Water Resources Research

RESEARCH ARTICLE
10.1029/2021WR030938

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

C. Winter[1], L. Tarasova[2], S. R. Lutz[1,3], A. Musolff[1], R. Kumar[4], and J. H. Fleckenstein[1,5]

[1]Department for Hydrogeology, Helmholtz Centre for Environmental Research-UFZ, Leipzig, Germany, [2]Department for Catchment Hydrology, Helmholtz Centre for Environmental Research-UFZ, Leipzig, Germany, [3]Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, The Netherlands, [4]Department of Computational Hydrosystems, Helmholtz Centre for Environmental Research-UFZ, Leipzig, Germany, [5]Hydrologic Modelling Unit, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany

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.

Correspondence to:

C. Winter,
carolin.winter@ufz.de

Citation:

Winter, C., Tarasova, L., Lutz, S. R., Musolff, A., Kumar, R., & Fleckenstein, J. H. (2022). Explaining the variability in high-frequency nitrate export patterns using long-term hydrological event classification. *Water Resources Research*, *58*, e2021WR030938. https://doi.org/10.1029/2021WR030938

Received 29 JUL 2021
Accepted 6 JAN 2022

Author Contributions:

Conceptualization: C. Winter, L. Tarasova, S. R. Lutz, A. Musolff
Data curation: C. Winter, R. Kumar
Formal analysis: C. Winter, L. Tarasova
Funding acquisition: J. H. Fleckenstein
Investigation: C. Winter
Methodology: C. Winter, L. Tarasova
Project Administration: J. H. Fleckenstein
Supervision: S. R. Lutz, A. Musolff, J. H. Fleckenstein
Validation: C. Winter

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

Visualization: C. Winter
Writing – original draft: C. Winter
Writing – review & editing: C. Winter, L. Tarasova, S. R. Lutz, A. Musolff, R. Kumar, J. H. Fleckenstein

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).

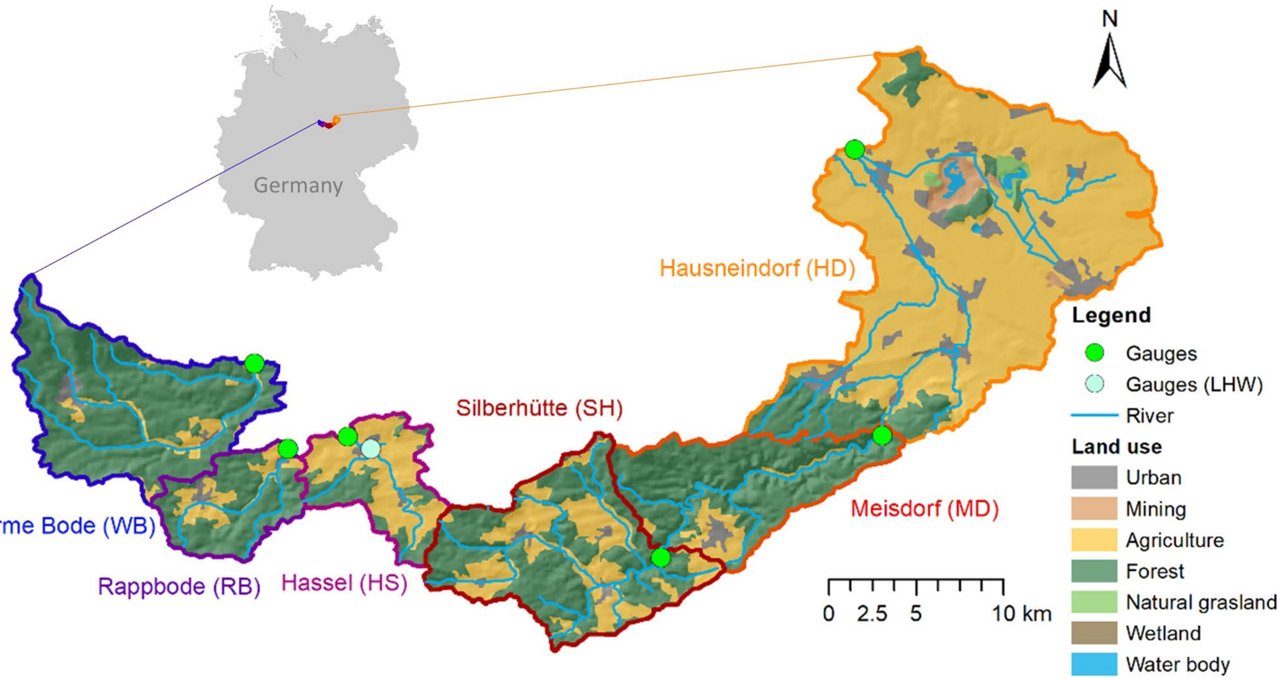

Figure 1. Map of the study site, showing all six mesoscale catchments (WB, RB, HS, SH, MD, and HD) with their respective land use.

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				Elevation range	Mean slope
				Agriculture	Forest	Urban	Other		
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*

