme Bode (WB), Rappbode (RB) and Hassel (HS) are part of the Rappbode Reservoir Observatory (Rinke et al., 2013), whereas Silberhütte (SH), Meisdorf (MD) and Hausneindorf (HD) are three subsequent gauging stations of the nested Selke River catchment. All six catchments are located in the Harz Mountains and the Harz foreland in Saxony-Anhalt, Germany (Figure 1). They have contrasting characteristics in regard to their size, land use, elevation, and mean annual precipitation (Table 1).

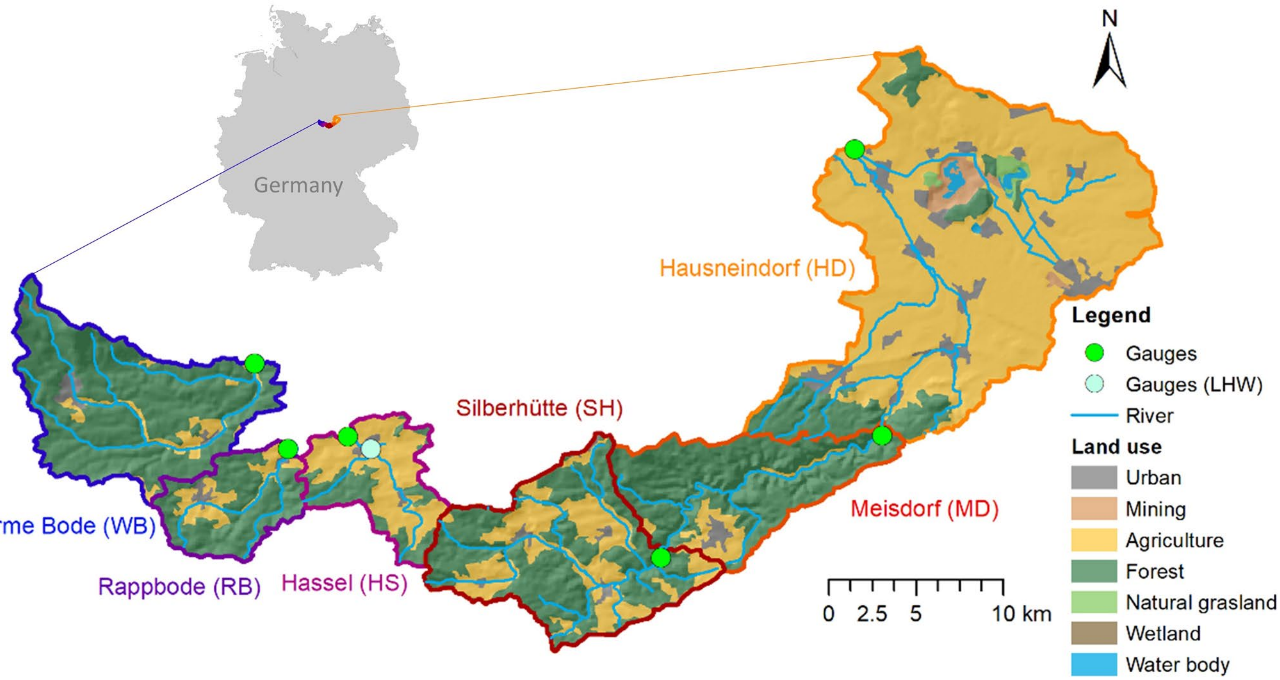

Figure 1. Map of the study site, showing all six mesoscale catchments (WB, RB, HS, SH, MD, and HD) with their respective land use.

2.2. Data

2.2.1. Long-Term Daily Data

We used long-term daily hydro-meteorological data (Figures S1–S6 in Supporting Information S1) to classify runoff events and to analyze potential trends in the characterization of runoff events. Daily discharge data was provided by the State Office of Flood Protection and Water Management of Saxony-Anhalt (LHW) and calculated to specific discharge [mm d^{-1}]. In all catchments except HS and HD, discharge data is available from 1955 until 2018. In HS and HD, discharge data records started in 1968 and 1980, respectively, and lasted until 2018. Daily precipitation data over these time periods were provided by Germany's National Meteorological Service (Deutscher Wetterdienst, DWD) as interpolated station data at a spatial resolution of 1 km^2 (REGNIE; Rauthe et al., 2013). Daily average temperatures were interpolated to a 4 km grid from the DWD stations by External Drift Kriging using elevation as an explanatory variable (Zink et al., 2017). Daily soil moisture and snow water equivalent were calculated using the mesoscale Hydrological Model (mHM, Kumar et al., 2013; Samaniego et al., 2010; Zink et al., 2017).

Table 1
Characteristics of the Six Studied Mesoscale Catchments Within the Bode River Catchment

	Area	Mean annual precipitation	Mean annual temperature	Land use and land cover: Agriculture	Forest	Urban	Other	Elevation range	Mean slope
Catchment	[km^2]	[mm yr^{-1}]	[°C]	[%]	[%]	[%]	[%]	[m.a.s.l.]	[%]
WB	101.1	1,111.9	6.6	5.9	90.2	2.9	1.0	429–957	7.7
RB	39.1	969.3	7.1	19.5	74.7	4.1	1.7	454–636	6.8
HS	42.0	820.9	7.0	59.8	35.6	4.5	0.1	436–604	4.8
SH	102.5	726.6	6.7	34.6	62.2	3.2	0.0	335–597	6.9
MD	178.6	693.0	7.2	23.2	73.6	3.1	0.1	196–597	8.4
HD	460.1	589.4	8.1	54.8	36.7	6.1	2.4	68–597	4.9

2.2.2. High-Frequency Hourly Data

High-frequency hourly data were used to analyze exported nitrate loads and CQ relationships within and between runoff events from 2013 to 2017. Discharge data at a temporal resolution of 15 min were provided by the LHW, which we aggregated to hourly values [mm h^{-1}]. Similar to nitrate concentration data (see below), a moving average was applied over a 5-hr window to reduce noise in the raw data and to stay consistent with the procedure applied in previous studies that used parts of the same data (e.g., Musolff et al., 2021; Rode, Angelstein, et al., 2016). Hourly precipitation data as reprocessed radar data were provided by the DWD with precipitation amounts adjusted to station observations and a spatial resolution of 1 km^2 (RADOLAN; Winterrath et al., 2017). Due to a lack of hourly temperature data, we reconstructed those from the daily data by using hourly weights based on month-specific sine functions obtained from long-term minimum and maximum temperatures to resemble the diurnal cycle of temperature. Hourly snow water equivalent and soil moisture data were simulated using mHM (Zink et al., 2017).

Nitrate concentration data were collected between 2013 and 2017 via TRIOS ProPS-UV sensors at 15 min intervals (Kong et al., 2019; Rode, Angelstein, et al., 2016), which we aggregated to hourly averages. Data from the WB catchment were previously published by Kong et al. (2019) and Musolff et al. (2021), data from the three Selke catchments (SH, MD, and HD) were previously published by Musolff et al. (2021), Rode, Angelstein, et al. (2016), Winter et al. (2021), and X. Yang, Jomaa, et al. (2018). For the processing of the nitrate concentration data, we refer to the references above and to our Supporting Information (Text S1 in Supporting Information S1). Briefly, raw data was restricted to a realistic range (0–100 mg N L^{-1}), outliers were removed (Grubbs, 1950), a moving average was applied over a 5-hr window to smooth the data and concentrations were calibrated against grab samples analyzed in the lab (R^2 0.80–0.91, Figures S7 and S8 in Supporting Information S1). Note that the LHW gauging station at HS, where long-term and high-frequency discharge data were measured, is located upstream of the measurement point for concentration data, thus delineating a catchment size of around 29 km^2 for discharge data compared to 42 km^2 for measured concentration data (Figure 1, Table 1). Nevertheless, area-specific discharge data [mm h^{-1}] from upstream and downstream measurement points (available downstream between 2013 and 2014) showed a good agreement in their temporal dynamics with a R^2 of 0.88 and in absolute values with a small percentage bias of −3.0% (Figure S9 in Supporting Information S1). We thus found area-specific discharge from the upstream station data to be suitable for further analysis at the downstream station.

2.3. Runoff Event Identification and Classification

Runoff events were separated and classified using the recently developed approach by Tarasova et al. (2018, 2020), which allows for an automated separation and classification of runoff events. The approach is explained in detail in the cited studies and is, therefore, only briefly described here. As a first step, events from daily long-term and high-frequency data were identified using an automated event separation approach from Tarasova et al. (2018). Then, we adopted the event classification framework from Tarasova et al. (2020), developed for daily data resolution (Figure 2). Each runoff event was classified by the characteristics of the inducing precipitation event (Figure 2a, Layer 1) and the pre-event wetness state of the catchment (Figure 2a, Layer 2). The nature of precipitation events was identified by the ratio of meltwater volume (M_{vol}) and total precipitation volume (i.e., sum of rainfall and snowmelt, P_{vol}). Using a threshold of $M_{vol}/P_{vol} = 0.05$ (Figure 2a), events were classified as *Rain* or *Snow*-influenced events. The temporal distribution of precipitation was characterized by means of the temporal coefficient of variation of the precipitation rate (CV_{temp}) and by the ratio between the maximum precipitation rate during an event and precipitation volume (P_{max}/P_{vol}). Events with a $CV_{temp} > 1$ and $P_{max}/P_{vol} > 0.5$ were defined as *intensity-dominated* and all other events as *volume-dominated* (Figure 2a). Third, the wetness state of a catchment was characterized by means of antecedent soil moisture (SM_{ant}). Using a threshold of maximum κ, with κ representing the catchment-specific curvature of the nonlinear relationship between event runoff coefficients and soil moisture (Tarasova et al., 2020), events were classified as *Wet* or *Dry* events (Figure 2a). In total, this classification resulted in five event classes (Figure 2b): (a) snow-influenced events (*Snow*), (b) rain-induced events that were *volume-dominated* and occurred under wet antecedent soil moisture conditions (*Rain-Wet-Vol*), (c) rain-induced events that occurred under wet antecedent conditions and were *intensity dominated* (*Rain-Wet-Int*), (d) rain-induced events that occurred under dry antecedent conditions and were *volume-dominated* (*Rain-Dry-Vol*) and (e) rain-induced events that occurred under dry antecedent conditions and were *intensity dominated*

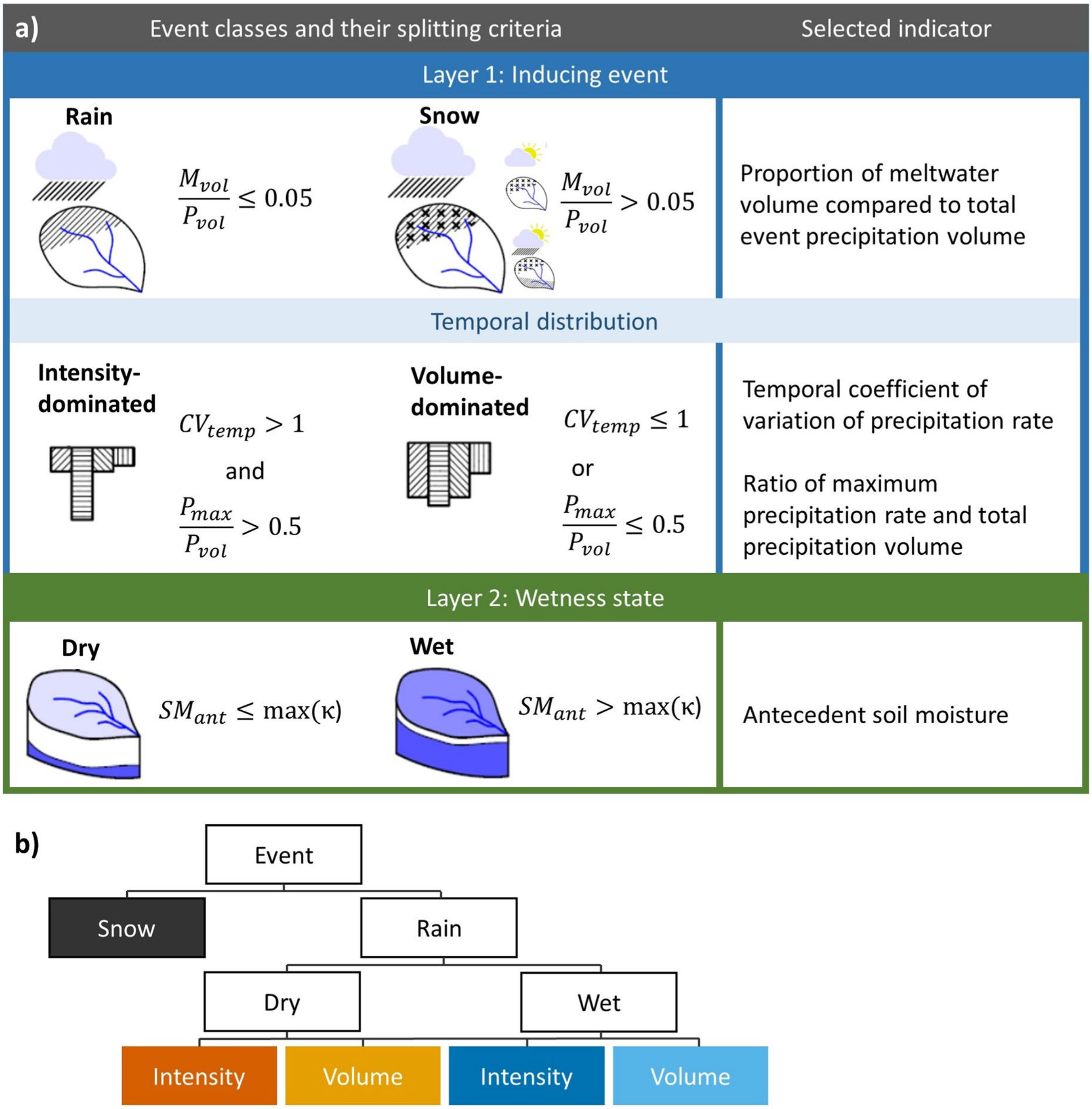

Figure 2. (a) Event characteristics and thresholds for the classification of events. Threshold for the wetness state of the catchments is defined by the maximum of κ, which represents the catchment-specific curvature of the nonlinear relationship between event runoff coefficients and soil moisture. (b) The resulting event classes. Modified from Tarasova et al. (2020, CC BY 4.0).

(*Rain-Dry-Int*). To assure comparability of event classes between two data sets of different resolutions, we classified events using the daily time series (1955–2018) and then assigned the respective classes to the corresponding events from the hourly time series (2013–2017).

2.4. Long-Term Trends in Event Characteristics

We used the non-parametric Mann-Kendall test (Kendall, 1998; Mann, 1945) to detect monotonic trends in the continuous event characteristics and event classes with a significance level of 5%. We considered the following continuous event characteristics: (a) antecedent soil moisture (SM_{ant}), (b) the ratio of meltwater volume and precipitation volume (M_{vol}/P_{vol}), and (c) the ratio of maximum precipitation and precipitation volume (P_{max}/P_{vol}), which is an indicator for *intensity*- or *volume-dominated* events, respectively (Figure 2a). To reduce inter-event variability between those characteristics, we calculated seasonal averages for each year and analyzed these for seasonal long-term trends. Similarly, we analyzed seasonal trends in the annual contribution and total number of (a) *Snow* events (vs. *Rain* events), (b) *Rain-Dry* (vs. *Rain-Wet*) events, and (c) *Intensity-dominated* (vs. *Volume-dominated*) events.

