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

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Abstract

Runoff events play an important role for nitrate export from catchments, but the variability of nutrient 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 soil moisture, snowmelt and the temporal organization of rainfall, in six neighboring mesoscale catchments with contrasting land use types. We related these event characteristics to nitrate export patterns from high-frequency nitrate concentration monitoring (2013 - 2017) using concentration-discharge relationships. Our results show that small rainfall-induced events with dry antecedent conditions exported lowest nitrate concentrations and loads but exhibited highly variable concentration-discharge 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, large 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 homogenous export patterns by high catchment wetness that activated a high number of flow paths. Long-term hydro-meteorological data indicated an increase of events with dry antecedent conditions in summer and decreased snow-influenced events. These trends will likely continue and lead to an increased nitrate concentration variability during low-flow seasons and to changes in the timing of largest nitrate export peaks during high-flow seasons.

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Key Points:

- Hydrological event classification enables transferability of dominant drivers of event-scale nitrate export patterns across catchments
- Small events with low antecedent wetness exported low nitrate concentrations with highly variable CQ relationships
- Large events with high antecedent wetness exported high nitrate concentrations and loads with chemostatic patterns across all catchments

Abstract

Runoff events play an important role for nitrate export from catchments, but the variability of nutrient 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 soil moisture, snowmelt and the temporal organization of rainfall, in six neighboring mesoscale catchments with contrasting land use types. We related these event characteristics to nitrate export patterns from high-frequency nitrate concentration monitoring (2013 - 2017) using concentration-discharge relationships. Our results show that small rainfall-induced events with dry antecedent conditions exported lowest nitrate concentrations and loads but exhibited highly variable concentration-discharge 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, large 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 homogenous export patterns by high catchment wetness that activated a high number of flow paths. Long-term hydro-meteorological data indicated an increase of events with dry antecedent conditions in summer and decreased snow-influenced events. These trends will likely continue and lead to an increased nitrate concentration variability during low-flow seasons and to changes in the timing of largest nitrate export peaks during high-flow seasons.

Plain Language Summary

Runoff events play an important role for nitrate exports 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 biogeochemically controlled 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. Long-term trends indicate a decrease of soil moisture in summer and a decrease of snow-influenced events. These trends might cause an increasing variability in nitrate concentrations during summer and change the timing of large 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 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 on 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 (Tarasova et al., 2020; Kirchner et al. 2004). Those analyses 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 et al., 2018). Moreover, in a temperate climate, runoff events can be generated by precipitation events of different nature, such as pure 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, we can know measure water quality at the same temporal resolution as water quantity to analyze in detail the impact of runoff event characteristics on nitrate export patterns (Kirchner et al., 2004; Rode et al., 2016a). Here 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 as such (for example peak discharge). To maintain 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 the high frequency measurements and conducted detailed analysis on nutrient mobilization and transport during runoff events and confirmed the important role of runoff events for nutrient export (e.g., Blaen et al., 2017; Burns et al., 2019; Rose et al., 2018, Fovet et al., 2018, Knapp et al., 2020). For example, Casson et al., (2010) and Pellerin et al. (2012) showed that large rain-on-snow events can account for a disproportional amount of annually exported large 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. These examples show that nitrate export patterns can be related to event characteristics, such as the contribution of meltwater or antecedent conditions, whereas this relationship can be highly variable between catchments of different configurations e.g., with regrads to land use and nitrate availability.

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 (e.g., 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 newly activated discharge zones (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). Nevertheless, 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 is still missing. Furthermore, studies that relate hydrological runoff events with nutrient transport are generally limited to relatively short time periods, which is often not more than one or two years (e.g., Bieroza et al., 2018; Bowes et al., 2015; Carey et al., 2014). Therefore, it mostly remains unclear if analyzed event characteristics are representative for the long-term catchment behaviour and if runoff event characteristics might change over longer time scales.

In this study, we explore to what extend runoff event characteristics govern nitrate export during and across runoff events in different catchments. 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 organization of rainfall to nitrate concentrations and loads. For this we used a 5-year 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 TERestrial 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).