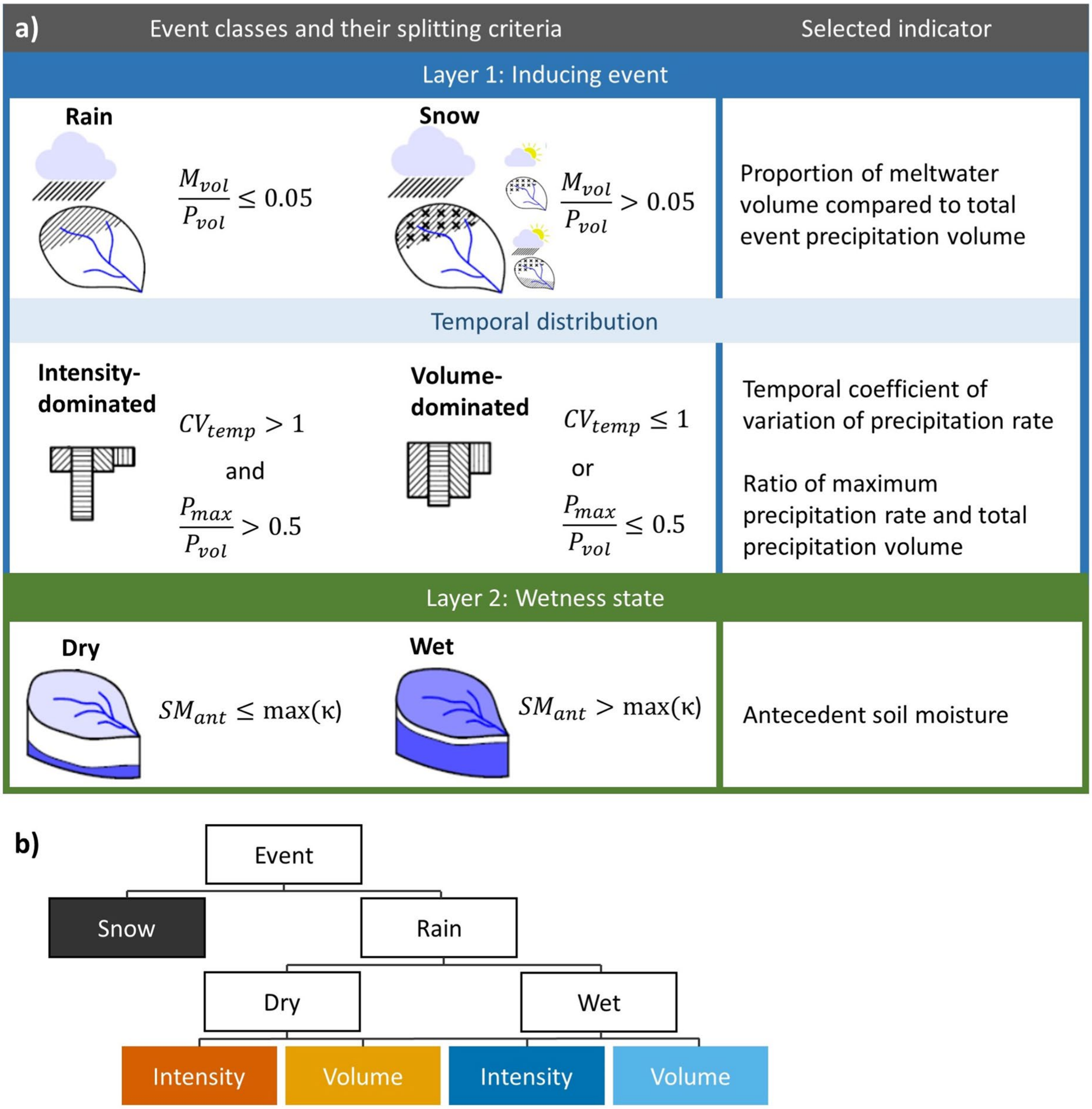

Figure 2. (a) Event characteristics and thresholds for the classification of events. Threshold for the wetness state of the catchments is defined by the maximum of *κ*, which represents the catchment-specific curvature of the nonlinear relationship between event runoff coefficients and soil moisture. (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%

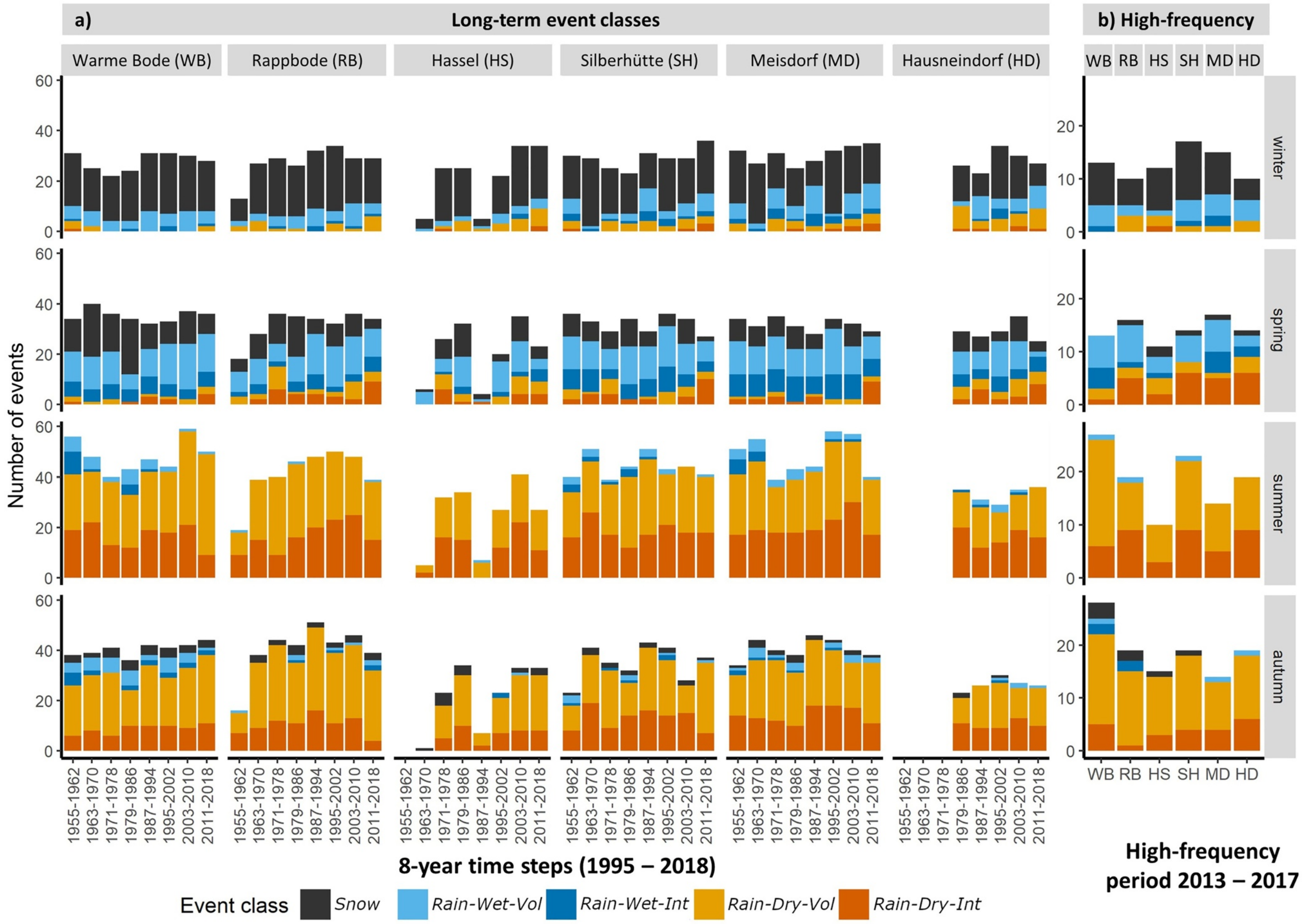

Figure 3. Seasonal absolute frequency of event classes (*y*-axis) in the six study catchments, showing (a) long-term changes between 8-year periods from 1955 until 2018 and (b) the period of high-frequency data from 2013 until 2017. Periods in panel (a) with no or very few events in HS and HD indicate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

10.1029/2021WR030938

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).