2.5. Nitrate Export

2.5.1. Descriptors of Nitrate Export

To characterize nitrate transport from the high-frequency data, we chose four descriptors for the event scale: (a) median nitrate concentration (C_{med} in mg N L^{-1}), (b) average loads per event in kg N ha^{-1} yr^{-1} (this unit was chosen for a better comparison between catchments and events of different duration), (c) inter-event CQ slopes and (d) event-specific CQ slopes. Event-specific CQ slopes were assessed by fitting the parameter b from the following power-law relationship after Godsey et al. (2009) and Musolff et al. (2015) to the data of the individual events:

$$C(t) = aQ(t)^b \tag{1}$$

where $C(t)$ represents the time series of nitrate concentrations during a specific event in mg N L^{-1}, $Q(t)$ represents the time series of discharge in mm h^{-1}, and a and b represent the intercept and linear slope of the CQ relationship in the log-log space. A parameter $b < 0$ describes a negative CQ slope, that is, decreasing concentrations with increasing discharge and therefore a dilution pattern. A parameter $b > 0$ describes a positive CQ slope, that is, increasing concentrations with increasing discharge and therefore an accretion pattern. Both scenarios are accounted for as chemodynamic patterns (Godsey et al., 2009; Musolff et al., 2015, 2017). If parameter b is close to zero, there is no clear directional relationship. This pattern can be described as chemostatic under the assumption that the coefficient of variation of concentrations is much smaller than that of discharge (Godsey et al., 2009; Musolff et al., 2015, 2017). Similar to the event-specific CQ slope, we analyzed the CQ relationship across all events within each catchment (i.e., the inter-event CQ slope) using the power law model from Equation 1 with C_{med} and Q_{med} of each event instead of $C(t)$ and $Q(t)$ within each specific event.

2.5.2. Statistical Analysis

All computations and statistical analyses were conducted in R (R Core Team, 2020). We used the non-parametric Kruskal-Wallis test (Kruskal & Wallis, 1952) to test for differences in loads, C_{med}, Q_{med} and the CQ slope between event classes and the Pairwise Wilcoxon Test (Wilcoxon, 1945) with Holms correction for multiple comparisons (Holm, 1979) to test for differences in-between the event classes, both at the significance level of 5%. In order to test the impact of event classes on the inter-event CQ slope, we tested the simple linear ln(C_{med})-ln(Q_{med}) regression against a linear regression model that includes event classes and their interactions with ln(Q_{med}). Both models were compared via the sample-size corrected Akaike Information Criterion (AICc; Akaike, 1973; Hurvich & Tsai, 1989; Sugiura, 1978). If accounting for event classes led to a substantial improvement (i.e., AICc decreased at least by 2, similar to Marinos et al., 2020) their impact was regarded as considerable. Otherwise, the added value from event classes compared to a simple CQ model was negligible for nitrate export estimations.

3. Results

3.1. Long-Term and High-Frequency Runoff Event Characteristics

In total, we identified and classified 5,872 events over the long-term period (on average 14.5–19.0 events per catchment and year) and 388 events over the high-frequency time period (on average 9.6–16.2 events per catchment and year). Event classes generally differed more strongly between seasons than between catchments (Figure 3). In both long-term and high-frequency event classes, winter (December–February) was dominated by *Snow* and *Rain-Wet-Vol* events. Spring (March–May) showed the most even distribution of event classes and was the season with the highest percentage of *Rain-Wet-Vol* and *Rain-Wet-Int* events. Summer (June–August) and autumn (September–November) were dominated by *Rain-Dry-Vol* events and *Rain-Dry-Int* events. Differences between catchments reflect a decreasing percentage of *Snow* events and an increasing percentage of *Rain-Dry-Vol* and *Rain-Dry-Int* events from west to east (WB to HD catchment; Figure 3). Across all seasons of the long-term event classes, more than half of all events in the six catchments were classified as *Rain-Dry* events (from 51.2% in WB to 61.9% in HD). Around a fifth up to a quarter of all observed events were classified as *Snow* events (from 17.7%

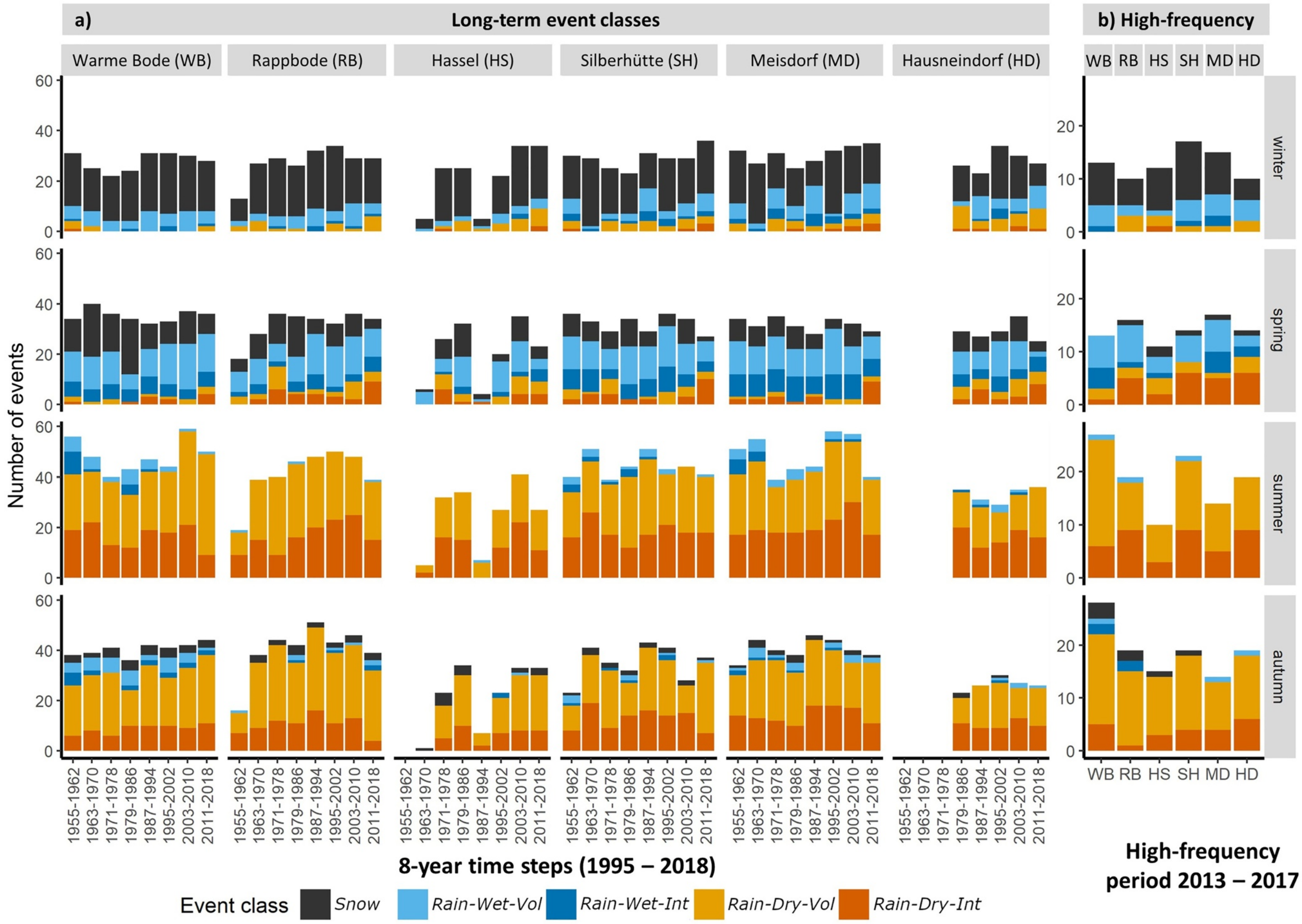

Figure 3. Seasonal absolute frequency of event classes (*y*-axis) in the six study catchments, showing (a) long-term changes between 8-year periods from 1955 until 2018 and (b) the period of high-frequency data from 2013 until 2017. Periods in panel (a) with no or very few events in HS and HD indicate missing discharge data.

in MD to 25.0% in WB), and the proportion of *Rain-Wet* events ranged between 14.0% in HS and 23.9% in WB. Rain-induced events were more frequently *volume*-than *intensity-dominated*.

Runoff events had an average duration of 11.2 ± 9.1 days for long-term data and 11.2 ± 8.9 days during the period of high-frequency data, with considerable differences between event classes (Figure S10 in Supporting Information S1). *Intensity-dominated* events (*Rain-Dry-Int* and *Rain-Wet-Int*) were shortest, lasting in average 5.5 ± 4.7 days and 8.6 ± 6.5 days for long-term data, respectively, followed by *Rain-Dry-Vol* events that lasted in average, 10.0 ± 8.1 days. *Rain-Wet-Vol* and *Snow* events were the longest events, lasting in average 14.4 ± 8.8 and 18.2 ± 10.2 days.

3.1.1. Long-Term Trends and Changes in Event Characteristics

In agreement with increasing temperature due to climate change (IPCC, 2013), Mann Kendall trends analysis indicated a decrease in the number and proportion of *Rain-Wet* events in summer, which was significant in half of the catchments (WB, SH, and MD; Table S1 in Supporting Information S1). This decrease goes along with a significant decrease in antecedent soil moisture in spring and/or summer in WB, RB, and MD catchments. Moreover, the number and/or proportion of *Snow* events decreased significantly in spring in WB, RB, SH, and MD catchments (Table S1 in Supporting Information S1). These trends go along with a significant decrease in the proportion of meltwater volume per event (M_{vol}/P_{vol}) in winter and spring in all catchments except HS. Only one catchment (WB) showed a significant decrease in the number and proportion of *intensity*- vs. *volume-dominated* events, which occurred during summer. In contrast, the RB, SH, and MD catchments showed a significant increase in P_{max}/P_{vol} during summer, but no significant trend in the total number or proportion of *intensity*- or *volume-dominated* events (Table S1 in Supporting Information S1).

3.2. Nitrate Export During Runoff Events

Runoff event and nitrate export characteristics differed between catchments. Event runoff decreased roughly from west to east, along the precipitation gradient (Table 1) with highest average Q_{med} in the WB catchment (1.1 mm hr^{-1}) and lowest average Q_{med} in the HD catchment (0.3 mm hr^{-1}). Nitrate export during runoff events varied across catchments in line with their land use patterns (Table 1). Catchments with the highest percentage of agricultural land use exported in average highest C_{med} (HS and HD with 2.5 mg N L^{-1} and 2.3 mg N L^{-1}), followed by mixed land use catchments (MD and SH with 1.6 mg N L^{-1} and 1.5 mg N L^{-1}) and lowest average C_{med} was observed in the dominantly forested catchments RB and WB (0.6 mg N L^{-1} and 0.7 mg N L^{-1}).

3.2.1. Nitrate Loads

Runoff events had a prominent role for annual nitrate export. The cumulative duration of all identified events from the high-frequency data was on average 39.6% (30.8%–48.1% depending on the catchment) of the analyzed time period (2013–2017), while they accounted on average for 51.2% (44.8%–63.3%) of all nitrate loads (Text S2 in Supporting Information S1). In relation to catchment area (Table 1), the HS catchment transported highest median nitrate loads across all event classes (5.5 kg N ha^{-1} yr^{-1}) followed by HD (1.8 kg N ha^{-1} yr^{-1}), MD (1.7 kg N ha^{-1} yr^{-1}), WB (1.6 kg N ha^{-1} yr^{-1}), SH (1.4 kg N ha^{-1} yr^{-1}) and lowest median loads were exported from RB catchment (1.0 kg N ha^{-1} yr^{-1}). Between event classes, lowest loads were transported during *Rain-Dry-Int* and *Rain-Dry-Vol* events, which were responsible for around 25.6% (14.8% in MD up to 41.6% in HD) of all event-driven loads. Highest loads were transported during *Rain-Wet* and *Snow* events, which were responsible for around 74.4% (58.4%–85.2%) of all event-driven loads (Figure 4). Kruskal Wallis test showed significant differences in exported nitrate loads between the event classes in all catchments. Results of the pairwise Wilcoxon Test indicated that these differences are mainly driven by the differences between *Rain-Dry-Int* or *Rain-Dry-Vol* events and *Rain-Wet-Vol* or *Snow* events, whereas no significant difference between *Rain-Dry-Vol* and *Rain-Dry-Int* events, nor between *Rain-Wet-Vol* and *Snow* events were detected. *Rain-Wet-Int* events were generally too low in their frequency (n = 1–7) to be compared reliably (Figure 4).

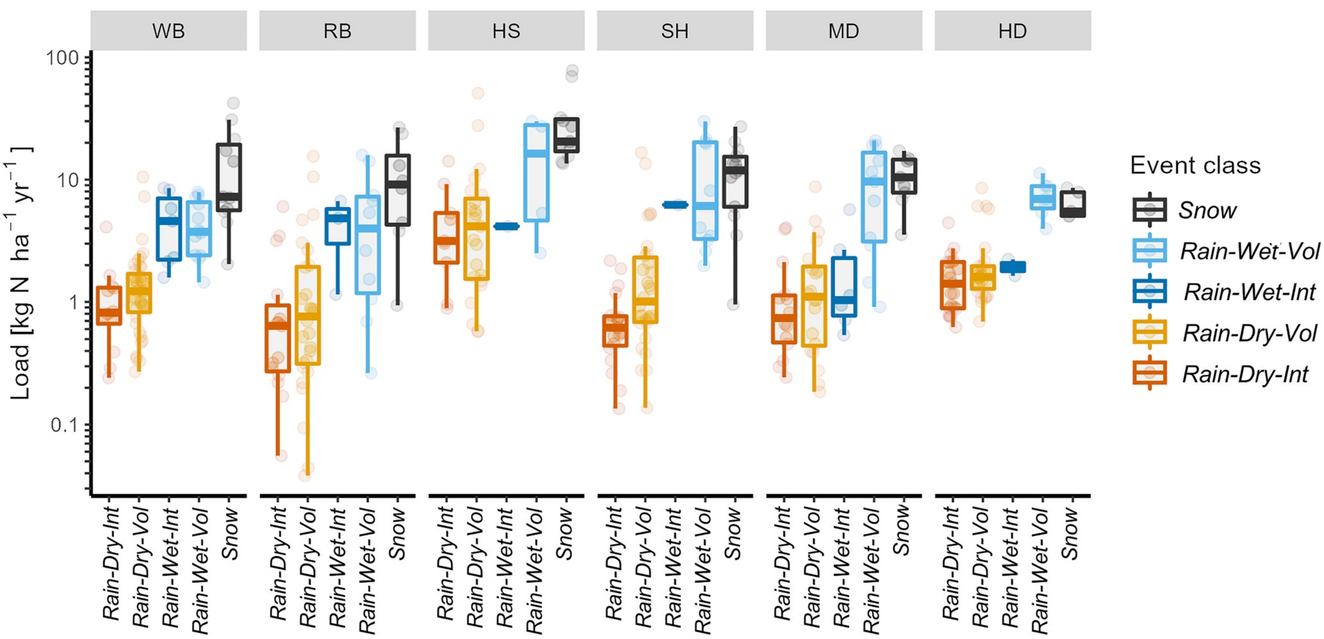

Figure 4. Nitrate loads per area (on logarithmic scale) transported during runoff events, divided into catchments and runoff event classes.