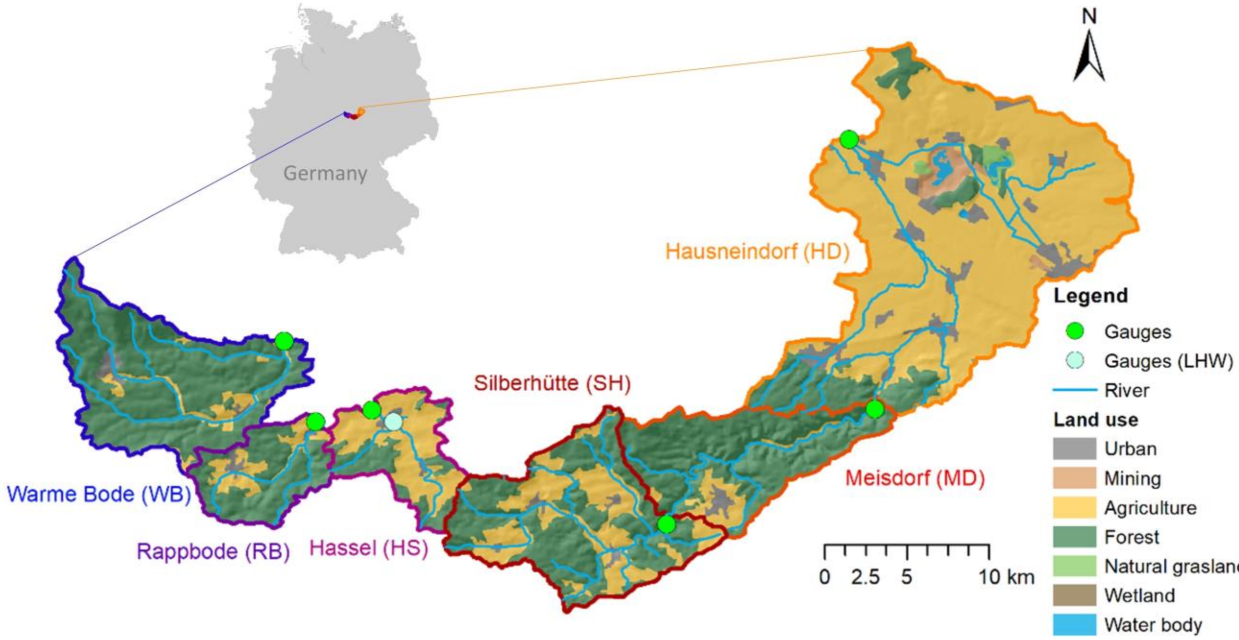

Figure 1. Map of the study site, showing all six mesoscale catchments (WB, RB, HS, SH, MD and HD) with their respective their land use.

Table 1. Characteristics of the six studied mesoscale catchments within the Bode River catchment.

Catchment	Area	Mean annual precipitation	Mean annual temperature	Land use and land cover				Elevation range	Mean Slope
				Agriculture	Forest	Urban	Other		
	[km²]	[mm yr^{-1}]	[°C]	[%]	[%]	[%]	[%]	[m.a.s.l.]	[%]
WB	101.1	1111.9	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 Data

2.2.1 Long-term daily data

Long-term daily data (Figure S1–S6) were used to classify runoff events and to analyse potential trends in these. 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 km² (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).

2.2.2 High-frequency hourly data

High-frequency hourly data were used to analayse exported nitrate loads and concentration-discharge relationships within and between runoff events from 2013 to 2017. Discharge data at a temporal resolution of 15 minutes 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-hour window to smooth the data. 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 km² (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 was simulated using mHM (Zink et al., 2017).

Nitrate concentration data between 2013 and 2017 was collected via TRIOS ProPS-UV sensors at 15 min. intervals (Kong et al., 2019; Rode, et al., 2016a), 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 Rode et al. (2016b), X. Yang et al. (2018), Winter et al. (2021) and Musolff et al. (2021). For the processing of the nitrate concentration data we refer to the references above and to our supporting information (Text S1). Briefly, raw data was restricted to a realistic range (0 – 100 mg L^{-1}), outliers were removed, a moving average was applied over a 5-hour window to smooth the data and concentrations were calibrated against grab samples analyzed in the lab (R^2 0.80 - 0.91, Figute S7 and S8). 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 km² for discharge data compared to 42 km² 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). 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 organization 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 non-linear relationship between event runoff coefficients and soil moisture (Tarasova et al., 2020), events were classified as *Wet* od *Dry* events (Figure 2a). In total, this classification resulted in five event classes (Figure 2b): i) snow-influenced events (*Snow*), ii) rain-induced events that were *volume dominated* and occurred under wet antecedent soil moisture conditions (*Rain-Wet-Vol*), iii) rain-induced events that occurred under wet antecedent conditions and were *intensity dominated* (*Rain-Wet-Int*), iv) rain-induced events that occurred under dry antecedent conditions and were *volume dominated* (*Rain-Dry-Vol*) and v) rain-induced events that occurred under dry antecedent conditions and were *intensity dominated* (*Rain-Dry-Int*). To assure comparability of event classes between two datasets of different resolution, 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).