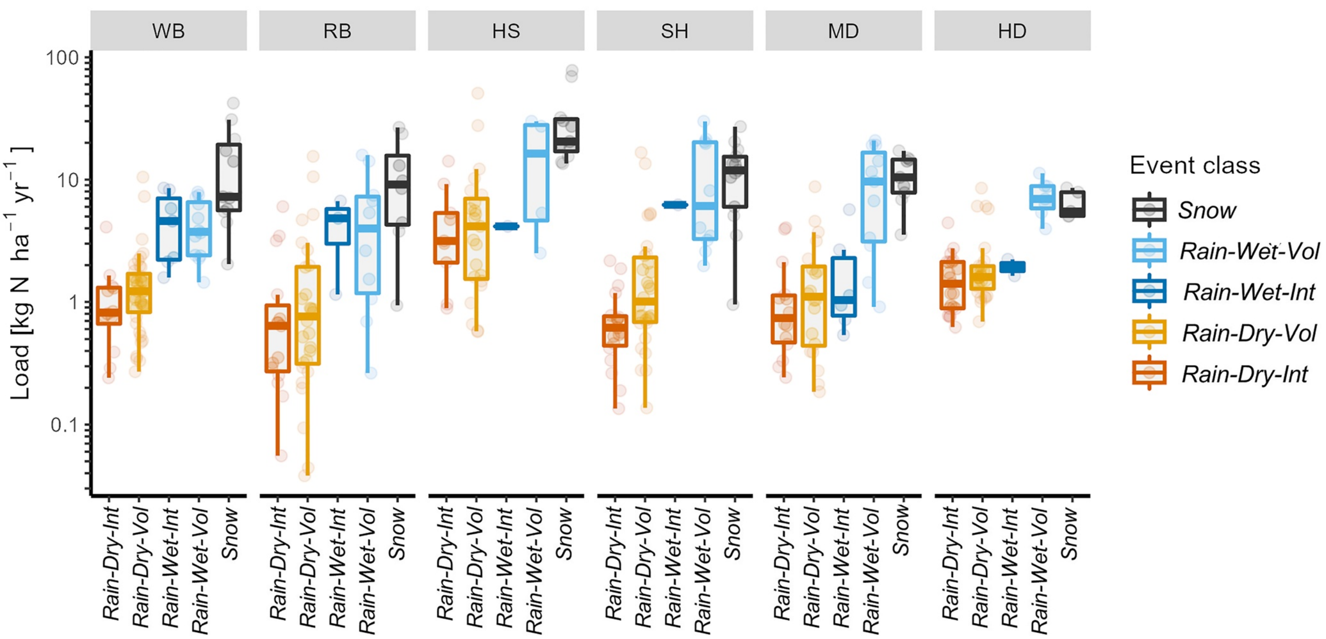

Figure 4. Nitrate loads per area (on logarithmic scale) transported during runoff events, divided into catchments and runoff event classes.

10.1029/2021WR030938

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.

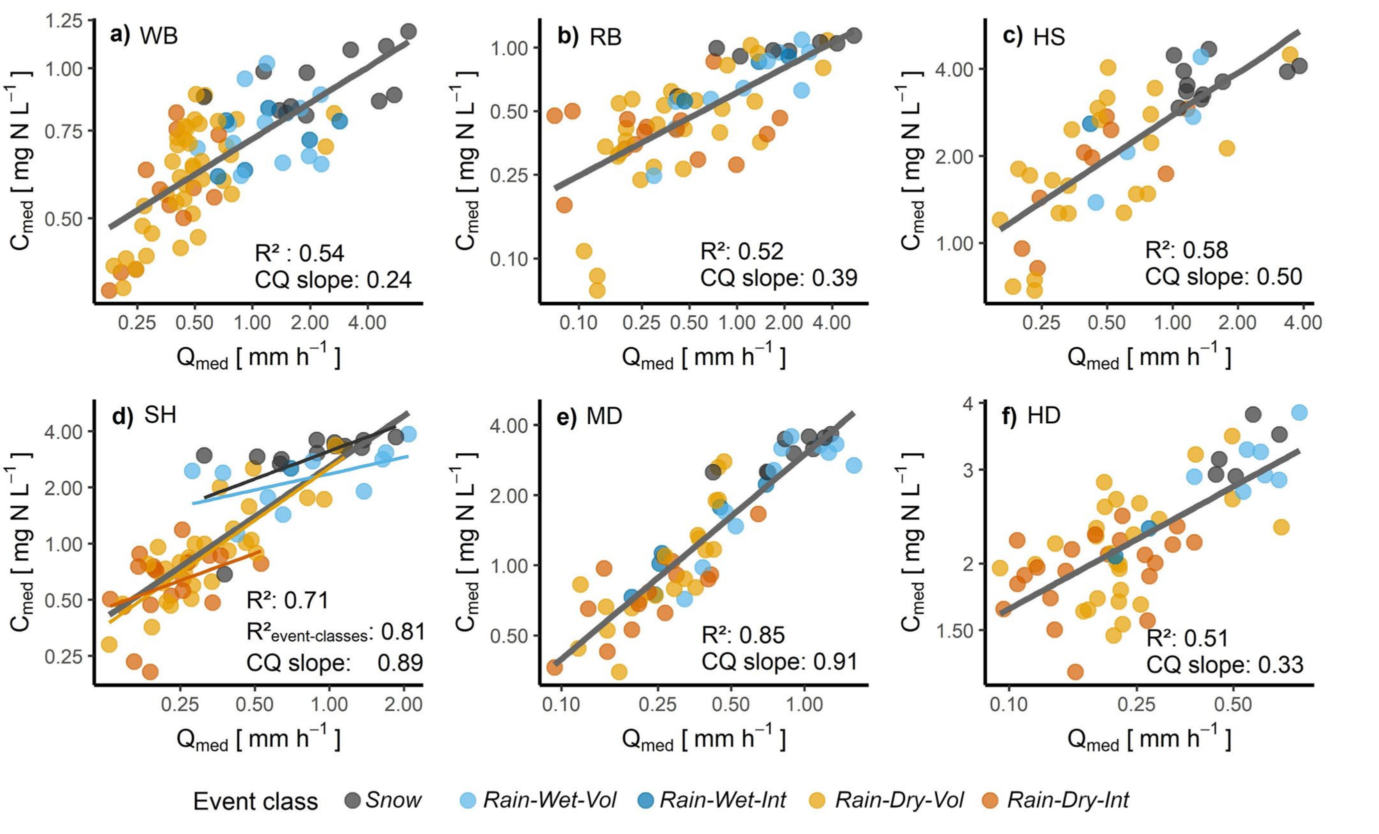

Figure 5. Median discharge (Q_{med}) and nitrate concentrations (C_{med}) for each runoff event with log-scale *x*- and *y*-axis, separated into the six catchments (a–f). Colors indicate the five different event classes, gray lines show the linear relationship between ln(C_{med}) and ln(Q_{med}) and 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)).