3.2.2. Inter-Event Concentration-Discharge Relationships

The inter-event CQ relationship is characterized by the slope between $\ln(C_{med})$ and $\ln(Q_{med})$ of all events within one catchment. It shows consistently positive CQ relationships in the log-log space, indicating that C_{med} increased with Q_{med} but with a different slope depending on the catchment (Figure 5). In line with transported loads (Figure 4), *Rain-Dry-Vol* and *Rain-Dry-Int* events are mainly located in the lower part of the CQ relationship, representing low-magnitude events (low Q_{med}) with low concentrations (low C_{med}) that occur mainly during summer and autumn (Figure 3). *Rain-Wet-Vol* and *Snow* events that occurred mainly in winter and spring (Figure 3) are located on the upper part of the CQ relationship, showing the highest Q_{med} and C_{med} (Figure 5). Additionally, some *Rain-Dry-Vol* events are located at the upper end of the CQ relationship. These events occurred mainly during autumn and often extended into the winter period with higher Q_{med} and C_{med}. *Rain-Wet-Int* events occurred only occasionally and represent mainly events of a lower magnitude in winter and spring with medium C_{med} and Q_{med}, plotting in between the other event classes.

The inter-event CQ relationship could account for most of the variance in C_{med} with an R^2 varying between 0.51 and 0.91 (Figure 5). Except for the SH catchment, adding information on event classes to the model did not improve its performance in terms of AICc compared to a simple CQ model. This indicates that Q_{med} was the most powerful predictor of C_{med} and no or only a small part of additional variance was explained by the event classes themselves. In the SH catchment, event classes clearly improved the linear regression model (AICc decreased by 13.6 units). While no clear differences between *Rain-Dry-Vol* and *Rain-Dry-Int* events nor between *Rain-Wet-Vol* and *Snow* events are visible (Figure S11 in Supporting Information S1), the main event class differences in SH was a higher intercept of *Rain-Wet-Vol* and *Snow* events compared to *Rain-Dry-Int* and *Rain-Dry-Vol* events.

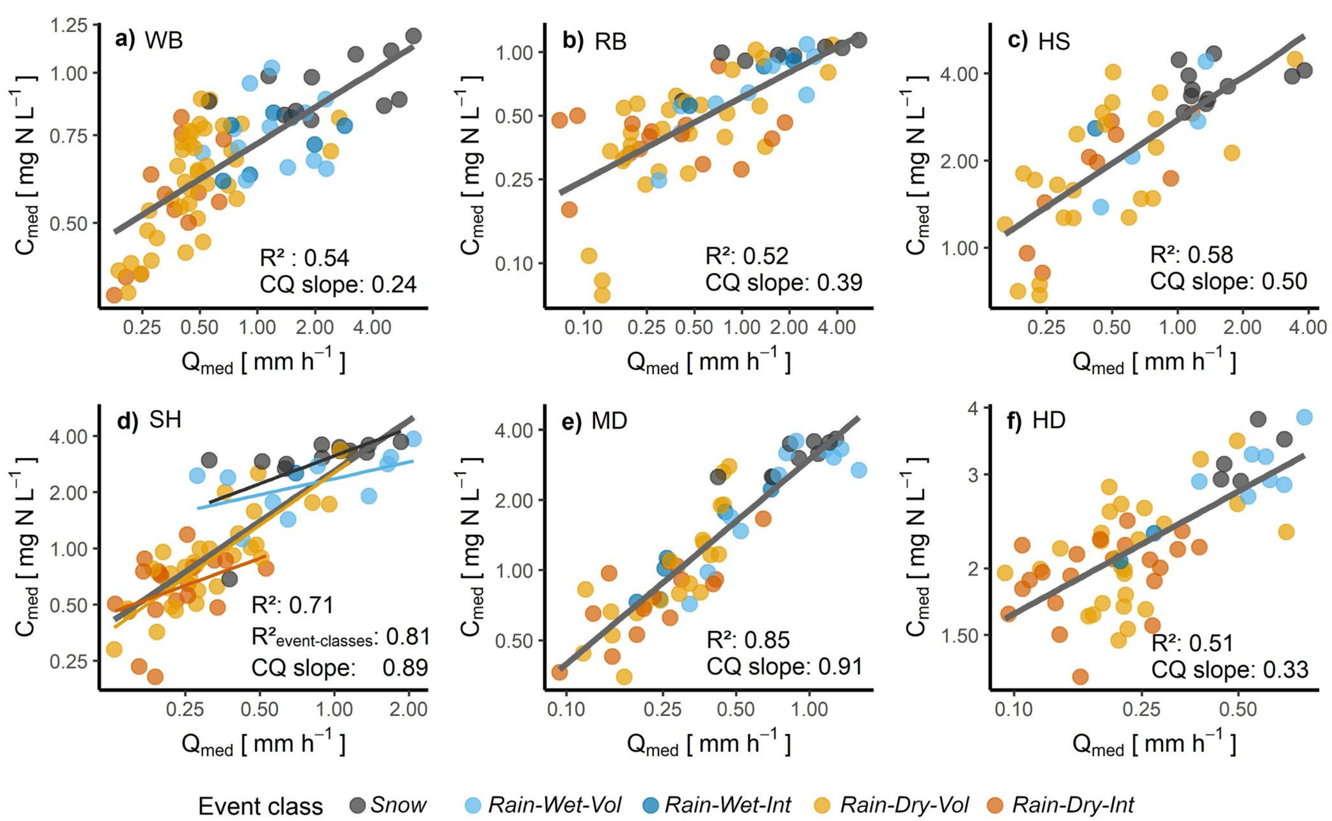

Figure 5. Median discharge (Q_{med}) and nitrate concentrations (C_{med}) for each runoff event with log-scale *x*- and *y*-axis, separated into the six catchments (a–f). Colors indicate the five different event classes, gray lines show the linear relationship between $\ln(C_{med})$ and $\ln(Q_{med})$ and colored lines show individual linear relationships between $\ln(C_{med})$ and $\ln(Q_{med})$ for each event class, only shown when event classes clearly improved the linear regression model (differences in AICc >2; (d)).

3.2.3. Event-Specific Concentration-Discharge Relationships

Across all catchments, most events (72.4%) were characterized by a positive event-specific CQ slope, indicating an increase of nitrate concentrations with increasing discharge (Figure 6). We found that event-specific CQ slopes in all catchments showed a large variability between low-magnitude events (low Q_{med}), whereas CQ slopes for high-magnitude events (higher Q_{med}) collapse to a slightly positive CQ slope that is roughly between 0.1 and 0.3, close to a chemostatic pattern (Figure 6a). Some catchment-specific differences can be observed between CQ slopes during low-magnitude events (Figure 6b). The more forested and pristine catchments dominantly showed positive CQ slopes, whereas the agriculturally dominated catchments HS and HD tended toward close-to-zero or negative CQ slopes.

Rain-Dry-Int and *Rain-Dry-Vol* events cause most of the variability between event-specific CQ slopes (Figure 6). These two event classes are distinguished by the temporal distribution of the inducing rainfall, being either *intensity-* or *volume-dominated*. To assess whether the difference in the temporal distribution of rainfall explains any additional variability in event-specific CQ slopes of low-magnitude events, we compared both classes using the Kruskal-Wallis test (Kruskal & Wallis, 1952). We found significantly higher event-specific CQ slopes for *Rain-Dry-Int* events compared to *Rain-Dry-Vol* events in half of the catchments (Figure 7; WB, SH, and MD), all of them showing >60% forest cover (Table 1). Median event-specific CQ slopes for *Rain-Dry-Vol* events were 0.18, 0.32, and 0.05 in WB, SH, and MD, respectively, and 0.39, 0.51, and 0.35 for *Rain-Dry-Int* events. In contrast, no

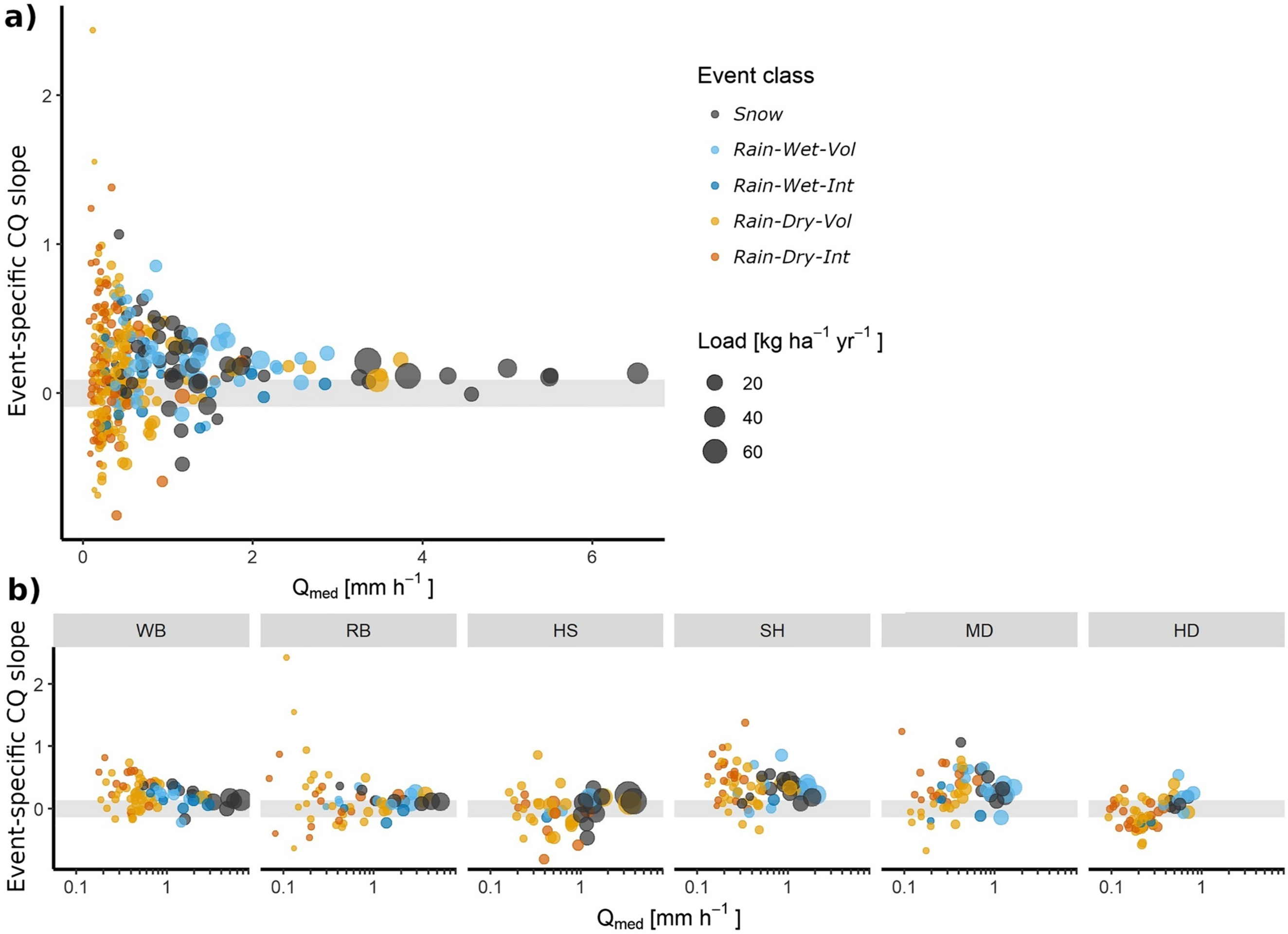

Figure 6. Event-specific CQ slopes (slope of nitrate concentrations and discharge in the log-log space) against the specific median discharge (Q_{med}) of each event shown for all catchments in one plot (a) and with logarithmic *x*-axis and separated by catchments to visualize differences in events with low Q_{med} between catchments (b). Colors of dots indicate the five event classes, dot sizes indicate the event load. Gray-shaded areas indicate event-specific CQ slopes close to zero (between −0.1 and 0.1).

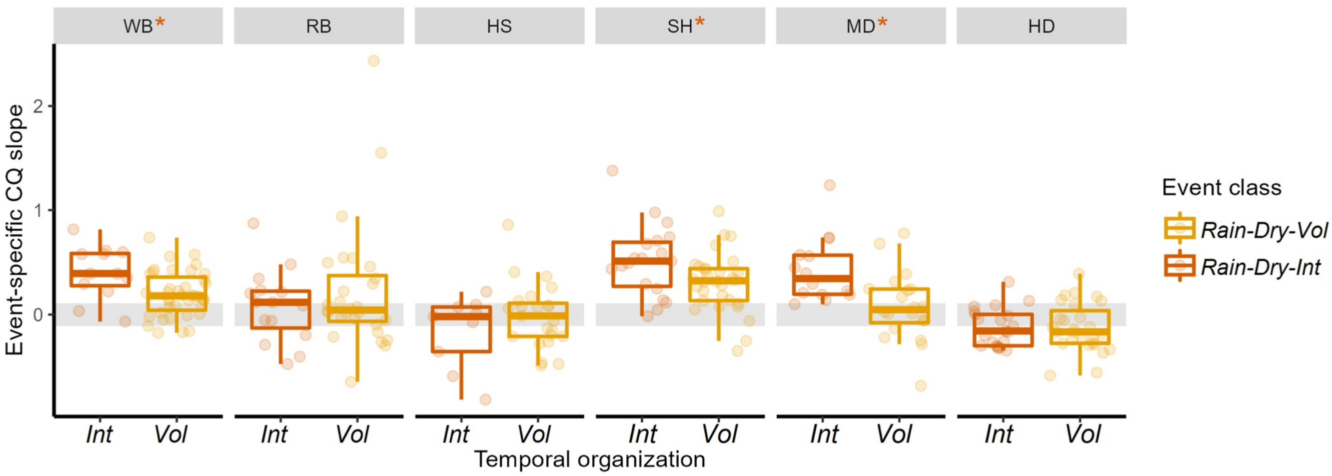

Figure 7. Event-specific CQ slopes (slope between nitrate concentrations and discharge in the log-log space) for all six study catchments and the two event classes Rain-Dry-Int and Rain-Dry-Vol, representing rain-induced runoff events that occurred under dry antecedent soil moisture conditions with either intensity- or volume-dominated rainfall. Orange asterisks in the header indicate significant ($p < 0.05$) differences between the event classes for a particular catchment. Gray-shaded areas indicate event-specific CQ slopes close to zero (between −0.1 and 0.1).

significant difference in C_{med} and Q_{med} between *Rain-Dry-Int* and *Rain-Dry-Vol* events could be detected (Figure S12 in Supporting Information S1), except for the SH catchment, where C_{med} and Q_{med} were significantly higher during *Rain-Dry-Vol* events.

4. Discussion

4.1. Impact of Runoff Event Characteristics on Nitrate Export

The aim of this study was to thoroughly assess how much of the inter-event variability in nitrate export patterns can be explained by event characteristics and runoff formation classes across a range of hydro-meteorological conditions and different types of catchments. We argue that the extensive data set used in combination with a systematic runoff event classification and a nitrate export characterization using CQ relationships leads to a broader transferability of the identified, dominant drivers of event-scale nitrate export patterns beyond the catchments analyzed in this study.