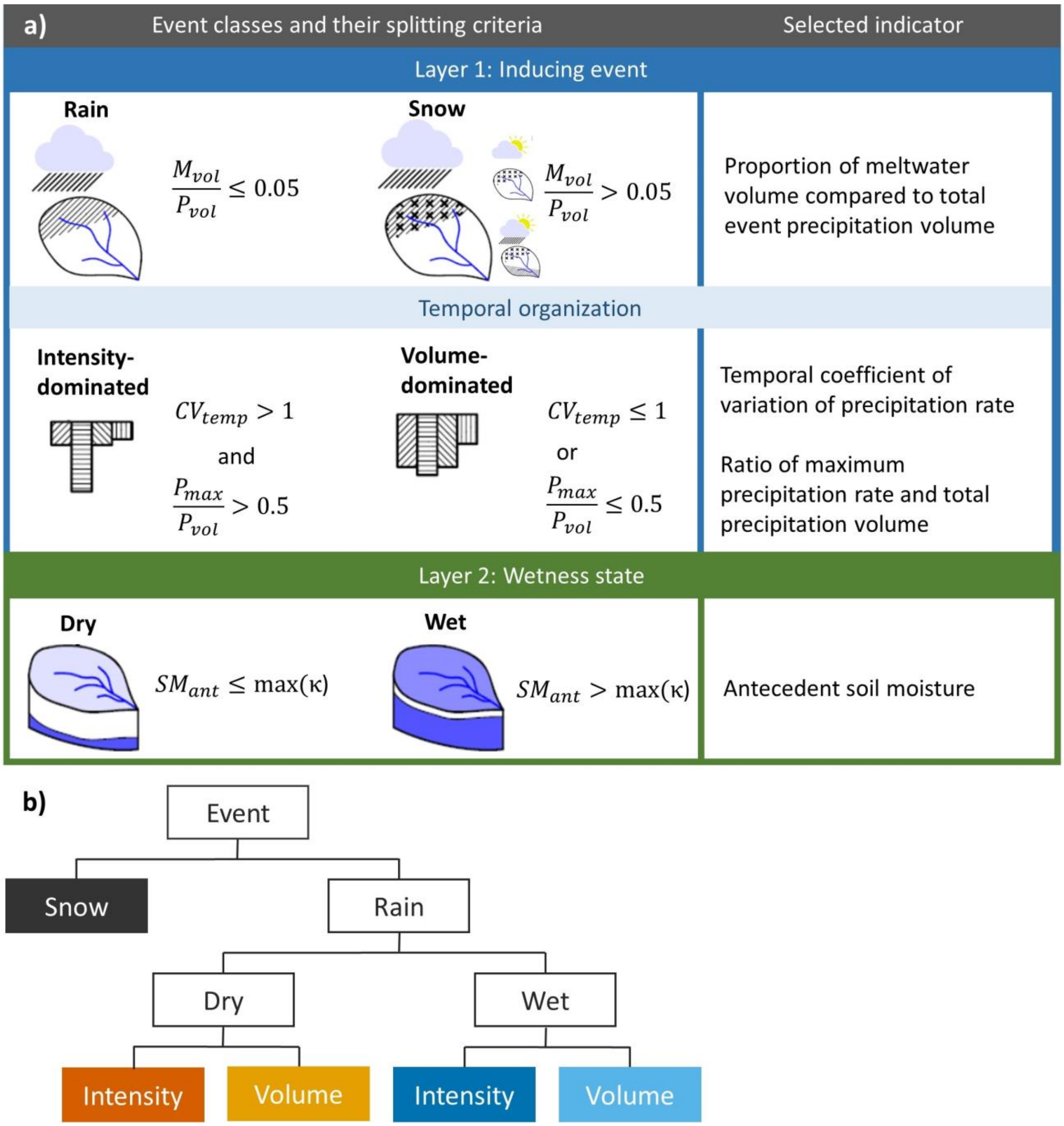

Figure 2. a) Event characteristics and thresholds for the classification of events. Threshold for the wetness state of the catchments is defined by the maximum of κ, which represents the catchment-specific curvature of the nonlinear relationship between event runoff coefficients and soil moisture. b)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