10.1029/2021WR030938

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

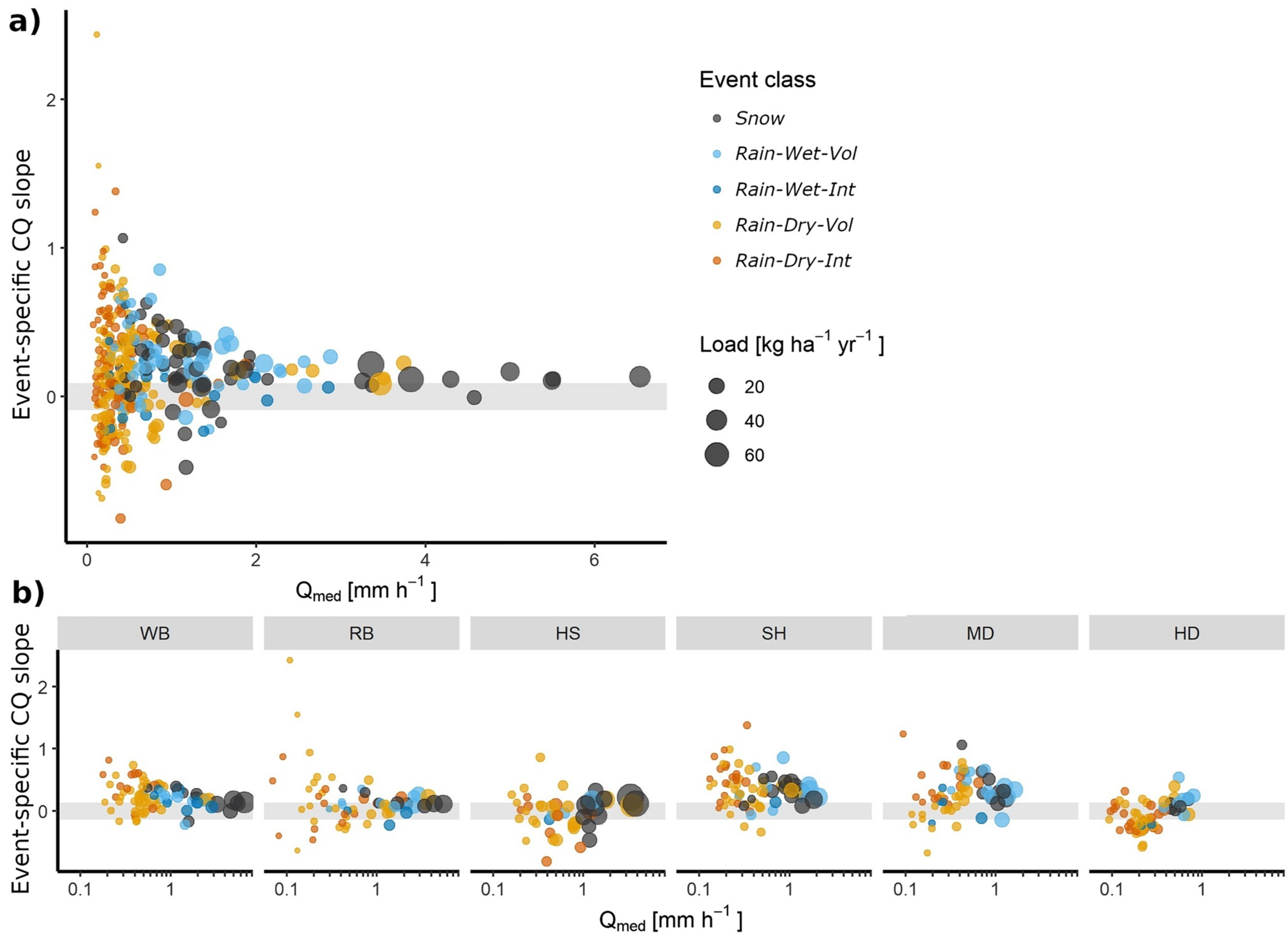

Figure 6. Event-specific CQ slopes (slope of nitrate concentrations and discharge in the log-log space) against the specific median discharge (Q_{med}) of each event shown for all catchments in one plot (a) and with logarithmic *x*-axis and separated by catchments to visualize differences in events with 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).

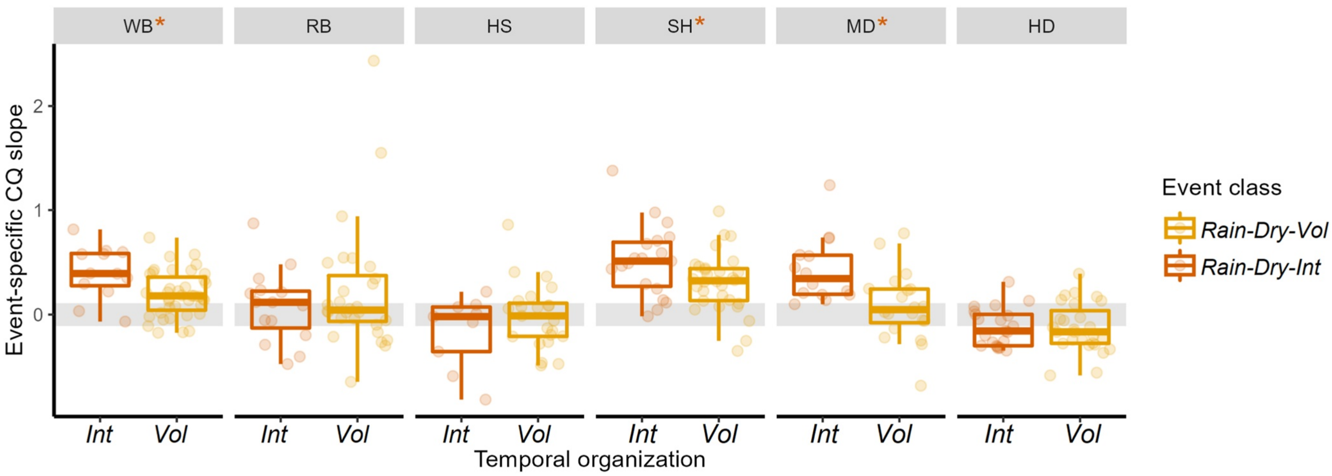

Figure 7. Event-specific CQ slopes (slope between nitrate concentrations and discharge in the log-log space) for all six study catchments and the two event classes Rain-Dry-Int and Rain-Dry-Vol, representing rain-induced runoff events that occurred under dry antecedent soil moisture conditions with either 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