Our results show that the average level of exported nitrate concentrations and loads during an event are catchment specific, depending on the land use and related N input. Higher export was observed in catchments with more agricultural land use, which have a higher N input through fertilizer application, whereas lower export was found in the more forested catchments, were N input, stemming from atmospheric deposition and biological fixation, is typically lower (Ebeling et al., 2021). However, we could also show very similar patterns in event-scale nitrate export across all catchments that were strongly dependent on the event magnitude (in regard to runoff) and season (Figure 8). Low-magnitude events during summer and autumn exported lowest concentrations and loads and high-magnitude events in winter and spring exported highest nitrate concentrations and loads (Figure 8a). The variability of event-specific CQ slopes decreased with increasing event magnitude, indicating an increasing homogenization of the dominant drivers for nutrient export for increasing event magnitudes (Figure 8b).

In the following, we discuss the impact of runoff event characteristics on nitrate export during those different conditions in more detail. Furthermore, we discuss the transferability of results to other areas and how well the analyzed runoff event characteristics from the high-frequency period (2013–2017) represent the long-term runoff event characteristics. Moreover, we discuss the observed trends in long-term runoff event characteristics and their implications for future nitrate export.

4.1.1. Low-Magnitude Events

Low-magnitude and often relatively short rain-induced events occurred mainly during summer and autumn and coincided with dry antecedent soil moisture conditions, classified as *Rain-Dry-Int* or *Rain-Dry-Vol*. These events

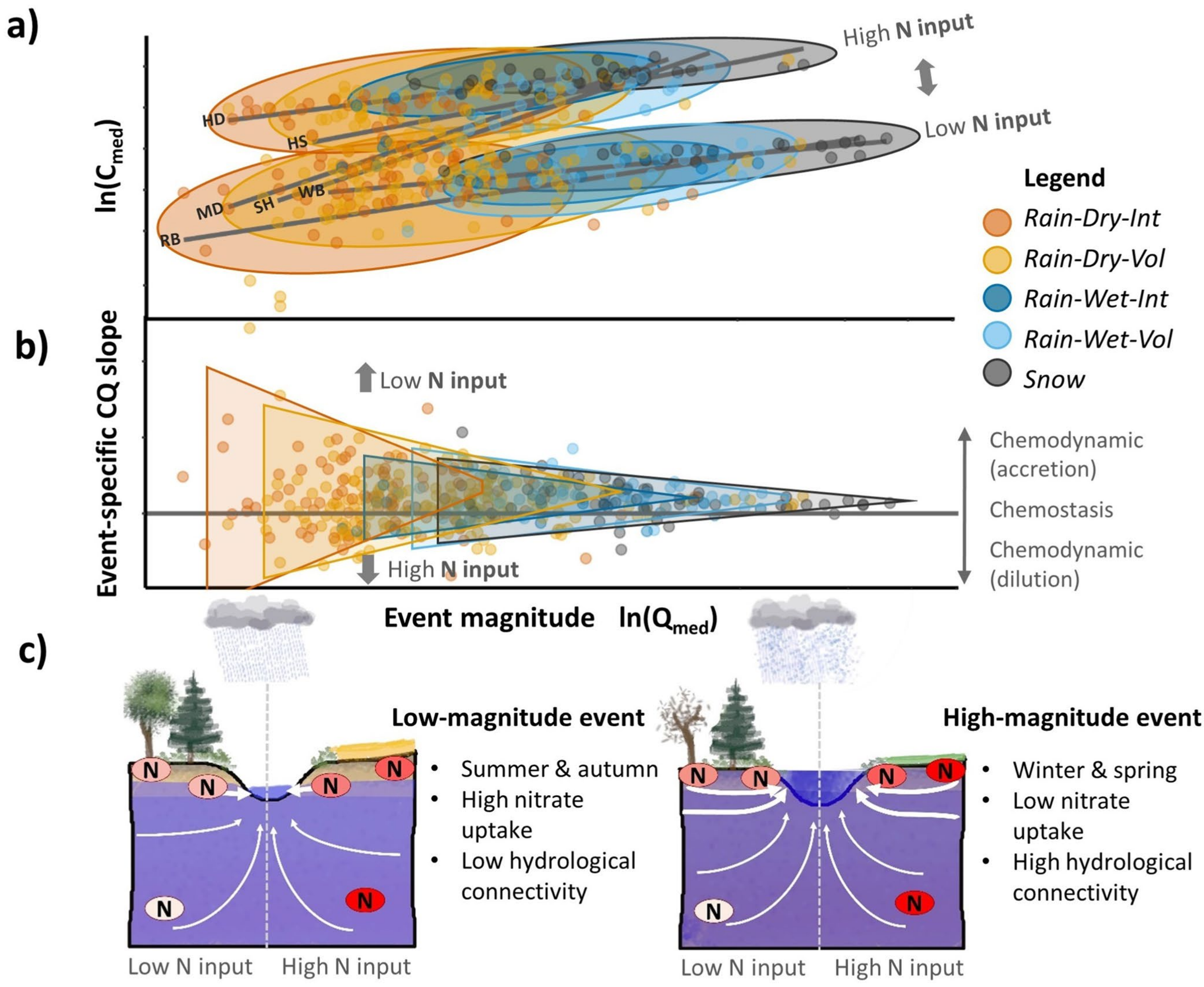

Figure 8. Framework of the relationship between runoff event classification and nitrate export characteristics. (a) The inter-event CQ relationship with median event-scale nitrate concentrations and discharge (C_{med} and Q_{med}). Gray lines show the inter-event CQ slope for the individual catchments in this study. Catchments with higher N input (i.e., more agricultural land use) show a higher intercept than catchments with lower N input (i.e., more forest). (b) The event-specific CQ slopes for all catchments and their decreasing variability with higher event magnitude (Q_{med}). Event-specific CQ slopes for low-magnitude events tended to be more positive for catchments with low N input and more negative for catchments with high N input. (c) Concept of potential underlying mechanisms in regard to catchment wetness enhancing hydrological connectivity and biogeochemically controlled nitrate source availability in catchments of overall low vs. high N input (i.e., forest vs. agricultural land use).

exported lowest nitrate concentrations and loads and showed highly variable event-specific CQ slopes. We can explain these relatively low nitrate loadings by a decreased hydrological connectivity (i.e., a low fraction of activated flow paths) with lower antecedent soil moisture and by a lower nitrate availability due to higher biogeochemical removal and biological uptake in summer and autumn, compared to winter and spring. As a result from decreased hydrological connectivity, only nitrate sources in close proximity to the stream network and from sources connected via deeper groundwater flow paths are connected to the stream network (Musolff et al., 2015; Stieglitz et al., 2003; J. Yang, Heidbüchel, et al., 2018). These flow paths during the dry period are generally characterized by longer transit times and thus enable more nitrate uptake and removal via denitrification (Ebeling et al., 2021; Ehrhardt et al., 2019; Kumar et al., 2020; Nguyen et al., 2021). As a result from increased biological activity with higher temperatures, nitrate uptake and removal increases, especially in streams and in the riparian zones (Baird et al., 1995; Lutz et al., 2020; Rode, Angelstein et al., 2016), which can lead to reduced nitrate availability compared to colder seasons. While certainly both nitrate availability and hydrological connectivity play a role for event-scale nitrate export, it is beyond the scope of this study to fully disentangle their individual contributions.

Seasonal differences in discharge and concentrations shaped the inter-event CQ relationship that was positive across catchments, reflecting higher concentrations during high flow in winter and spring and lower concentrations during low-flow conditions in summer and autumn. At the event level, CQ slopes can reveal complementary information on the underlying processes of nitrate mobilization and transport within seasons (Godsey et al., 2019; Musolff et al., 2021; Winter et al., 2021). We found large variability in event-specific CQ slopes during low-magnitude events, which we explain by an increased relevance of different environmental factors such as (a) catchment characteristics and the spatial distribution and connectivity of N sources within a catchment, (b) riparian and in-stream biogeochemical processes and (c) the spatial and temporal distribution of the inducing precipitation event. In regard to catchment characteristics, we could show that the more forest-dominated catchments (WB, RB, SH, MD, Figure 1) showed mainly positive event-specific CQ slopes during low-magnitude events, whereas the more agriculturally dominated catchments (HS and HD) tended towards negative event-specific CQ slopes (Figure 6b). The dilution patterns in the agricultural catchments can be explained by relatively high base-flow concentrations (reflecting high N input from fertilization) and the spatial distribution of N sources within these catchments. For example, Musolff et al. (2021) argued that due to large buffer strips (100 m) in the HS catchment, there are no or only few nitrate sources in the riparian zones. Hence, events of low magnitude that activate only proximate flow paths from this area could cause the observed dilution pattern. In the HD catchment, Winter et al. (2021) found that a disproportionally large part of event runoff is generated in the upstream area that is mainly covered by forests and thus exports lower nitrate concentrations. Runoff from this area can thus dilute higher concentrations in base flow, which are largely generated by groundwater from the downstream agricultural areas. Hence, the preferential mobilization from certain areas of lower N availability, here riparian zones or upstream areas, can cause a dilution pattern in catchments with an overall high N input. In contrast, the dominant accretion pattern in the more forested catchments might be explained by a flushing of proximate shallow nitrate sources, likely from the upper soil layers of the riparian zones as also suggested by Musolff et al. (2021) for the WB catchment and a sub-catchment of RB. In regard to in-stream and near-stream processing, several studies argued that biogeochemical processes such as nitrate uptake and denitrification in-stream or in the riparian zones have a stronger relative impact on nitrate export during low-magnitude events (e.g., Marinos et al., 2020; Moatar et al., 2017). Hence, variability in these processes through, for example, varying instream temperature (Rode, Angelstein, et al., 2016) or in the riparian zone partly due to stream water infiltration (Lutz et al., 2020; Nogueira et al., 2021) might be responsible for the observed higher variability between event-specific CQ slopes. This is supported by a study from Heathwaite and Bieroza (2021), who found that nutrient export dynamics during low-magnitude events can be considerably influenced by diurnal cycling.

By separating runoff event classes into *intensity*- and *volume-dominated* precipitation, we could show that the impact of the temporal distribution of precipitation can explain another part of the variability in mobilization patterns during low-magnitude events. *Intensity-dominated* events (*Rain-Dry-Int*) showed higher event-specific CQ slopes compared to *volume-dominated* events (*Rain-Dry-Vol*) in half of the catchments. Those catchments comprise forested or mixed land use and showed overall positive event-specific CQ slopes for both *Rain-Dry-Int* and *Rain-Dry-Vol* events (Figures 1 and 7). Both event classes are rain-induced with dry antecedent conditions. During *Rain-Dry-Int* events however, runoff is generated by a shorter and rather intense rainfall, whereas during *Rain-Dry-Vol* events, the duration of rainfall is typically longer with a lower ratio of the maximum precipitation rate compared to the total precipitation volume (Tarasova et al., 2020). As argued further above, nitrate mobilized during low-magnitude events in those forested catchments may mainly stem from shallow and proximate N sources (Musolff et al., 2021). One possible explanation for the difference in event-specific CQ slopes might be that relatively short but intensive runoff events preferentially activate proximate and shallow flow paths and mobilize those shallow N sources. This mobilization then causes an increase in nitrate concentrations that is reflected by the positive event-specific CQ slope. Longer *volume-dominated* events might create a higher, yet delayed hydrological connectivity with more distant sources than those near-stream N source zones, which is reflected in a decreasing event-specific CQ slope. As such, CQ slopes during *volume-dominated* events approximate more chemostatic patterns and show a higher similarity with higher-magnitude runoff events under wet antecedent conditions (see Section 4.1.2).

4.1.2. High-Magnitude Runoff Events

In contrast to low-magnitude events in summer and autumn, runoff events in winter and spring were mainly snow-influenced (*Snow*) or rain-induced (<5% snowmelt) and generated by *volume-dominated* precipitation under wet antecedent conditions (*Rain-Wet-Vol*, Figures 2 and 3). These two event classes were found to be the largest runoff events in regard to median discharge (Q_{med}) and caused the highest nitrate concentrations and loads (Figures 4 and 5). Approximately three quarters of all event-driven loads were exported during *Snow* and *Rain-Wet-Vol* events, which is in agreement with other studies that reported exceptionally high nitrate export during large rain-on-snow events (Crossman et al., 2016; Koenig et al., 2017; Sebestyen et al., 2009; Seybold et al., 2019). These results underline the important role of *Snow* and *Rain-Wet-Vol* event classes for nitrate export and show that missing information on the winter period, which is often the case (e.g., Blaen et al., 2017; Carey et al., 2014; Knapp et al., 2020; Wollheim et al., 2017), can lead to a lack of information about the most relevant events for the export of nitrate loads.

In temperate climates, rain-on-snow events often form the largest runoff events of the year due to the cumulative effect of rainfall and additional input from snowmelt (Casson et al., 2014; Pellerin et al., 2012). Nevertheless, we identified *Rain-Wet-Vol* events (not influenced by snowmelt) that caused comparable or even higher Q_{med}, especially in the Selke catchment (Figures 5d–5f). Those events transported comparably high nitrate loads (Figure 4), fell on the same or a very similar inter-event CQ slope (Figure 5) and showed similar event-specific CQ slopes (Figure 6) as the *Snow* events. This indicates that both event classes, *Snow* and *Rain-Wet-Vol*, activate the same or very similar N sources within a catchment, despite their differences in the meltwater fraction.

Similar to Stieglitz et al. (2003), we argue that high-magnitude events during winter and spring can activate all relevant nitrate sources within a catchment, including distant sources (Bowes et al., 2015) and shallow and younger N sources (Fovet et al., 2018; Musolff et al., 2017, 2015; J. Yang, Heidbüchel, et al., 2018). During winter and spring, discharge and antecedent soil moisture are generally higher, which leads to more active flow paths compared to summer and autumn (Stieglitz et al., 2003; J. Yang, Heidbüchel, et al., 2018). At the same time, lower temperatures cause a reduced N demand of ecosystems that can result in a higher nitrate source availability (Baird et al., 1995; Rode, Angelstein, et al., 2016). Together, the flow path activation in a highly saturated catchment and a relatively high nitrate availability can explain the high nitrate concentrations and loads observed in the studied catchments (Figures 4 and 5). Moreover, they can explain the low variability in event specific-CQ slopes (Figure 6), because if all flow paths are activated and sufficient nitrate sources are available, no changes in nitrate mobilization through bypassing, activation of additional N sources or source depletion can occur.