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: i) antecedent soil moisture (SM_{ant}), ii) the ratio of meltwater volume and precipitation volume (M_{vol}/P_{vol}) and iii) 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 i) *Snow* events (vs. *Rain* events), ii) *Rain-Dry* (vs. *Rain-Wet*) events and iii*)* *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: i) median nitrate concentration (C_{med}), ii) average loads per event in kg ha^{-1} yr^{-1} (this unit was chosen for a better comparison between catchments and events of different duration), iii) inter-event CQ slopes and iv) 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 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, i.e., decreasing concentrations with increasing discharge and therefore a dilution pattern. A parameter $b > 0$ describes a negative CQ slope, i.e., 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 eq. 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 5872 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 was dominated by *Snow* and *Rain-Wet-Vol* events. Spring showed the greatest variability of event classes and was the season with the highest percentage of *Rain-Wet-Vol* and *Rain-Wet-Int* events. Summer and autumn 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% 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). *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.

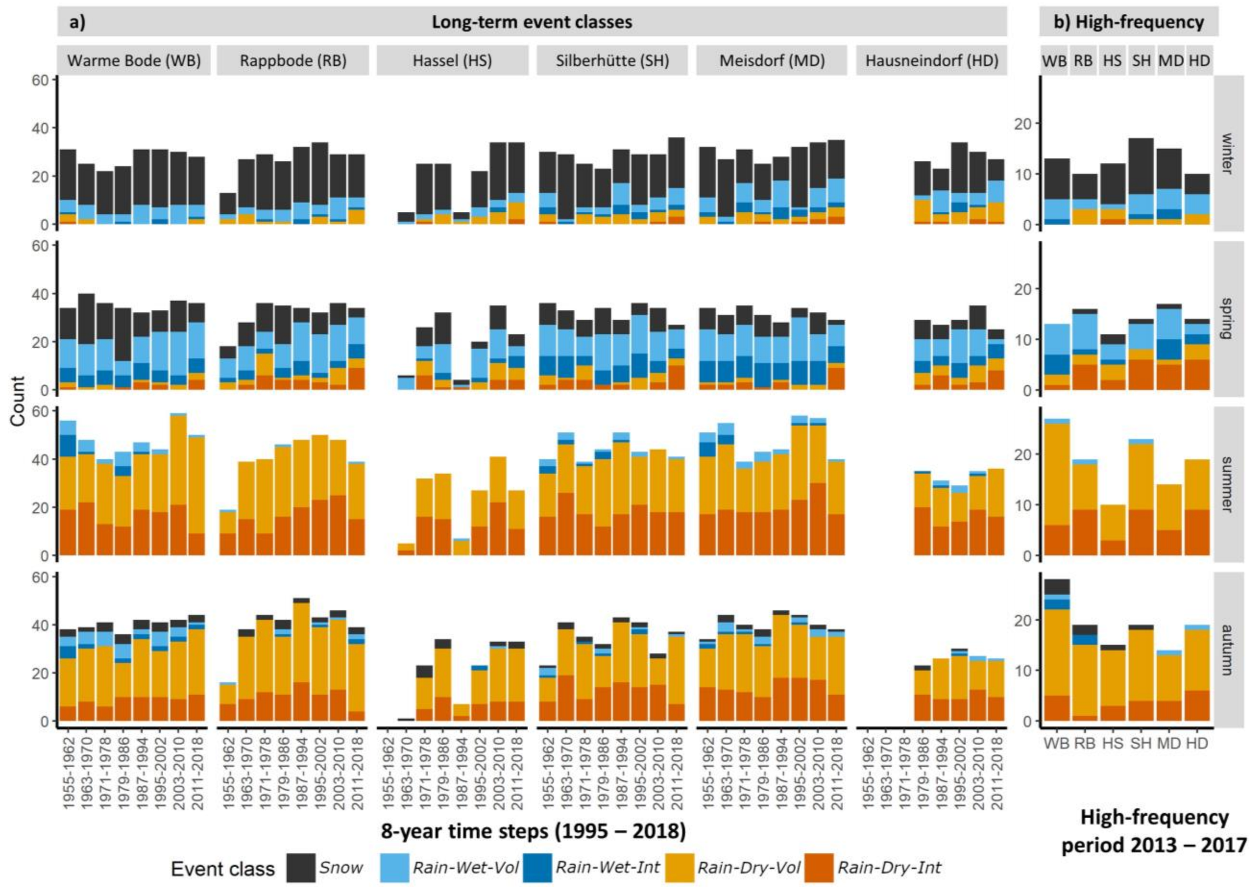

Figure 3. Seasonal absolute frequency of event classes (y axis) in the six study catchments, showing a) long-term changes between 8-year periods from 1955 until 2018 and b) the period of high-frequency data from 2013 until 2017. Periods in panel a) with no or very few events in HS and HD indicate missing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