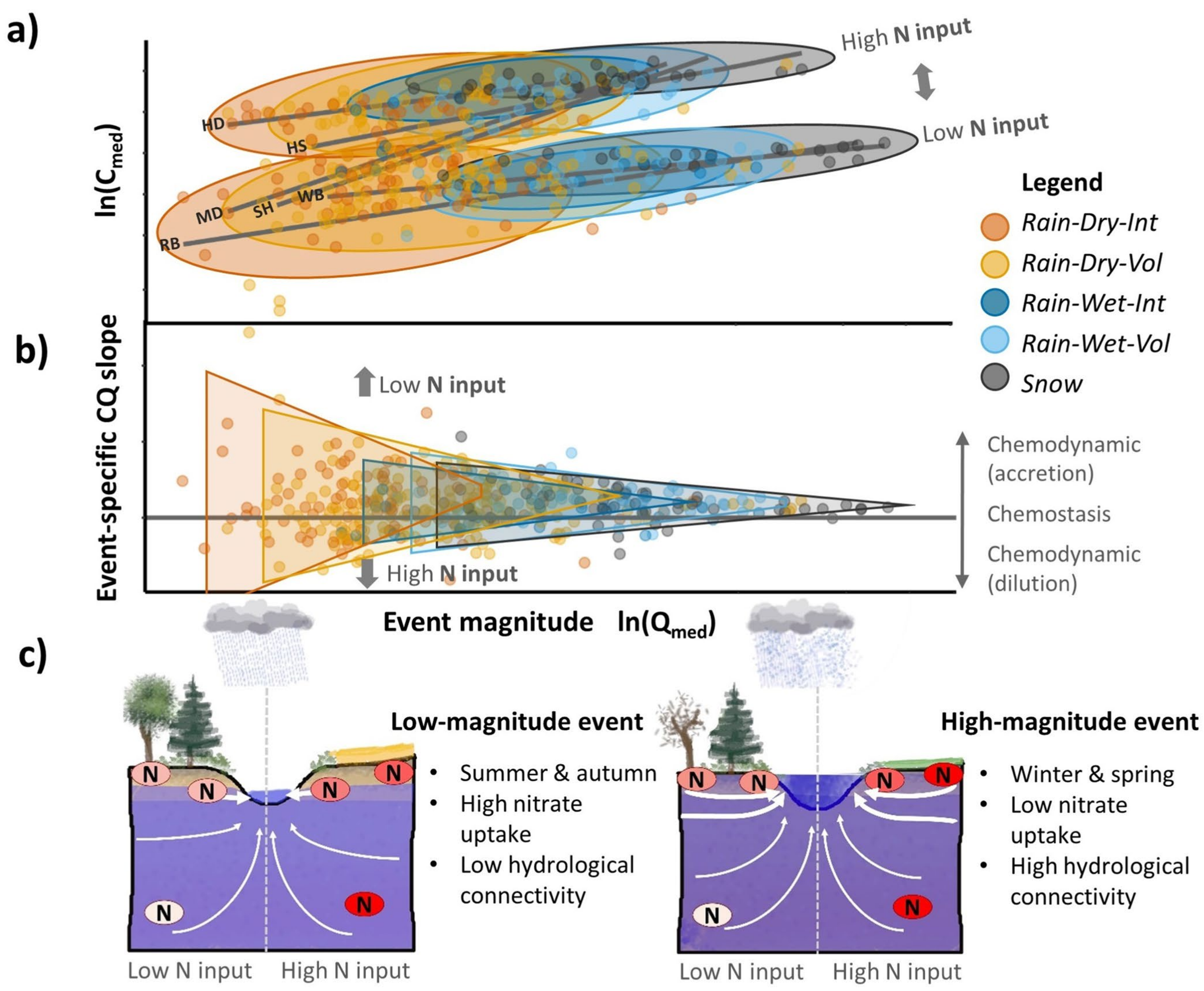

Figure 8. Framework of the relationship between runoff event classification and nitrate export characteristics. (a) The inter-event CQ relationship with median event-scale nitrate concentrations and discharge (C_{med} and Q_{med}). Gray lines show the inter-event CQ slope for the individual catchments 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.

Acknowledgments

Funding for this study was provided by the Helmholtz Research Program, Topic 5 Landscapes of the Future, subtopic 5.2 Water resources and the environment and by the Helmholtz International Research School TRACER (HIRS-0017). The authors cordially thank the State Office of Flood Protection and Water Quality of Saxony-Anhalt (LHW) for the provision of discharge data and Germany's National Meteorological Service (Deutscher Wetterdienst, DWD) for the provision of meteorological data sets. Furthermore, the authors thank Michael Rode, Karsten Rinke, Xiangzhen Kong, and Kurt Friese for the provision of high-frequency and lab data from TERENO observational facilities.

References

Akaike, H. (1973). Maximum likelihood identification of Gaussian autoregressive moving average models. *Biometrika*, *60*(2), 255–265. https://doi.org/10.2307/2334537

Baird, D., Ulanowicz, R. E., & Boynton, W. R. (1995). Seasonal nitrogen dynamics in Chesapeake Bay: A network approach. *Estuarine, Coastal, and Shelf Science*, *41*(2), 137–162. https://doi.org/10.1006/ecss.1995.0058

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. *Geophysical Research Letters*, *37*(23). https://doi.org/10.1029/2010GL045168

Berghuijs, W. R., Harrigan, S., Molnar, P., Slater, L. J., & Kirchner, J. W. (2019). The relative importance of different flood-generating mechanisms across Europe. *Water Resources Research*, *55*(6), 4582–4593. https://doi.org/10.1029/2019WR024841

Bieroza, M. Z., Heathwaite, A. L., Bechmann, M., Kyllmar, K., & Jordan, P. (2018). The concentration-discharge slope as a tool for water quality management. *Science of the Total Environment*, *630*, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256

Blaen, P. J., Khamis, K., Lloyd, C., Comer-Warner, S., Ciocca, F., Thomas, R. M., et al. (2017). High-frequency monitoring of catchment nutrient exports reveals highly variable storm event responses and dynamic source zone activation. *Journal of Geophysical Research: Biogeosciences*, *122*(9), 2265–2281. https://doi.org/10.1002/2017JG003904

Bowes, M. J., Jarvie, H. P., Halliday, S. J., Skeffington, R. A., Wade, A. J., Loewenthal, M., et al. (2015). Characterizing phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships. *Science of the Total Environment*, *511*, 608–620. https://doi.org/10.1016/j.scitotenv.2014.12.086