Remarkably, the event-specific CQ slopes during high-magnitude events did not show any signs of dilution (Figure 6). Other studies have reported such dilution pattern during precipitation events across the whole year including high-magnitude events, which might indicate source depletion (Kincaid et al., 2020; Vaughan et al., 2017) or high base flow concentrations from deeper groundwater that are diluted by water with lower concentration from newly activated zones (Fovet et al., 2018; Rose et al., 2018). Here, we consistently reported slightly positive CQ slopes (roughly 0.1–0.3) that reflect a milder increase of concentrations compared to that of discharge, indicating increasingly chemostatic export patterns with increasing event runoff. This is further supported by the fact that the event-specific coefficient of variation of concentrations is much smaller than that of discharge (Musolff et al., 2015) with a median ratio of 0.28 for high-magnitude events ($Q_{med} > 1$ mm hr^{-1}). These patterns provide strong evidence for a transport rather than a source limitation of nitrate in all six catchments (Basu et al., 2010), even in the forest dominated catchments, which is alarming in terms of water quality. In the agricultural catchments (HS and HD), fertilization is likely the main nitrate source. In the mixed land use catchments (SH and MD) and the more forested catchments (WB and RB) smaller patches of agriculture and the overall high atmospheric N deposition in the Harz Mountains (Kuhr et al., 2014; Winter et al., 2021) are likely to be the dominant nitrate sources. In addition, long transit times and chemostatic export patterns in the agricultural lowland catchment HD indicate substantial N legacies belowground, which might keep nitrate concentrations at a high level independent from the event size (Winter et al., 2021). On the contrary, shorter transit times in the upper Harz Mountain catchments likely prevent such accumulation of long-term legacies (Ehrhardt et al., 2019; Nguyen et al., 2021; Winter et al., 2021; J. Yang, Heidbüchel, et al., 2018). Still, our results suggest that even without such long-term legacies, younger nitrate sources that get connected to the stream network during high-magnitude events provide sufficient supply to maintain chemostatic export patterns. Additionally, Ohte et al. (2004) and Sebestyen et al. (2009) showed that atmospheric N stored in the snowpack can considerably contribute to nitrate export during snow-influenced events in a forested catchment. However, the strikingly similar nitrate export patterns during *Snow* and *Rain-Wet-Vol* events with comparable event size hint at similar nitrate sources for both event classes and thus not at the melting snowpack as a key source.

4.2. Long-Term Trends of Event Characteristics and Their Implications for Nutrient Export Patterns

We analyzed nitrate export patterns for a 5-yr period of high-frequency nitrate concentration data (2013–2017), which is not sufficient to estimate any long-term trends. However, in this study, we bring together a short-term high-frequency analysis with long-term runoff event characterization and classification from daily data, which allowed us to detect long-term trends in runoff event characteristics and to discuss their possible impact on nitrate export patterns.

We found a decrease of soil moisture in summer, which aligned along a decrease of wet compared to dry events. This is in agreement with increasing summer temperatures over Europe (Briffa et al., 2009; IPCC, 2013) and other studies that report a decreasing contribution of summer precipitation (Szwed, 2019) and an increased risk for summer droughts in large parts of Europe (Hari et al., 2020; Pal et al., 2004). Here, we found that runoff events generated during dry catchment conditions are associated with a lower event magnitude (i.e., lower event runoff) proportionally lower nitrate concentrations and loads and a higher variability in event-specific CQ slopes, compared to wet conditions. Therefore, possibly drier antecedent conditions resulting from increasing future temperatures (IPCC, 2018; Pal et al., 2004) might lead to a decrease in nitrate export in summer periods but also to a higher variability in concentrations, due to more variable and partly higher event-specific CQ slopes. However, also nitrate availability is likely to be affected by changing climatic conditions with nitrate uptake and removal rates, but also mineralization, either increasing with increasing temperatures or decreasing because of soils drying out (Hartmann et al., 2013; Mosley, 2015). N that is not exported nor taken up during dry seasons is accumulated in the catchment and can be mineralized and flushed with rewetting in autumn (Mosley, 2015). First runoff events after especially dry summer periods were often reported to cause disproportionally high nitrate export peaks, which can cause severe water quality deteriorations and further increase the inter-annual variability of nitrate concentrations (Jarvie et al., 2003; Morecroft et al., 2000; Mosley, 2015; Oborne et al., 1980). In summary, we see evidence for an increased variability of nitrate concentrations and export dynamics with increasingly dry conditions in summer and autumn.

In addition to the increasingly dry summer conditions, we found a decrease in the contribution and number of snow-influenced events (*Snow*) as well as a decrease in the proportion of meltwater during winter and spring. These events exported highest nitrate loads; hence from the perspective of hydrological transport, a decrease of high nitrate export peaks could be expected, which was also reported by Sebestyen et al. (2009) for a mountainous forested catchment. However, winter precipitation is predicted to substantially increase in most of Europe (Stahl et al., 2010). The resulting larger rain-induced events could potentially counterbalance the decreased number of *Snow* events and trigger similarly high event runoff and nitrate export, as observed in the SH, MD, and HD catchments (Figures 5d–5f). As such, the timing of nitrate export peaks would not be restricted to the melting period but to the entire high flow season in winter and early spring, given sufficient nitrate supply. Additionally, several studies predict that an earlier start of snowmelt due to increasing temperatures causes a time shift of discharge and nitrate export peaks towards earlier in the year (Clow, 2010; IPCC, 2014; Sebestyen et al., 2009). In summary, we do not see clear evidence for a change in nitrate loading during high-magnitude winter and spring events but we do see evidence for a change in the timing of nitrate export peaks.

4.3. How Representative Are the Obtained Results for These and Other Catchments?

The classification of runoff events from long-term time series in this study allowed for a consistent characterization of typical hydro-meteorological and catchment-state conditions, their seasonality, and temporal changes (i.e., trends) in their configuration beyond the limited time period of available high-frequency nitrate measurements. To our knowledge, this placement of short-term nitrate export dynamics into a larger context of long-term runoff event characteristics has never been conducted before. Runoff event classes from the shorter and more recent high-frequency period (with available nitrate concentration data) deviated from the long-term average runoff event classes mainly in their proportion of *Rain-Dry* events (which mainly increased in summer) and in their proportion of snow-influenced events (which mainly decreased in spring). These deviations can help us understand possible trajectories of runoff event characteristics and their impact on nitrate export in the future. Additionally, these long-term runoff event characteristics allow us to embed the observed catchments into a larger group of catchments with very similar runoff event characteristics, classified by Tarasova et al. (2020). The six studied catchments match well with the clusters that characterize runoff events in the Central Uplands of Germany (including the Harz Mountains where this study is located) and in the Alpine Foreland (Tarasova et al., 2020). Over a time period from 1979 to 2002, the majority of runoff events in these clusters were *Rain-Dry* events, while approximately 15%–25% were snow-influenced events (*Snow*) and the number of events characterized by *volume-dominated* rainfall prevailed over *intensity-dominated* rainfall (Tarasova et al., 2020). This is well in line with our results that include more recent years (until 2018) and show >50% *Rain-Dry* events, 18%–25% *Snow* events, and more events characterized by *volume-dominated* rainfall than *intensity-dominated* rainfall. Based on this, we argue that our observed runoff event classes are representative for many upland areas and forelands of higher mountain ranges in a temperate climate.

To get a representative picture of nitrate export during those runoff events, one needs to consider that export also depends on additional factors, such as the amount and distribution of N sources within a catchment, which are strongly driven by land use patterns (Dupas et al., 2019; Musolff et al., 2017) as well as biogeochemical processing. By analyzing the impact of these representative runoff event characteristics on nitrate export across different hydro-climatic conditions and in six catchments that span a significant range of different land use types and other characteristics (Table 1), we are confident that the presented results are generally transferable to other upland areas and mountain forelands in a temperate climate. However, the analysis of long-term runoff event characteristics in combination with concentration data of five years only, does not allow inference on long-term trajectories of nitrate transport. We cannot easily assume a biogeochemical stationarity at decadal or longer time scales. However, there is evidence of this stationarity in catchments with high N loadings and thus ubiquitous and strong N sources that reflect in chemostatic export patterns (Basu et al., 2010). This may be the case in our catchments but may not be transferable to catchments with limited N availability or a different N input history.

Nonetheless, by including an extended set of hydro-meteorological variables that goes beyond the limited set of event characteristics used in previous studies, we could disentangle a large part of the variability in nitrate export patterns and create results that are better transferable to other catchments and time periods, assuming that catchment functioning for nitrate cycling and retention remains similar. A hydrological classification can thus be seen as one prerequisite for creating transferrable results to better compare the partly contradicting results between different studies (e.g., Knapp et al., 2020; Koenig et al., 2017; Rose et al., 2018; Vaughan et al., 2017; Winter et al., 2021) and to create a more coherent picture of the hydrological processes that shape nitrate export dynamics.

5. Conclusions

In this study, we conducted a rigorous assessment of the impact of runoff event characteristics and their classes on high-frequency nitrate export across multiple years, hydro-climatic conditions, and across six contrasting mesoscale catchments. We used long-term runoff event characteristics to embed the relationship between event runoff and nitrate export into a larger hydrological description of events and catchments. This new framework allowed us to identify potential long-term trends in nitrate export and their implications under a changing climate. We found that nitrate export differed substantially between runoff events with different characteristics, and strong drivers being event magnitude and a pronounced seasonality. With our findings, we argue that the variability and timing of nitrate export is likely to change with a changing frequency of event types that is driven by future global warming that is, projected changes in temperatures and other hydro-meteorological conditions.

Lowest nitrate concentrations and loads were transported during low-magnitude rain-induced events with dry antecedent soil moisture (*Rain-Dry-Int* and *Rain-Dry-Vol*), which occurred mainly during summer and autumn. These lower nitrate loadings, compared to high-flow seasons, can be explained by a small fraction of active flow paths, longer transit times, and a lower nitrate availability through higher uptake and denitrification rates during the vegetation period. Additionally, we found an increasing variability of event-specific CQ slopes with decreasing event size. We explain this high variability by an increased relevance of different environmental factors for nitrate export dynamics, such as the spatial distribution of nitrate sources and their connectivity to the streams, as well as the spatial and temporal distribution of precipitation (i.e., *volume-* or *intensity-dominated*) and biogeochemical processes in-stream and in the riparian zone. Consequently, more frequent dry spells will likely lead to more variable and less predictable water quality in rivers and streams.

In contrast, highest nitrate concentrations and loads were exported during high-magnitude snowmelt-induced (*Snow*) or *volume-dominated* rain-induced events under wet antecedent conditions (*Rain-Wet-Vol*), which occurred mainly during winter and spring. Nitrate mobilization, represented by event-specific CQ slopes, was surprisingly homogeneous among high-magnitude events across all catchments and land-use types, showing a relatively small increase of nitrate concentrations compared to discharge (approximately chemostatic conditions). We explain this by the activation of all relevant flow paths within a catchment that facilitate the land-to-stream connection of all relevant N sources and by higher, not limiting, nitrate availability during the dormant seasons. As classes for high-magnitude events, that is, *Snow* and *Rain-Wet-Vol*, showed a very similar nitrate export behavior, we suggest that not the meltwater fraction, but instead other common characteristics such as event size, catchment saturation, and nitrate availability are the main drivers of nitrate export during high-magnitude runoff events. No dilution patterns (negative event-specific CQ slope) were observed for those events; hence, even forest-dominated catchments showed no sign of N source depletion, which could be a warning sign for future water quality trends. Increasing temperatures might cause a change in the timing of large nitrate export peaks within the high flow season, but we could not find evidence for a change in the amount of nitrate export in regard to hydrological transport, because declining snowfall (and consequently snow-influenced events) could potentially be compensated for by increasing winter rainfall.

Runoff event characteristics in this study are generic and hence comparable between catchments. Therefore, we argue that they are also representative for other upland or foreland areas in temperate climates. Covering a range of different catchment characteristics, for example, dominantly forested vs. mainly agricultural land cover, allowed us to analyze various catchment configurations and the respective event-driven nitrate export patterns and thus to represent a range of possible generic relationships between runoff event types and nitrate export. The potential of a hydrological event classification to create transferable results should be further exploited by analyzing event-driven nitrate export across even wider ranges of catchment characteristics and climatic conditions and by applying this approach to event-driven export of other solutes and particulates. Establishing robust relationships between runoff event characteristics and water quality dynamics, and relating them to long-term trends in runoff event characteristics, as introduced here, would be an informative tool for understanding possible directions of future changes in water quality.

Data Availability Statement

Supplementary figures and tables are available as Supplementary Information. The raw discharge data can be freely obtained from the State Office of Flood Protection and Water Quality of Saxony-Anhalt (LHW) under https://gld-sa.dhi-wasy.de/GLD-Portal/. The raw meteorological data sets can be freely obtained from Germanys National Meteorological Service (Deutscher Wetterddienst, DWD) under https://opendata.dwd.de/climate_environment/CDC/grids_germany/daily/regnie/ (daily precipitation) and https://opendata.dwd.de/climate_environment/CDC/grids_germany/hourly/radolan/reproc/2017_002/ (hourly precipitation). Gridded products based on Zink et al. (2017) are available from https://www.ufz.de/index.php?en=41160. Raw nitrate concentration data are archived in the TERENO database and are available upon request through the TERENO-Portal (www.tereno.net/ddp). All runoff event characteristics from the long-term and from the high-frequency data are available under http://www.hydroshare.org/resource/8409b4a5d40541b684d4bdafc0b16b43.

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Water Resources Research

Supporting Information for

Explaining the Variability in High-Frequency Nitrate Export Patterns Using Long-Term Hydrological Event Classification

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Contents of this file

Additional Supporting Information (Files uploaded separately)

Introduction

This supporting information provides figures that show all daily long-term data that was used to identify and classify runoff events (Figures S1 to S6) and a detailed description of the procedure of high-frequency data correction and quality checks (Text S1 and Figures S7 to S9). Furthermore, it provides information on the duration of runoff events per event class (Figure S10); information on the methodology to estimate annual nitrate loads (Text S2); an effect plot for the linear regression model including event classes for the SH catchment (Figure S11); a figure showing the differences in event-specific nitrate concentrations and discharge between event classes under dry antecedent conditions (Figure S12) and a table with τ-values and significance levels for monotonic long-term trends in runoff event characteristics (Table S1).