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). 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). 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 occured during summer. In contrast, the RB, SH and MD catchments showed a significant increase in P_{max}/P_{vol} during summer, but no significant trend in the total number or proportion of *intensity*- or *volume-dominated* events (Table S1).

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 h^{-1}) and lowest average Q_{med} in the HD catchment (0.3 mm h^{-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 and lowest percentage of forests exported in average highest C_{med} (HS and HD with 2.5 mg L^{-1} and 2.3 mg L^{-1}), followed by mixed land use catchments (MD and SH with 1.6 mg L^{-1} and 1.5 mg L^{-1}) and lowest average C_{med} was observed in the dominantly forested catchments RB and WB (0.6 mg L^{-1} and 0.7 mg 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 relation to catchment area (Table. 1), the HS catchment transported highest median nitrate loads across all event classes (5.5 kg ha^{-1} yr^{-1}) followed by HD (1.8 kg ha^{-1} yr^{-1}), MD (1.7 kg ha^{-1} yr^{-1}), WB (1.6 kg ha^{-1} yr^{-1}), SH (1.4 kg ha^{-1} yr^{-1}) and lowest median loads were exported from RB catchment (1.0 kg 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).

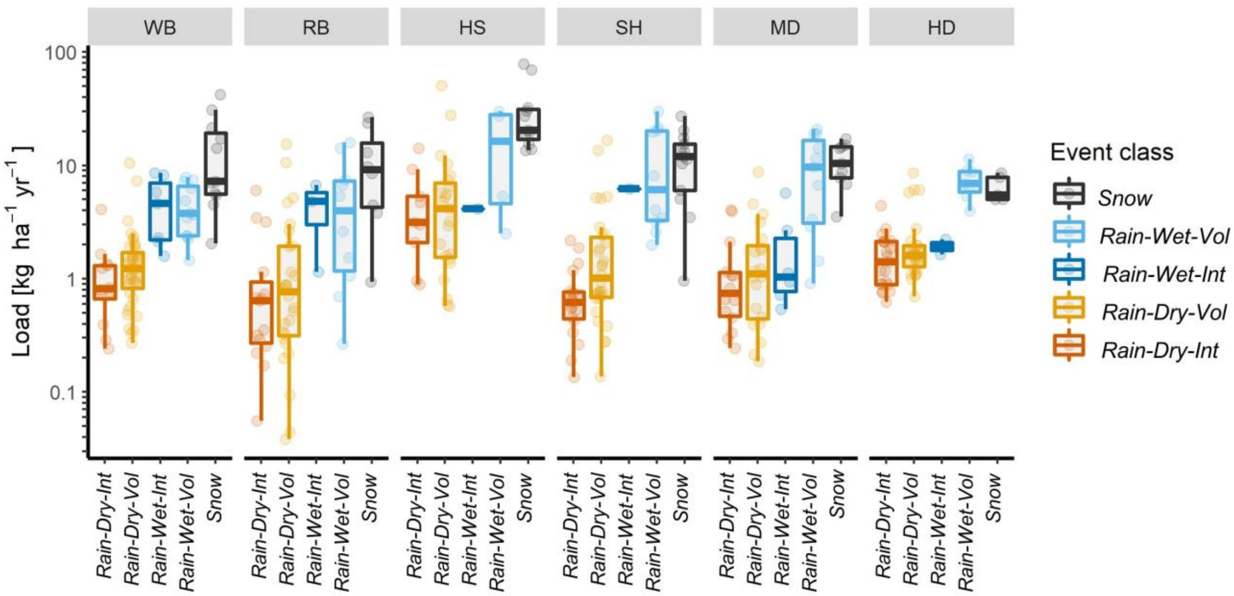

Figure 4. Nitrate loads (on logarithmic scale) transported during runoff events, divided into catchments and runoff event classes.