Briffa, K. R., van der Schrier, G., & Jones, P. D. (2009). Wet and dry summers in Europe since 1750: Evidence of increasing drought. *International Journal of Climatology*, *29*(13), 1894–1905. https://doi.org/10.1002/joc.1836

Burns, D. A., Pellerin, B. A., Miller, M. P., Capel, P. D., Tesoriero, A. J., & Duncan, J. M. (2019). Monitoring the riverine pulse: Applying high-frequency nitrate data to advance integrative understanding of biogeochemical and hydrological processes. *Wiley Interdisciplinary Reviews: Water*, *6*(4), e1348. https://doi.org/10.1002/wat2.1348

Carey, R. O., Wollheim, W. M., Mulukutla, G. K., & Mineau, M. M. (2014). Characterizing storm-event nitrate fluxes in a fifth order suburbanizing watershed using in situ sensors. *Environmental Science & Technology*, *48*(14), 7756–7765. https://doi.org/10.1021/es500252j

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, *8*(3), 559–568. https://doi.org/10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2

Casson, N. J., Eimers, M. C., & Buttle, J. M. (2010). The contribution of rain-on-snow events to nitrate export in the forested landscape of south-central Ontario, Canada. *Hydrological Processes*, *24*(14), 1985–1993. https://doi.org/10.1002/hyp.7692

Casson, N. J., Eimers, M. C., & Watmough, S. A. (2014). Sources of nitrate export during rain-on-snow events at forested catchments. *Biogeochemistry*, *120*(1), 23–36. https://doi.org/10.1007/s10533-013-9850-4

Clow, D. W. (2010). Changes in the timing of snowmelt and streamflow in Colorado: A response to recent warming. *Journal of Climate*, *23*(9), 2293–2306. https://doi.org/10.1175/2009JCLI2951.1

Crossman, J., Catherine Eimers, M., Casson, N. J., Burns, D. A., Campbell, J. L., Likens, G. E., et al. (2016). Regional meteorological drivers and long term trends of winter-spring nitrate dynamics across watersheds in northeastern North America. *Biogeochemistry*, *130*(3), 247–265. https://doi.org/10.1007/s10533-016-0255-z

Dupas, R., Abbott, B. W., Minaudo, C., & Fovet, O. (2019). Distribution of landscape units within catchments influences nutrient export dynamics. *Frontiers in Environmental Science*, *7*, 43. https://doi.org/10.3389/fenvs.2019.00043

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and controls of riverine nutrient export across German catchments. *Water Resources Research*, *57*(4), e2020WR028134. https://doi.org/10.1029/2020WR028134

Ehrhardt, S., Kumar, R., Fleckenstein, J. H., Attinger, S., & Musolff, A. (2019). Trajectories of nitrate input and output in three nested catchments along a land use gradient. *Hydrology and Earth System Sciences*, *23*(9), 3503–3524. https://doi.org/10.5194/hess-23-3503-2019

Elser, J. J. (2011). A world awash with nitrogen. *Science*, *334*(6062), 1504–1505. https://doi.org/10.1126/science.1215567

Fovet, O., Humbert, G., Dupas, R., Gascuel-Odoux, C., Gruau, G., Jaffrézic, A., et al. (2018). Seasonal variability of stream water quality response to storm events captured using high-frequency and multi-parameter data. *Journal of Hydrology*, *559*, 282–293. https://doi.org/10.1016/j.jhydrol.2018.02.040

Godsey, S. E., Hartmann, J., & Kirchner, J. W. (2019). Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. *Hydrological Processes*, *33*(24), 3056–3069. https://doi.org/10.1002/hyp.13554

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, *23*(13), 1844–1864. https://doi.org/10.1002/hyp.7315

Grubbs, F. E. (1950). Sample criteria for testing outlying observations. *The Annals of Mathematical Statistics*, 27–58.

Hari, V., Rakovec, O., Markonis, Y., Hanel, M., & Kumar, R. (2020). Increased future occurrences of the exceptional 2018–2019 Central European drought under global warming. *Scientific Reports*, *10*(1), 1–10. https://doi.org/10.1038/s41598-020-68872-9

Hartmann, A. A., Barnard, R. L., Marhan, S., & Niklaus, P. A. (2013). Effects of drought and N-fertilization on N cycling in two grassland soils. *Oecologia*, *171*(3), 705–717. https://doi.org/10.1007/s00442-012-2578-3

Heathwaite, A. L., & Bieroza, M. (2021). Fingerprinting hydrological and biogeochemical drivers of freshwater quality. *Hydrological Processes*, *35*(1), e13973. https://doi.org/10.1002/hyp.13973

Holm, S. (1979). A simple sequentially rejective multiple test procedure. *Scandinavian Journal of Statistics*, *6*(2), 65–70. https://www.jstor.org/stable/4615733

Hurvich, C. M., & Tsai, C.-L. (1989). Regression and time series model selection in small samples. *Biometrika*, *76*(2), 297–307. https://doi.org/10.1093/biomet/76.2.297

Inamdar, S. P., O'Leary, N., Mitchell, M. J., & Riley, J. T. (2006). The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. *Hydrological Processes*, *20*(16), 3423–3439. https://doi.org/10.1002/hyp.6141

IPCC. (2013). *Climate change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, et al. (Eds.)]. Cambridge University Press.

IPCC. (2014). Climate Change 2014. In *Mitigation of climate change*. *Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press.

IPCC. (2018). *Global warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty* [V. Masson-Delmotte, P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P. R. Shukla, et al. (Eds.)]. In Press.

Jarvie, H. P., Neal, C., Withers, P. J., Robinson, A., & Salter, N. (2003). Nutrient water quality of the Wye catchment, UK: Exploring patterns and fluxes using the Environment Agency data archives. *Hydrology and Earth System Sciences*, *7*(5), 722–743. https://doi.org/10.5194/hess-7-722-2003

Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., & Marshall, L. A. (2009). Hydrologic connectivity between landscapes and streams: Transferring reach-and plot-scale understanding to the catchment scale. *Water Resources Research*, *45*(4). https://doi.org/10.1029/2008WR007225

Kendall, C. (1998). Tracing nitrogen sources and cycling in catchments. In *Isotope tracers in catchment hydrology* (pp. 519–576). Elsevier.