Warme Bode (WB)

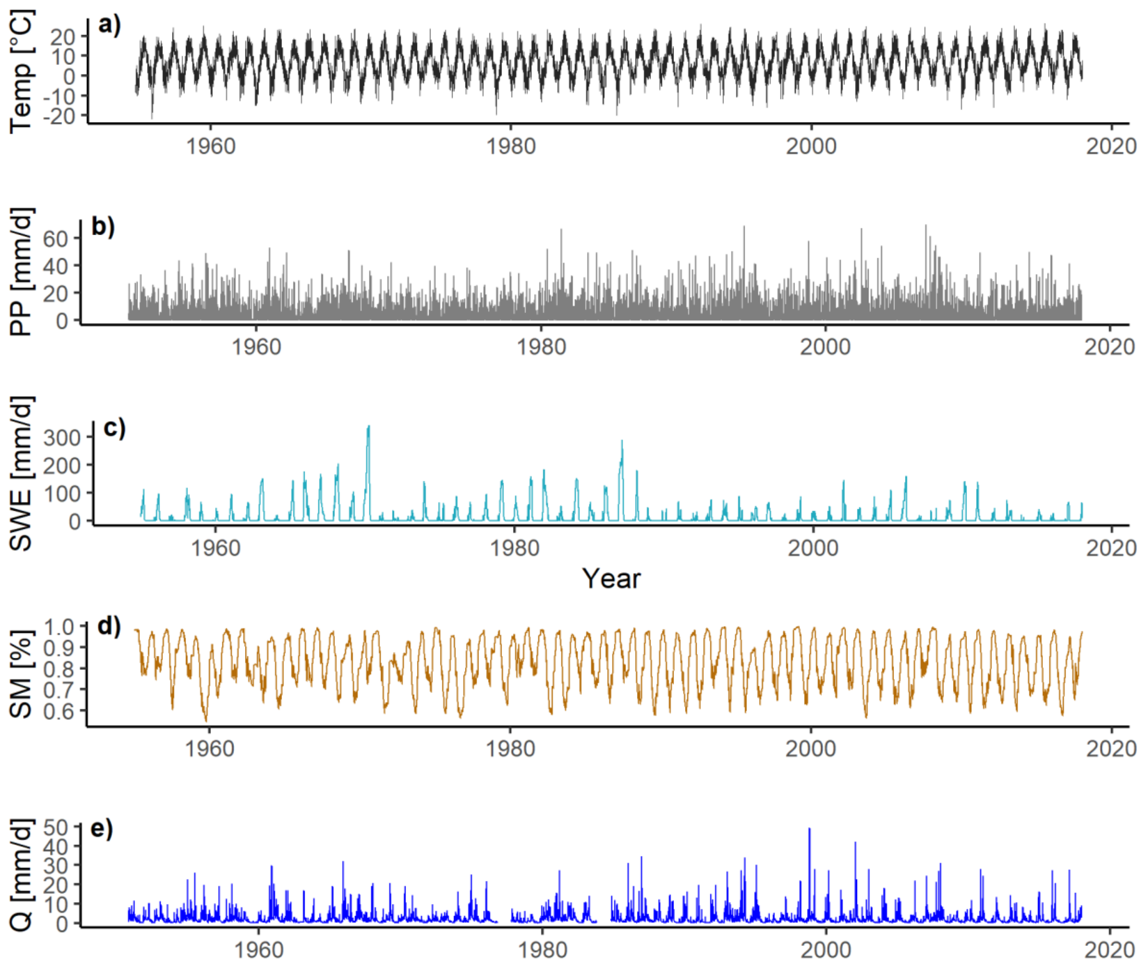

Figure S1. Daily long-term data from the WB catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM; Kumar et al., 2013; Samaniego et al., 2010; Zink et al., 2017).

Rappbode (RB)

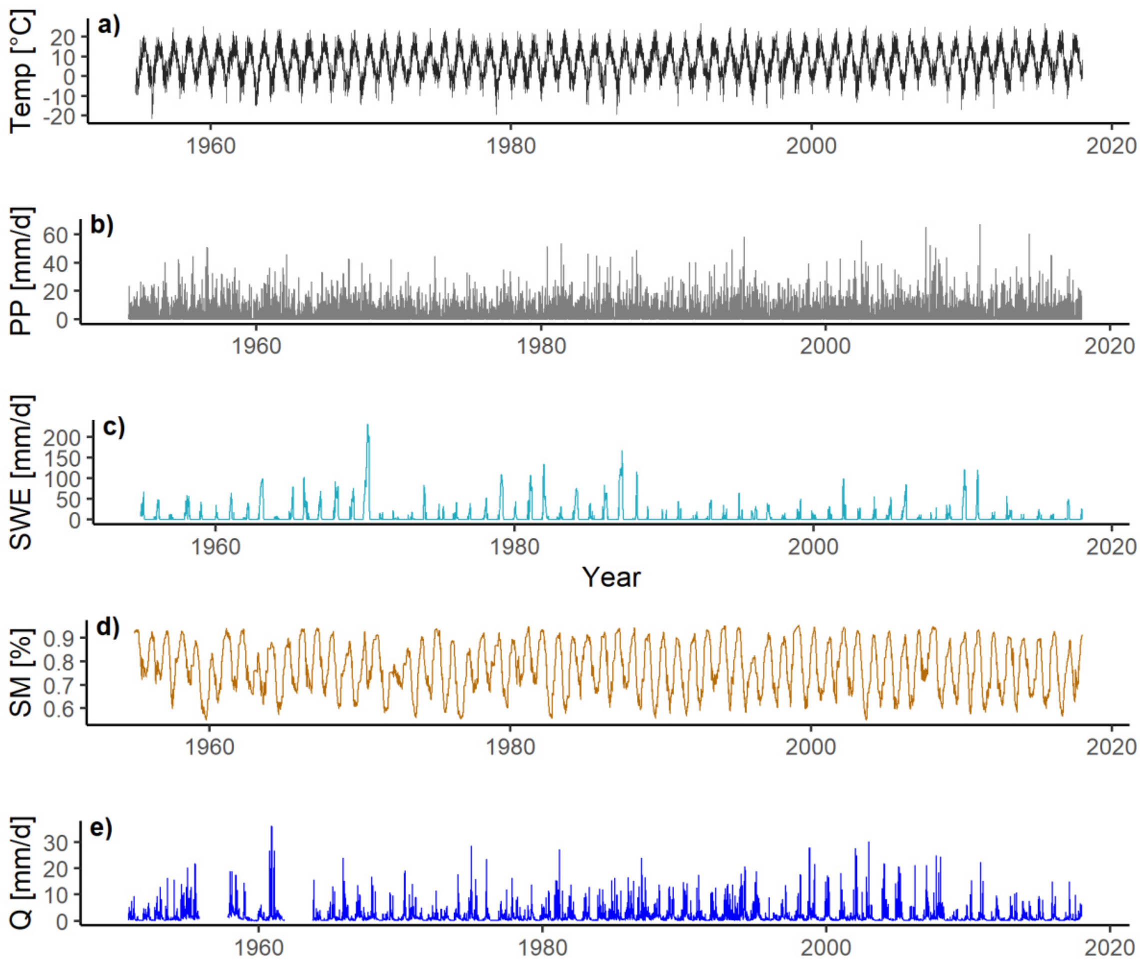

Figure S2. Daily long-term data from the RB catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM).

Hassel (HS)

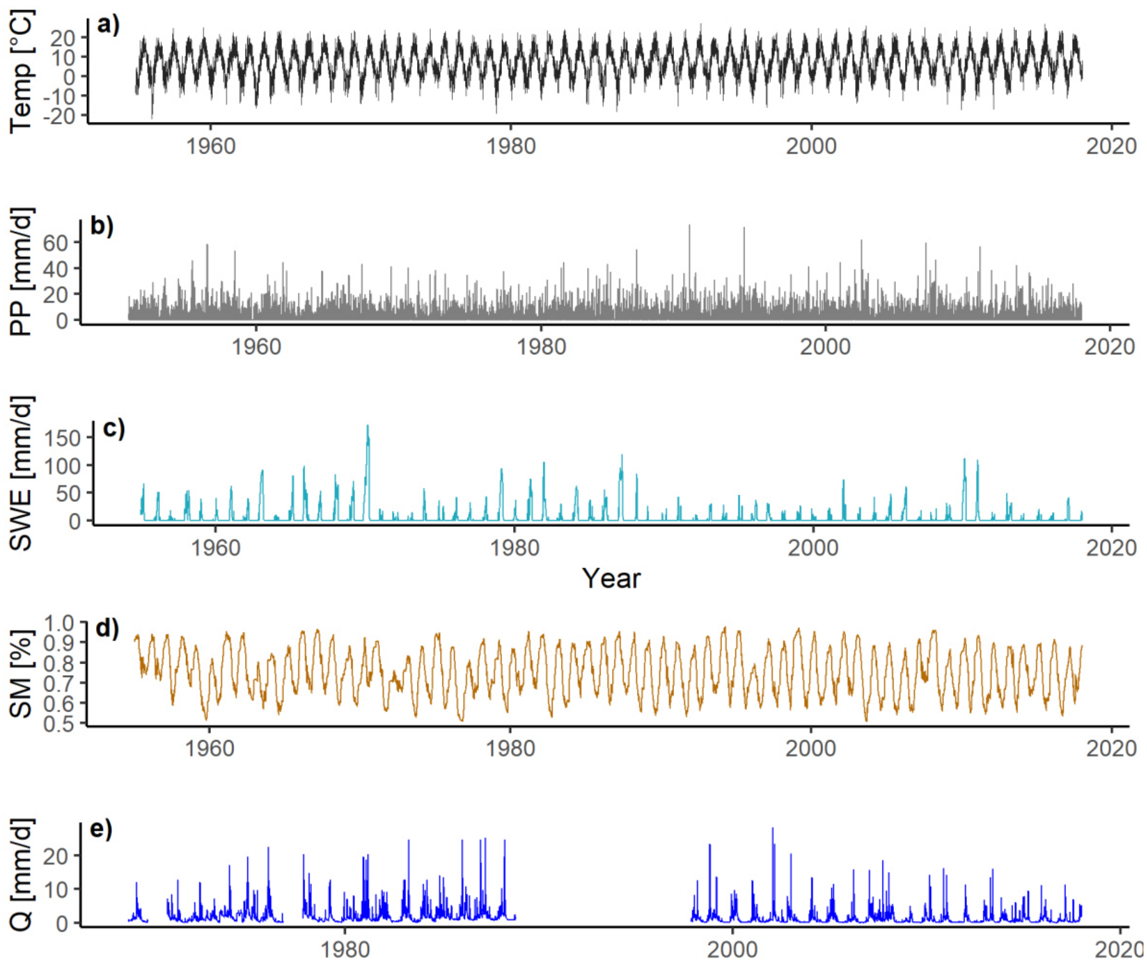

Figure S3. Daily long-term data from the HS catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM).

Silberhütte (SH)

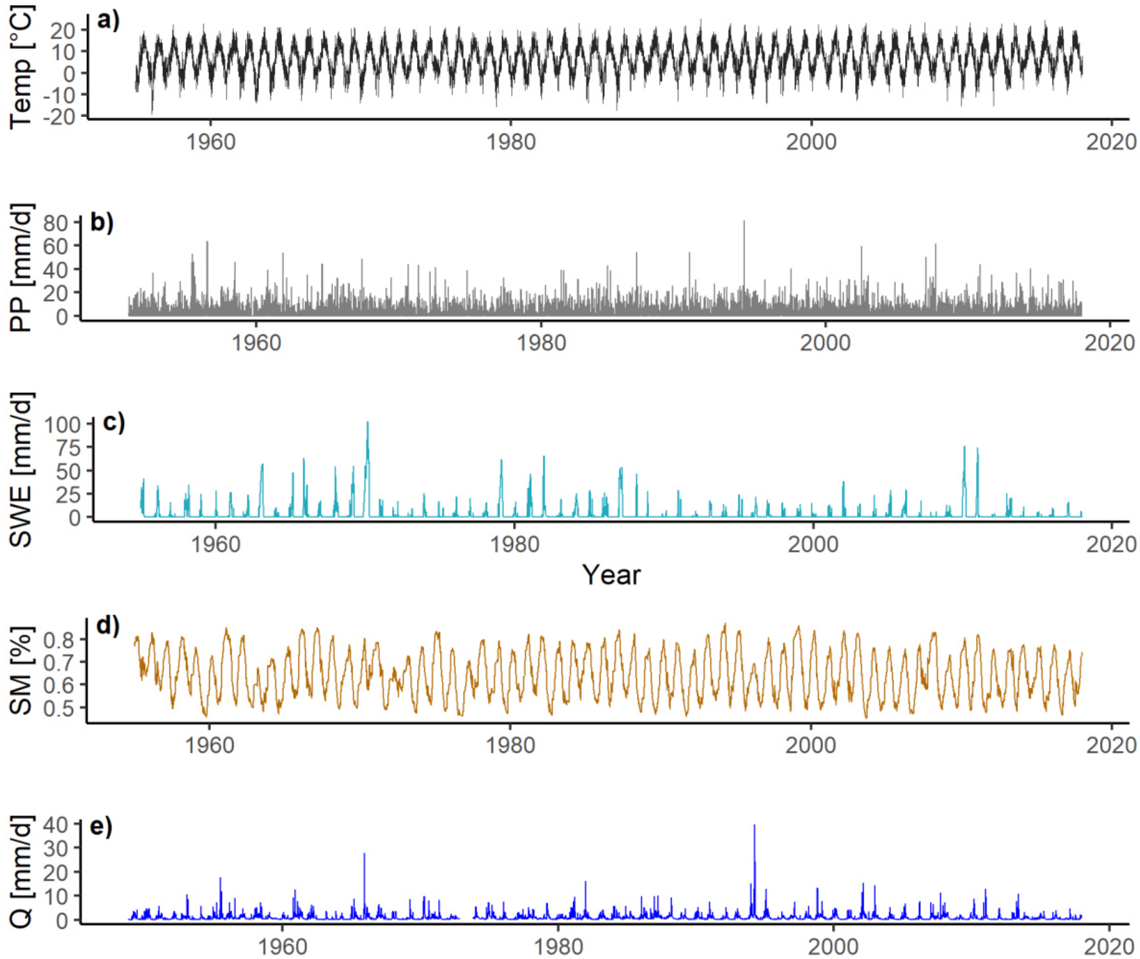

Figure S4. Daily long-term data from the SH catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM).

Meisdorf (MD)

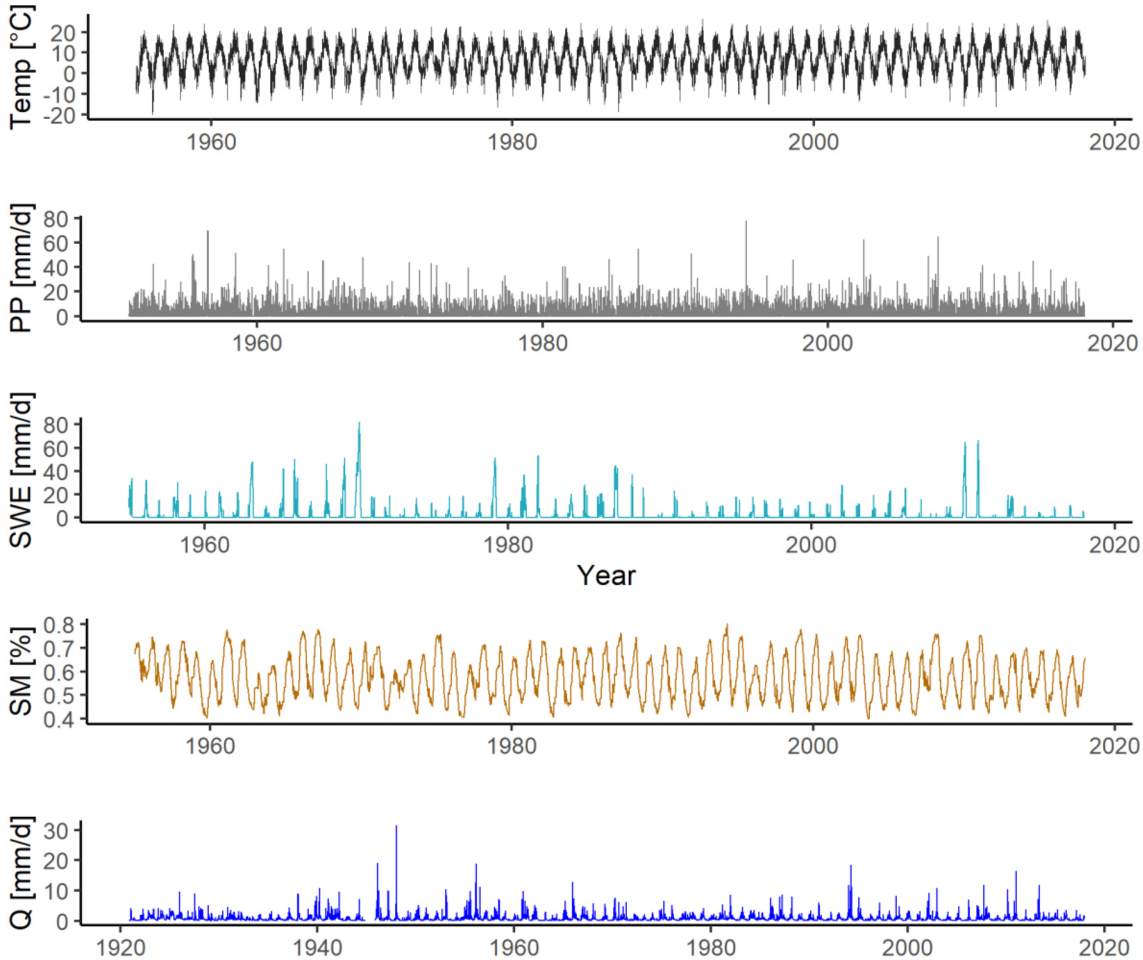

Figure S5. Daily long-term data from the MD catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM).