Kincaid, D. W., Seybold, E. C., Adair, E. C., Bowden, W. B., Perdrial, J. N., Vaughan, M. C., & Schroth, A. W. (2020). Land use and season influence event-scale nitrate and soluble reactive phosphorus exports and export stoichiometry from headwater catchments. *Water Resources Research*, *56*(10), e2020WR027361. https://doi.org/10.1029/2020WR027361

Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: The (high-frequency) wave of the future. *Hydrological Processes*, *18*(7), 1353–1359. https://doi.org/10.1002/hyp.5537

Knapp, J. L., von Freyberg, J., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics. *Hydrology and Earth System Sciences Discussions*, *24*(5), 1–27. https://doi.org/10.5194/hess-24-2561-2020

Koenig, L. E., Shattuck, M. D., Snyder, L. E., Potter, J. D., & McDowell, W. H. (2017). Deconstructing the effects of flow on DOC, nitrate, and major ion interactions using a high-frequency aquatic sensor network. *Water Resources Research*, *53*(12), 10655–10673. https://doi.org/10.1002/2017WR020739

Kong, X., Zhan, Q., Boehrer, B., & Rinke, K. (2019). High-frequency data provide new insights into evaluating and modeling nitrogen retention in reservoirs. *Water Research*, *166*, 115017. https://doi.org/10.1016/j.watres.2019.115017

Kruskal, W. H., & Wallis, W. A. (1952). Use of ranks in one-criterion variance analysis. *Journal of the American Statistical Association*, *47*(260), 583–621. https://doi.org/10.1080/01621459.1952.10483441

Kuhr, P., Kunkel, R., Tetzlaff, B., & Wendland, F. (2014). Räumlich differenzierte Quantifizierung der Nährstoffeinträge in Grundwasser und Oberflächengewässer in Sachsen-Anhalt unter Anwendung der Modellkombination GROWA-WEKU-MEPhos. *FZ Jülich, Endbericht Vom*, *25*.

Kumar, R., Heße, F., Rao, P. S. C., Musolff, A., Jawitz, J. W., Sarrazin, F., et al. (2020). Strong hydroclimatic controls on vulnerability to subsurface nitrate contamination across Europe. *Nature Communications*, *11*(1), 6302. https://doi.org/10.1038/s41467-020-19955-8

Kumar, R., Samaniego, L., & Attinger, S. (2013). Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations. *Water Resources Research*, *49*(1), 360–379. https://doi.org/10.1029/2012WR012195

Lutz, S. R., Trauth, N., Musolff, A., Van Breukelen, B. M., Knöller, K., & Fleckenstein, J. H. (2020). How important is denitrification in riparian zones? Combining end-member mixing and isotope modeling to quantify nitrate removal from riparian groundwater. *Water Resources Research*, *56*(1), e2019WR025528. https://doi.org/10.1029/2019WR025528

Mann, H. B. (1945). Non-parametric tests against trend. *Econometrica*, *13*, 245–259.

Marinos, R. E., Van Meter, K. J., & Basu, N. B. (2020). Is the river a chemostat?: Scale vs. land use controls on nitrate concentration-discharge dynamics in the upper Mississippi River Basin. *Geophysical Research Letters*, *47*(16), e2020GL087051. https://doi.org/10.1029/2020GL087051

Marshall, E., & Randhir, T. (2008). Effect of climate change on watershed system: A regional analysis. *Climatic Change*, *89*(3), 263–280. https://doi.org/10.1007/s10584-007-9389-2

Mekonnen, M. M., & Hoekstra, A. Y. (2020). Anthropogenic nitrogen loads to freshwater: A high-resolution global study. In *Just enough nitrogen* (pp. 303–317). Springer.

Minaudo, C., Dupas, R., Gascuel-Odoux, C., Roubeix, V., Danis, P.-A., & Moatar, F. (2019). Seasonal and event-based concentration-discharge relationships to identify catchment controls on nutrient export regimes. *Advances in Water Resources*, *131*, 103379. https://doi.org/10.1016/j.advwatres.2019.103379

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016WR019635

Morecroft, M. D., Burt, T. P., Taylor, M. E., & Rowland, A. P. (2000). Effects of the 1995–1997 drought on nitrate leaching in lowland England. *Soil Use and Management*, *16*(2), 117–123. https://doi.org/10.1111/j.1475-2743.2000.tb00186.x

Mosley, L. M. (2015). Drought impacts on the water quality of freshwater systems; review and integration. *Earth-Science Reviews*, *140*, 203–214. https://doi.org/10.1016/j.earscirev.2014.11.010

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *Geophysical Research Letters*, *44*(9), 4143–4151. https://doi.org/10.1002/2017GL072630

Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, *86*, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026

Musolff, A., Zhan, Q., Dupas, R., Minaudo, C., Fleckenstein, J. H., Rode, M., et al. (2021). Spatial and temporal variability in concentration-discharge relationships at the event scale. *Water Resources Research*, *57*(10), e2020WR029442. https://doi.org/10.1029/2020WR029442

Nguyen, T. V., Kumar, R., Lutz, S. R., Musolff, A., Yang, J., & Fleckenstein, J. H. (2021). Modeling nitrate export from a mesoscale catchment using StorAge selection functions. *Water Resources Research*, *57*(2), e2020WR028490. https://doi.org/10.1029/2020WR028490

Nogueira, G. E., Schmidt, C., Trauth, N., & Fleckenstein, J. H. (2021). Seasonal and short-term controls of riparian oxygen dynamics and the implications for redox processes. *Hydrological Processes*, *35*(2), e14055. https://doi.org/10.1002/hyp.14055

Oborne, A. C., Brooker, M. P., & Edwards, R. W. (1980). The chemistry of the river Wye. *Journal of Hydrology*, *45*(3), 233–252. https://doi.org/10.1016/0022-1694(80)90022-0

Ockenden, M. C., Deasy, C. E., Benskin, C. M. H., Beven, K. J., Burke, S., Collins, A. L., et al. (2016). Changing climate and nutrient transfers: Evidence from high temporal resolution concentration-flow dynamics in headwater catchments. *Science of the Total Environment*, *548–549*, 325–339. https://doi.org/10.1016/j.scitotenv.2015.12.086

Ohte, N., Sebestyen, S. D., Shanley, J. B., Doctor, D. H., Kendall, C., Wankel, S. D., & Boyer, E. W. (2004). Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique. *Geophysical Research Letters*, *31*(21). https://doi.org/10.1029/2004GL020908

Pal, J. S., Giorgi, F., & Bi, X. (2004). Consistency of recent European summer precipitation trends and extremes with future regional climate projections. *Geophysical Research Letters*, *31*(13). https://doi.org/10.1029/2004GL019836

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., & Bergamaschi, B. A. (2012). Taking the pulse of snowmelt: In situ sensors reveal seasonal, event, and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry*, *108*(1–3), 183–198. https://doi.org/10.1007/s10533-011-9589-8

Rauthe, M., Steiner, H., Riediger, U., Mazurkiewicz, A., & Gratzki, A. (2013). A Central European precipitation climatology—Part I: Generation and validation of a high-resolution gridded daily data set (HYRAS). *Meteorologische Zeitschrift*, *22*(3), 235–256. https://doi.org/10.1127/0941-2948/2013/0436

R Core Team. (2020). R: A language and environment for statistical computing. In *R Foundation for Statistical Computing*. https://www.R-project.org/

Rinke, K., Kuehn, B., Bocaniov, S., Wendt-Potthoff, K., Büttner, O., Tittel, J., et al. (2013). Reservoirs as sentinels of catchments: The Rappbode reservoir observatory (Harz Mountains, Germany). *Environmental Earth Sciences*, *69*(2), 523–536. https://doi.org/10.1007/s12665-013-2464-2

Rode, M., Angelstein, S. H. N., Anis, M. R., Borchardt, D., & Weitere, M. (2016). Continuous in-stream assimilatory nitrate uptake from high-frequency sensor measurements. *Environmental Science & Technology*, *50*(11), 5685–5694. https://doi.org/10.1021/acs.est.6b00943

Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W., et al. (2016). *Sensors in the stream: The high-frequency wave of the present*. ACS Publications. https://doi.org/10.1021/acs.est.6b02155

Rose, L. A., Karwan, D. L., & Godsey, S. E. (2018). Concentration-discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. *Hydrological Processes*, *32*(18), 2829–2844. https://doi.org/10.1002/hyp.13235

Samaniego, L., Kumar, R., & Attinger, S. (2010). Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale. *Water Resources Research*, *46*(5). https://doi.org/10.1029/2008WR007327

Sebestyen, S. D., Boyer, E. W., & Shanley, J. B. (2009). Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States. *Journal of Geophysical Research: Biogeosciences*, *114*(G2). https://doi.org/10.1029/2008JG000778

Seybold, E., Gold, A. J., Inamdar, S. P., Adair, C., Bowden, W. B., Vaughan, M. C., et al. (2019). Influence of land use and hydrologic variability on seasonal dissolved organic carbon and nitrate export: Insights from a multiyear regional analysis for the northeastern USA. *Biogeochemistry*, *146*(1), 31–49. https://doi.org/10.1007/s10533-019-00609-x

Stahl, K., Hisdal, H., Hannaford, J., Tallaksen, L., Van Lanen, H., Sauquet, E., et al. (2010). Streamflow trends in Europe: Evidence from a data set of near-natural catchments. *Hydrology and Earth System Sciences*, *14*(12), 2367–2382. https://doi.org/10.5194/hess-14-2367-2010

Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. *Global Biogeochemical Cycles*, *17*(4). https://doi.org/10.1029/2003GB002041

Sugiura, N. (1978). Further analysts of the data by akaike's information criterion and the finite corrections: Further analysts of the data by akaike's. *Communications in Statistics—Theory and Methods*, *7*(1), 13–26. https://doi.org/10.1080/03610927808827599

Szwed, M. (2019). Variability of precipitation in Poland under climate change. *Theoretical and Applied Climatology*, *135*(3), 1003–1015. https://doi.org/10.1007/s00704-018-2408-6

Tarasova, L., Basso, S., Wendi, D., Viglione, A., Kumar, R., & Merz, R. (2020). A process-based framework to characterize and classify runoff events: The event typology of Germany. *Water Resources Research*, *56*(5), e2019WR026951. https://doi.org/10.1029/2019WR026951

Tarasova, L., Basso, S., Zink, M., & Merz, R. (2018). Exploring controls on rainfall-runoff events: 1. Time series-based event separation and temporal dynamics of event runoff response in Germany. *Water Resources Research*, *54*(10), 7711–7732. https://doi.org/10.1029/2018WR022587

Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic vs. biogeochemical factors on solute export across impact gradients. *Water Resources Research*, *47*(10). https://doi.org/10.1029/2010WR009605

Trang, N. T. T., Shrestha, S., Shrestha, M., Datta, A., & Kawasaki, A. (2017). Evaluating the impacts of climate and land-use change on the hydrology and nutrient yield in a transboundary river basin: A case study in the 3S River Basin (Sekong, Sesan, and Srepok). *Science of the Total Environment*, *576*, 586–598. https://doi.org/10.1016/j.scitotenv.2016.10.138

Vaughan, M. C., Bowden, W. B., Shanley, J. B., Vermilyea, A., Sleeper, R., Gold, A. J., et al. (2017). High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. *Water Resources Research*, *53*(7), 5345–5363. https://doi.org/10.1002/2017WR020491

Wagena, M. B., Collick, A. S., Ross, A. C., Najjar, R. G., Rau, B., Sommerlot, A. R., et al. (2018). Impact of climate change and climate anomalies on hydrologic and biogeochemical processes in an agricultural catchment of the Chesapeake Bay watershed, USA. *Science of the Total Environment*, *637–638*, 1443–1454. https://doi.org/10.1016/j.scitotenv.2018.05.116

Wilcoxon, F. (1945). Individual comparisons by ranking methods. *Biometrics Bulletin*, *1*(6), 80–83. https://doi.org/10.2307/3001968

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

Winterrath, T., Brendel, C., Hafer, M., Junghänel, T., Klameth, A., Walawender, E., et al. (2017). *Erstellung einer radargestützten Niederschlagsklimatologie*. Deutscher Wetterdienst.

Wollheim, W. M., Mulukutla, G. K., Cook, C., & Carey, R. O. (2017). Aquatic nitrate retention at river network scales across flow conditions determined using nested in situ sensors. *Water Resources Research*, *53*(11), 9740–9756. https://doi.org/10.1002/2017WR020644

Wollschläger, U., Attinger, S., Borchardt, D., Brauns, M., Cuntz, M., Dietrich, P., et al. (2017). The Bode hydrological observatory: A platform for integrated, interdisciplinary hydro-ecological research within the TERENO Harz/Central German Lowland Observatory. *Environmental Earth Sciences*, *76*(1), 29. https://doi.org/10.1007/s12665-016-6327-5

Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F., & Fleckenstein, J. H. (2018). Exploring the dynamics of transit times and subsurface mixing in a small agricultural catchment. *Water Resources Research*, *54*(3), 2317–2335. https://doi.org/10.1002/2017WR021896

Yang, X., Jomaa, S., Zink, M., Fleckenstein, J. H., Borchardt, D., & Rode, M. (2018). A new fully distributed model of nitrate transport and removal at catchment scale. *Water Resources Research*, *54*(8), 5856–5877. https://doi.org/10.1029/2017WR022380

Zink, M., Kumar, R., Cuntz, M., & Samaniego, L. (2017). A high-resolution dataset of water fluxes and states for Germany accounting for parametric uncertainty. *Hydrology and Earth System Sciences*, *21*(3), 1769–1790. https://doi.org/10.5194/hess-21-1769-2017