Hausneindorf (HD)

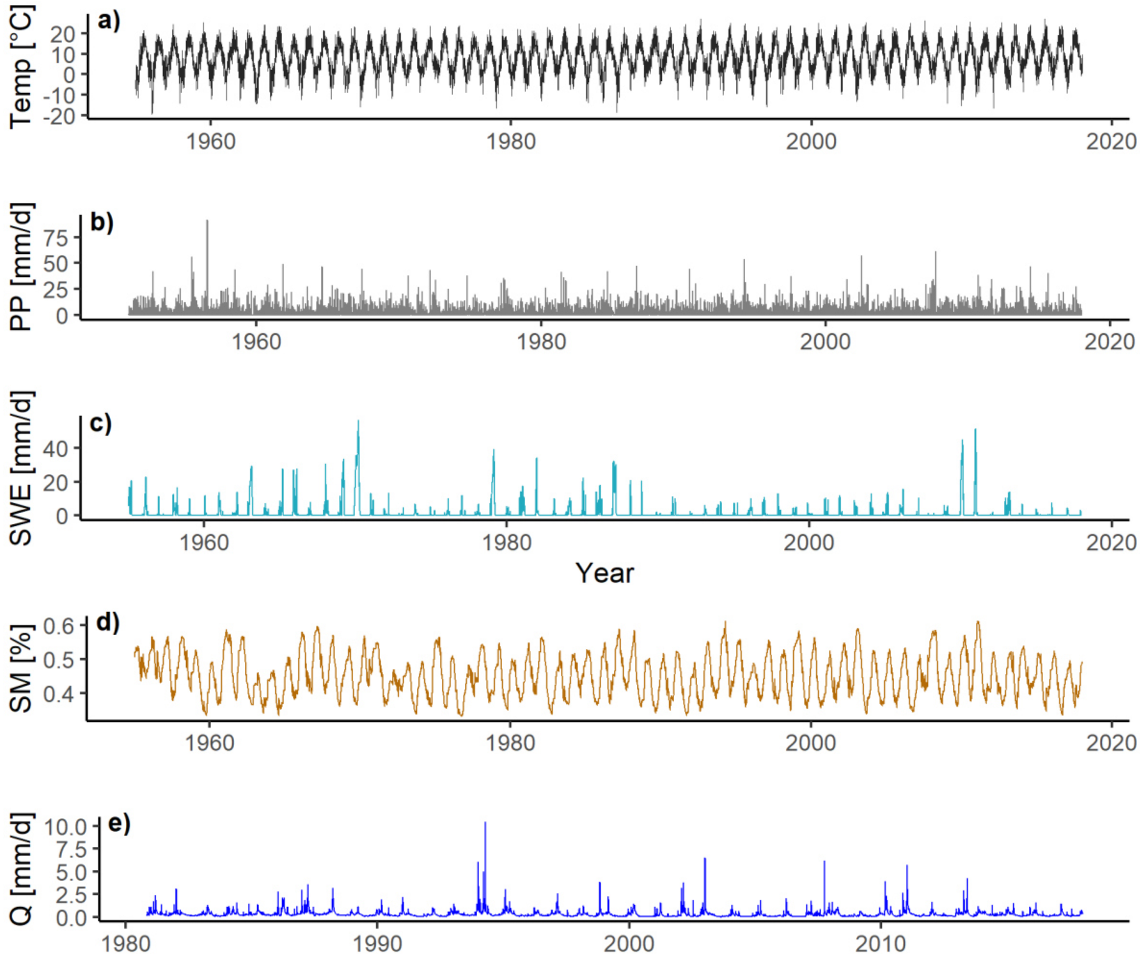

Figure S6. Daily long-term data from the HD catchment, used to identify, characterize and classify runoff events. a) Average daily temperature (Temp), b) precipitation (PP), c) snow water equivalent (SWE), d) soil moisture (SM) and e) specific discharge (Q). Temp, PP and Q were provided by public sources (see data availability statement in the main article), whereas SM and SWE were simulated using the hydrological Mesoscale Model (mHM).

Text S1.

High-frequency data correction and quality control

Continuous high-frequency nitrate concentration data were measured at 15 min intervals using TriOS ProPS-UV sensors. Data for the three Selke sub-catchments (SH, MD, HD) were previously published by Rode et al. (2016), Yang et al. (2018), Winter et al. (2021) and Musolff et al. (2021). A detailed description of the data preparation procedure can be found in Rode et al. (2016); sensor performance was high with an R^2 between 0.80 and 0.91 for the regression of grab samples and sensor-derived concentrations (Figure S7).

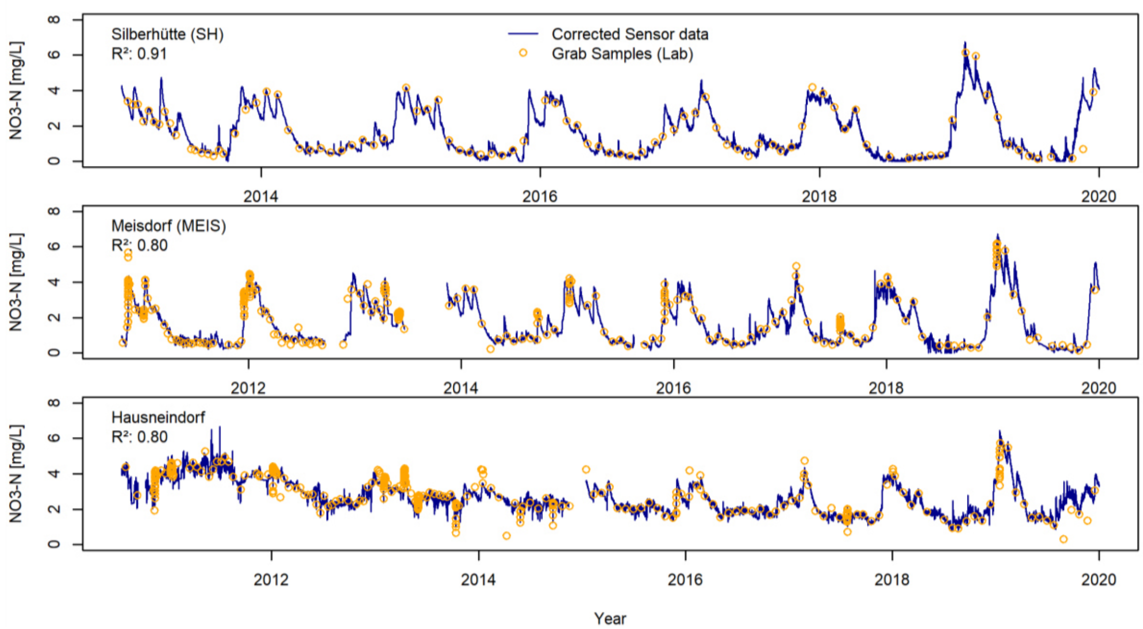

Figure S7. Nitrate concentration data, measured at a temporal resolution of 15 min for the three Selke sub-catchments Silberhütte, Meisdorf and Hausneindorf, depicted as blue lines. Grab samples, analyzed in the laboratory are depicted as orange dots. The coefficient of determination (R^2) given for each sub-catchment represents the agreement between high-frequency data and grab samples.

Data for the Warme Bode (WB) catchment were previously published by Kong et al. (2019) and Musolff et al. (2021). Sensor data for the catchments WB, RB and HS was prepared in 6 steps for this study:

1) NO_3-N concentration were restricted to a realistic range of 0 – 100 mg/L.
2) Outliers were detected and removed applying the Grubbs test (Grubbs, 1950) to a moving window of 100 values, using log-transformed concentration data.
3) A manual correction was applied to remove visual sensor failure, for example before and after sensor maintenance or to remove constant values over several days.
4) A moving average was applied over a 5-hour window to smooth the data.
5) Gap filling was applied for gaps < 2 hours using cubic spline interpolation (similar to Vaughan et al., 2017).

6) The resulting data was calibrated against lab measured grab samples using the average sensor values one hour before and after grab sampling.

After this procedure, sensor performance was high with a R^2 between 0.85 and 0.90 for corrected sensor data vs. grab samples (Figure S8).

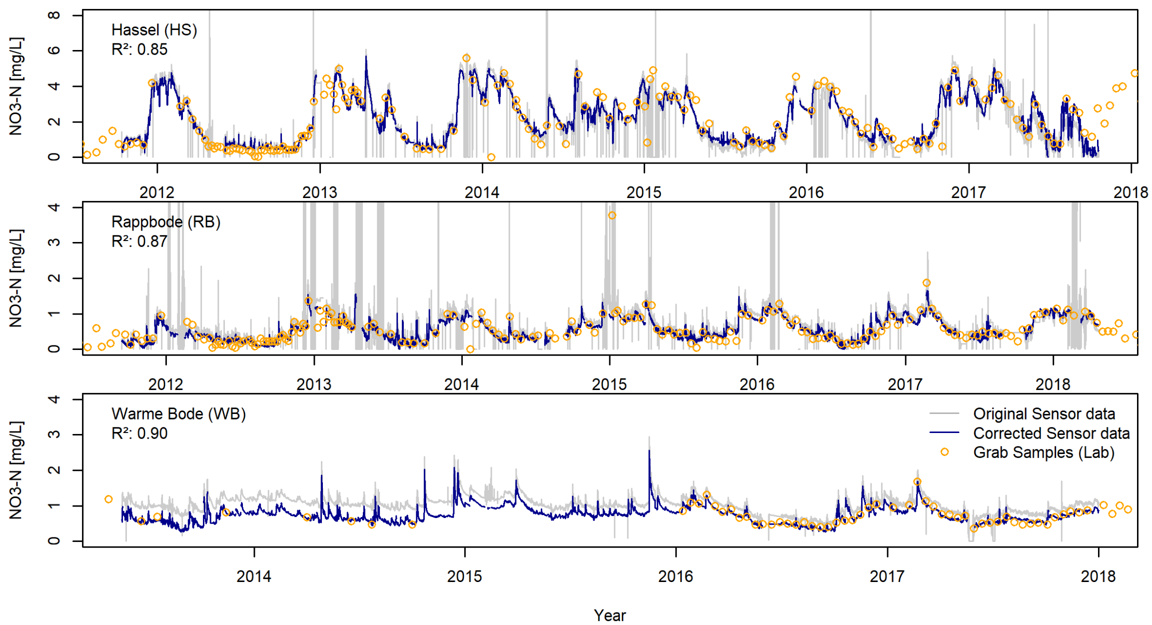

Figure S8. Original and corrected nitrate concentration data, measured at a temporal resolution of 15 min for the three catchments HS, RB and WB, depicted as grey blue lines, respectively. Grab samples analyzed in the laboratory are depicted as orange dots. The coefficient of determination (R^2) given for each catchment represents the agreement between high-frequency data and grab samples.

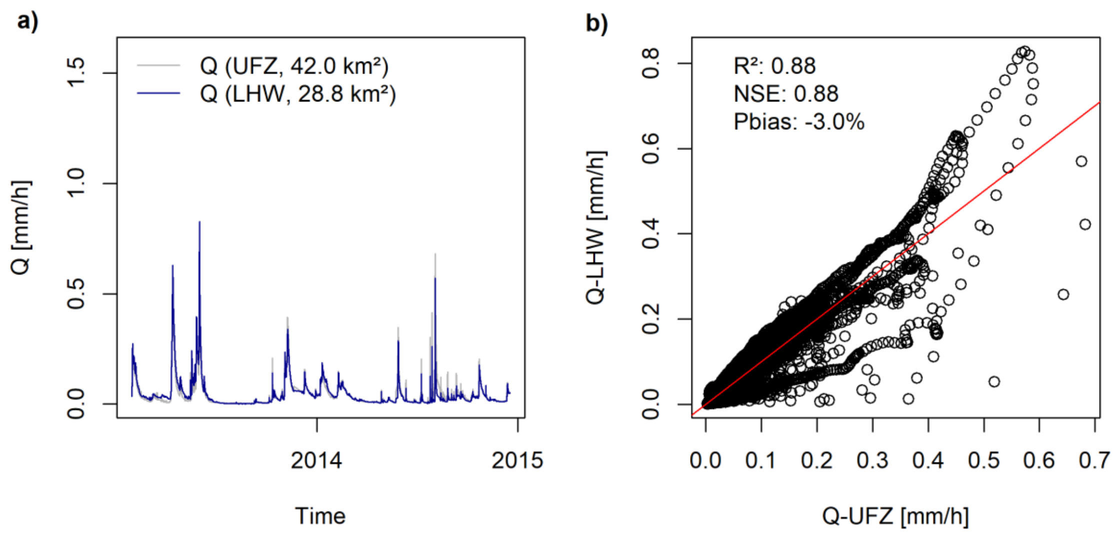

Figure S9. Specific discharge data [mm/h] for the HS catchment, measured between 2013 and 2014 at the same point as nitrate concentration (delineating a catchment area of 42.0 km^2, UFZ in S9a) and discharge data measured by the LHW at an upstream gauging station that delineates a catchment area of 28.8 km^2 and that is available over a longer time period. a) Both discharge times series over the common period of time 2013 – 2014). b) Fit of both area-specific discharge data sets, with the red line depicting the 1:1 line representing a perfect fit.

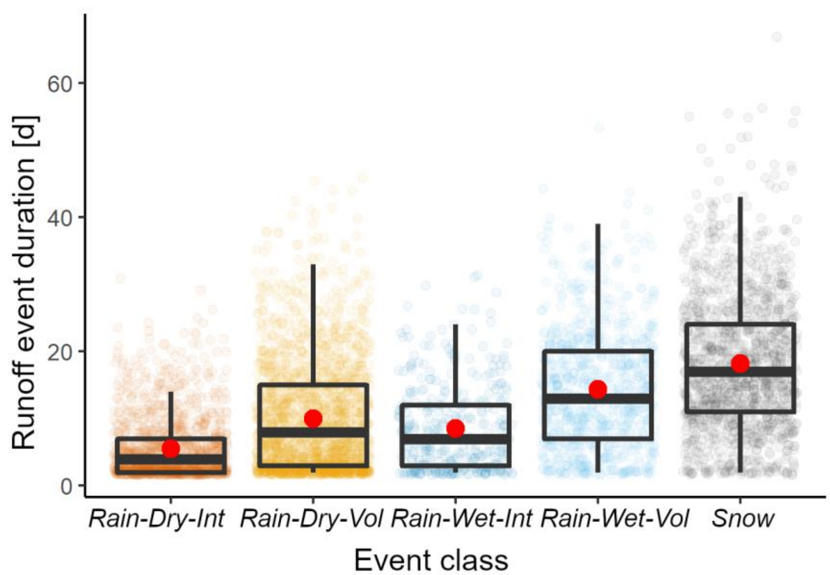

Figure S10. Duration of runoff events in days for all catchments over the long-term time period (1955 - 2018), divided by event classes. Transparent dots show the duration of single events and the colors indicate the event classes. Red dots indicate the average event duration for each event class.

Text S2.

Annual load estimations

Discharge data (Q) over the period of available nitrate concentration data (C) between 2013 and 2017 does not have any gaps and could thus be used for load calculations without further gap filling. In contrast, nitrate concentration data contained data gaps from sensor maintenance and outlier correction, etc. (see text S1). Therefore, for annual load estimations (not event driven loads), we filled all data gaps in C using the linear regression between ln(Q) and ln(C), restricted to positive C values below the 98th percentile of measured C data. With this approach, total loads for the period from 2013 to 2017 were: 297.14 t for WB catchment, 77.02 t for RB, 274.09 t for HS, 312.02 t for SH, 463.61 t for MD and 685.45 t for HD catchment.

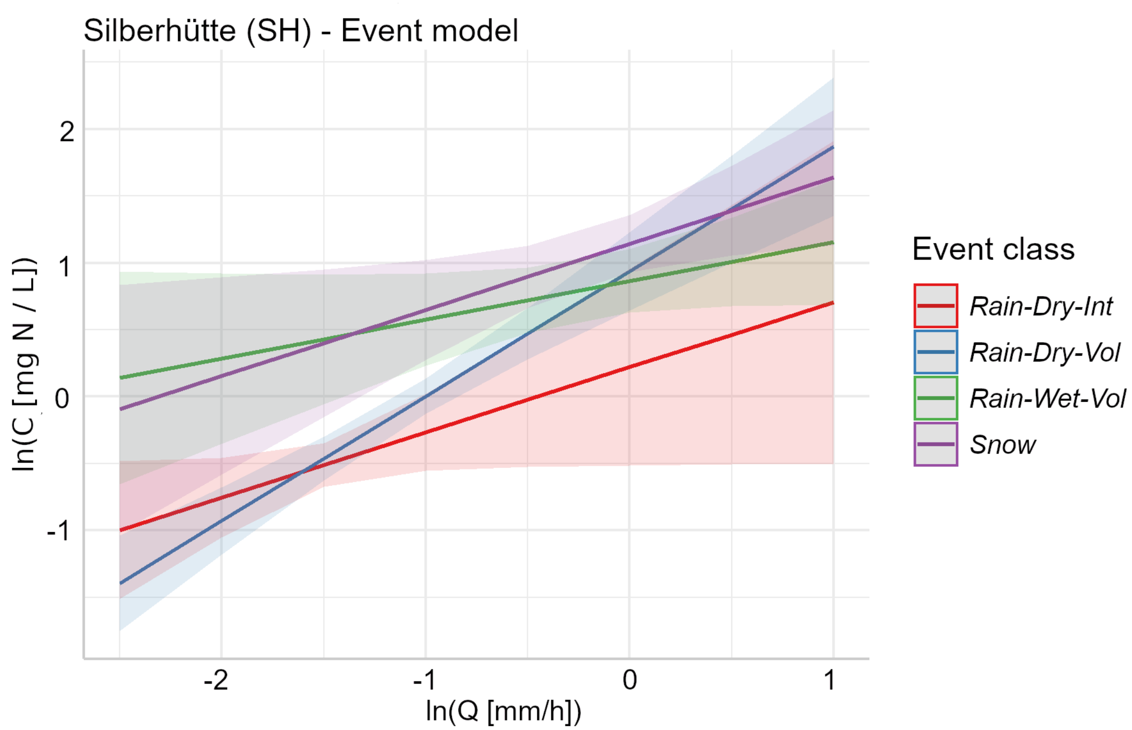

Figure S11. Effect plot for the SH catchment for the linear regression model that includes event classes. Only four out of five event classes are included in the model, because only one *Rain-Wet-Int* event was classified for this catchment and this event class was therefore excluded. The effect plot shows that uncertainty bands for *Rain-Dry* events largely overlap, same as uncertainty bands for *Snow* and *Rain-Wet-Vol* events. For this catchment, the model clearly improved with the addition of event classes (in terms of AICc), which can be explained by the difference between *Rain-Dry* events and *Rain-Wet-Vol* and *Snow* events.

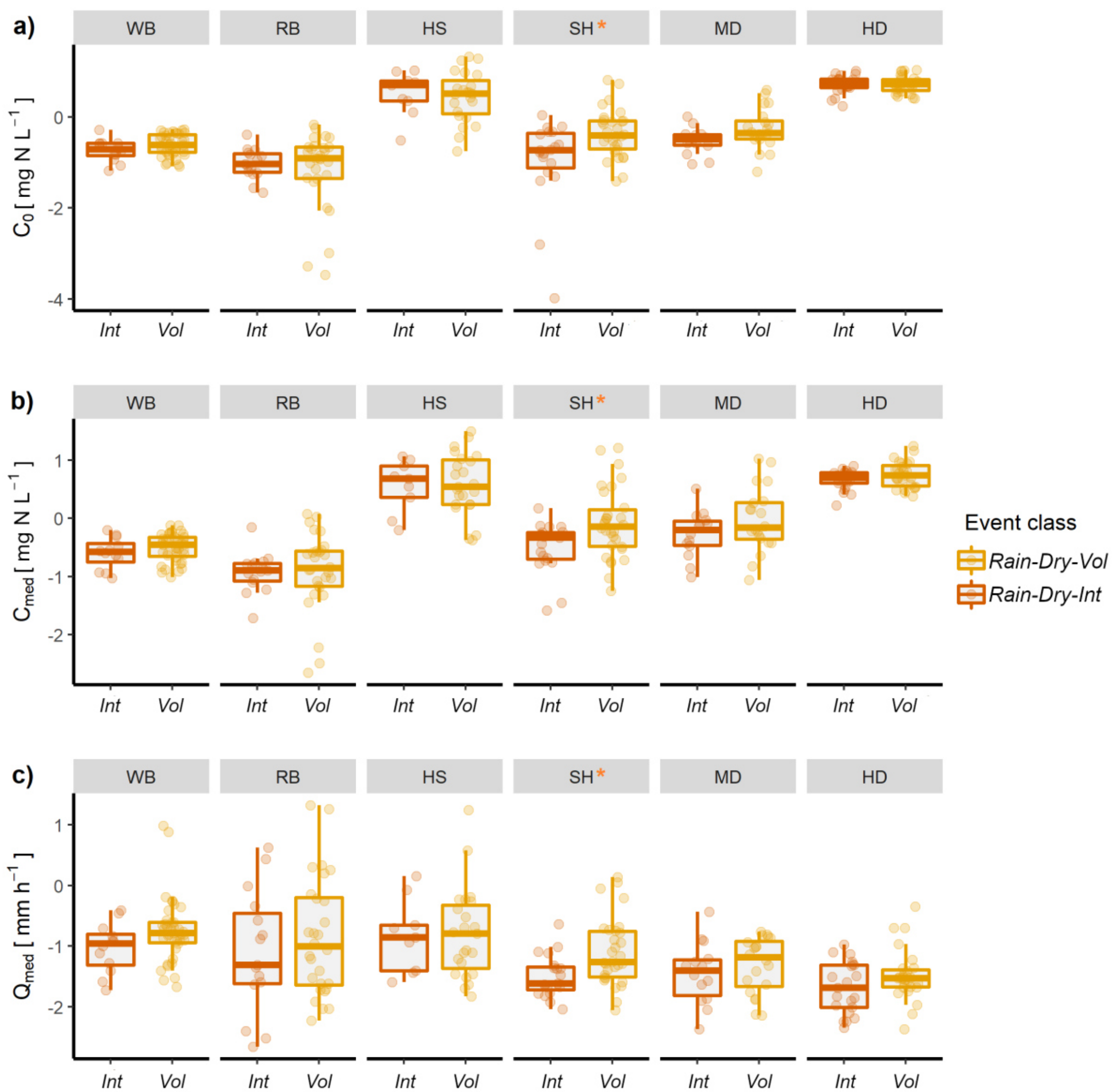

Figure S12. Differences in event characteristics for the Rain-Dry event classes (*Rain-Dry-Int* and *Rain-Dry-Vol*), divided into the six studied catchments (WB, RB, HS, SH, MD, HD). Panel a) shows nitrate concentrations at the start of a runoff event (C_0), panel b) shows median nitrate concentrations (C_{med}) and panel c) shows median discharge (Q_{med}) for each event. No significant differences (p-value < 0.05) could be detected by means of the Kruskal-Wallis rank sum test (Kruskal & Wallis, 1952), except for the SH catchment (indicated by the orange stars), where all variables (C_0, C_{med} and Q_{med}) were significantly higher for the Rain-Dry-Vol events.

Table S1. Tau values (τ) for monotonic long-term trends in runoff event characteristics and the proportion and total number of event classes, calculated via the Mann-Kendall trend test (Kendall, 1998; Mann, 1945).

Catchment	WB		RB		HS		SH		MD		HD	
Proportion of meltwater volume (M_{vol}/P_{vol})												
Winter	-0.10		**-0.13**	*	-0.08		**-0.19**	*	**-0.23**	*	**-0.25**	*
Spring	**-0.25**	*	**-0.20**	*	-0.12		-0.17		**-0.23**	*	**-0.27**	*
Summer	-		-		-		-		-		-	
Autumn	-0.04		0.06		-0.16		0.06		-0.06		-0.09	
Proportion *Snow*/*Rain* events												
Winter	-0.03		-0.18		-0.15		-0.16		**-0.20**	*	-0.07	
Spring	**-0.25**	*	**-0.23**	*	-0.16		-0.14		**-0.18**	*	-0.10	
Summer												
Autumn	-0.02		0.05		-0.20		-0.03		-0.11		-0.26	
Number of *Snow* events												
Winter	0.07		0.04		0.07		-0.01		-0.10		-0.08	
Spring	**-0.26**	*	**-0.22**	*	-0.19		**-0.21**	*	**-0.24**	*	-0.14	
Summer												
Autumn	0.00		0.05		-0.16		-0.03		-0.09		-0.26	
Antecedent soil moisture (SM_{ant})												
Winter	0.05		0.08		-0.02		-0.09		-0.07		**0.20**	
Spring	**-0.19**	*	-0.03		0.09		-0.13		**-0.18**	*	-0.08	
Summer	**-0.23**	*	**-0.18**	*	-0.03		-0.14		-0.13		-0.06	
Autumn	-0.12		-0.09		0.05		-0.04		0.00		0.15	
Proportion Rain-Wet/Rain-Dry events												
Winter	0.15		0.04		0.05		-0.03		-0.06		0.13	
Spring	-0.10		-0.04		0.05		-0.13		-0.19		-0.16	
Summer	**-0.29**	*	-0.04		-0.03		**-0.22**	*	**-0.23**	*	-0.16	
Autumn	-0.12		0.13		0.11		-0.05		0.03		0.23	
Number of Rain-Wet events												
Winter	0.04		0.08		0.07		-0.01		0.00		0.26	
Spring	0.07		0.15		0.01		-0.06		-0.06		-0.19	
Summer	**-0.31**	*	-0.03		-0.03		**-0.26**	*	**-0.24**	*	-0.15	
Autumn	-0.12		0.14		0.11		-0.05		0.04		0.23	
P_{max}/P_{vol}												
Winter	0.10		0.14		0.15		0.15		**0.19**	*	0.07	
Spring	0.12		**0.27**	*	0.00		0.00		0.00		0.00	
Summer	-0.05		**0.22**	*	0.14		**0.20**	*	**0.18**	*	-0.02	
Autumn	-0.01		-0.12		0.03		-0.03		-0.11		0.10	
Proportion Intensity-dominated/Volume-dominated												
Winter	-0.05		0.11		0.21		0.07		0.14		0.05	
Spring	-0.10		0.08		0.10		-0.01		-0.04		0.07	
Summer	**-0.22**	*	0.14		0.05		-0.07		0.06		-0.12	
Autumn	0.07		-0.11		-0.06		-0.03		-0.07		0.04	
Number of Intensity-dominated events												
Winter	-0.42		0.11		0.25		0.08		0.14		0.06	
Spring	0.00		0.15		0.12		-0.03		0.01		0.01	
Summer	**-0.21**	*	0.15		0.00		-0.11		0.01		-0.12	
Autumn	0.08		-0.44		0.09		-0.02		-0.01		0.09	

Note. Positive or negative τ-values indicate a positive or negative trend, respectively. Values printed in bold with an asterisks indicate a significant trend (p-value < 0.05), according to the Mann-Kendall tend test.

Table S2. Runoff event characteristics for all 5872 events from daily long-term data (1955 – 2018) are available under http://www.hydroshare.org/resource/8409b4a5d40541b684d4bdafc0b16b43.

Table S3. Runoff event characteristics for all 388 events from hourly data including nitrate concentration data (2013 – 2017) are available under http://www.hydroshare.org/resource/8409b4a5d40541b684d4bdafc0b16b43.

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Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., & Fleckenstein, J. H. (2021). Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales. *Water Resources Research*, *57*(1), e2020WR027992. https://doi.org/10.1029/2020WR027992

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List of Publications

Publications Included in this Thesis

Winter, C., Nguyen, V. T., Musolff, An., Lutz, S., Rode, M., Kumar, R., and Fleckenstein, J. H.: Droughts can reduce the nitrogen retention capacity of catchments, Hydrology and Earth System Sciences, 27(1), https://doi.org/10.5194/hess-27-303-2023, 2022.

Winter, C., Tarasova, L., Lutz, S. R., Musolff, A., Kumar, R., and Fleckenstein, J. H.: Explaining the Variability in High-Frequency Nitrate Export Patterns Using Long-Term Hydrological Event Classification, Water Resour. Res., 58, e2021WR030938, https://doi.org/10.1029/2021WR030938, 2022.

Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., and Fleckenstein, J. H.: Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales, Water Resour. Res., 57, e2020WR027992, https://doi.org/10.1029/2020WR027992, 2021.

Publications Not Included in this Thesis

Schnabel, F., Donoso, P. J., and **Winter, C.**: Short-term effects of single-tree selection cutting on stand structure and tree species composition in Valdivian rainforests of Chile, N. Z. J. For. Sci., 47, 21, https://doi.org/10.1186/s40490-017-0103-5, 2017.

(Eidesstattliche) Versicherungen und Erklärungen

(§ 8 Satz 2 Nr. 3 PromO Fakultät)

Hiermit versichere ich eidesstattlich, dass ich die Arbeit selbstständig verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe (vgl. Art. 64 Abs. 1 Satz 6 BayHSchG).

(§ 8 Satz 2 Nr. 3 PromO Fakultät)

Hiermit erkläre ich, dass ich die Dissertation nicht bereits zur Erlangung eines akademischen Grades eingereicht habe und dass ich nicht bereits diese oder eine gleichartige Doktorprüfung endgültig nicht bestanden habe.

(§ 8 Satz 2 Nr. 4 PromO Fakultät)

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