3.2.2 Inter-event concentration-discharge relatioships

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 small 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 smaller events 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 a 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), 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.

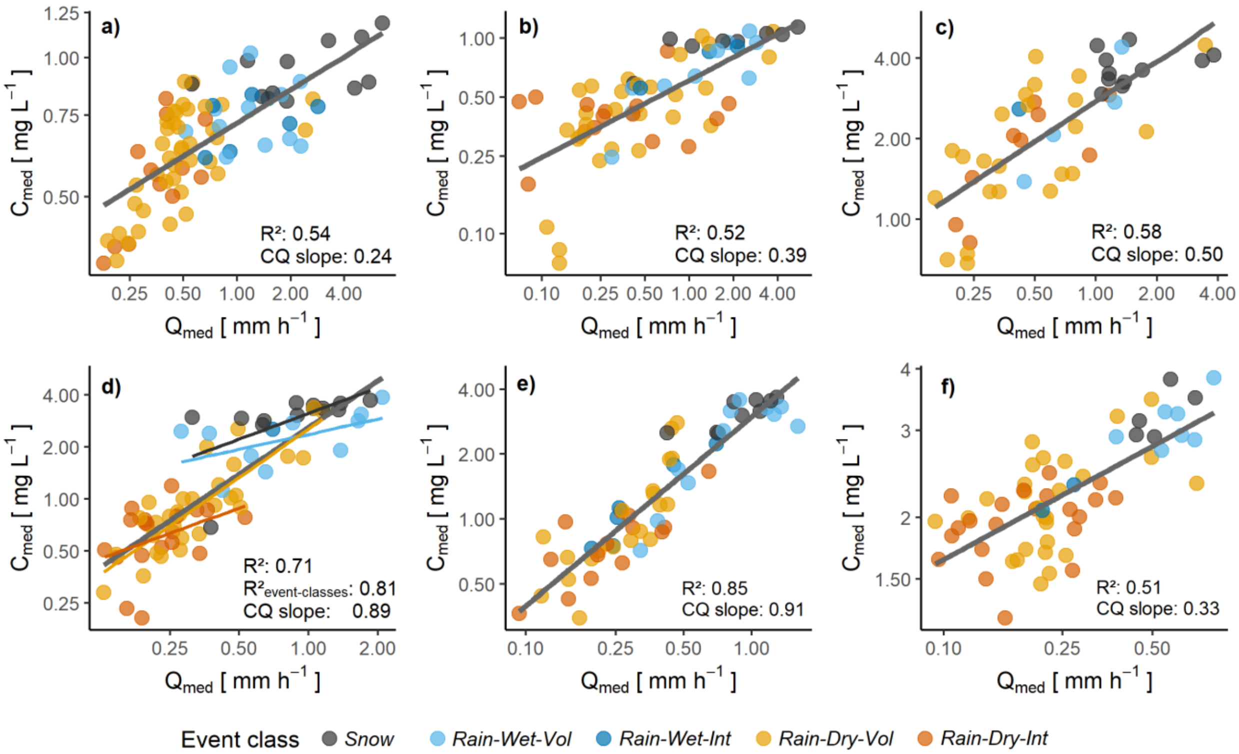

Figure 5. Median discharge (Q_{med}) and nitrate concentrations (C_{med}) for each runoff event with log-scale x- and y-axis, separated into the six catchments (a-f). Colors indicate the five different event classes, grey lines show the linear relationship between ln(C_{med}) and ln(Q_{med}) and colored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

3.2.3 Event-specific concentration-discharge relationships

Across all catchments, most events (72.4%) were characterized by a positive event-specific CQ slope, indicating an increase of nitrate concentrations with increasing discharge (Figure 6). We found that event-specific CQ slopes in all catchments showed a large variability between small events (low Q_{med}), whereas CQ slopes for larger 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 small events (Figure 6b). The more forested and pristine catchments dominantly showed positive CQ slopes, whereas the agriculturally dominated catchments HS and HD tended towards close-to-zero or negative CQ slopes.

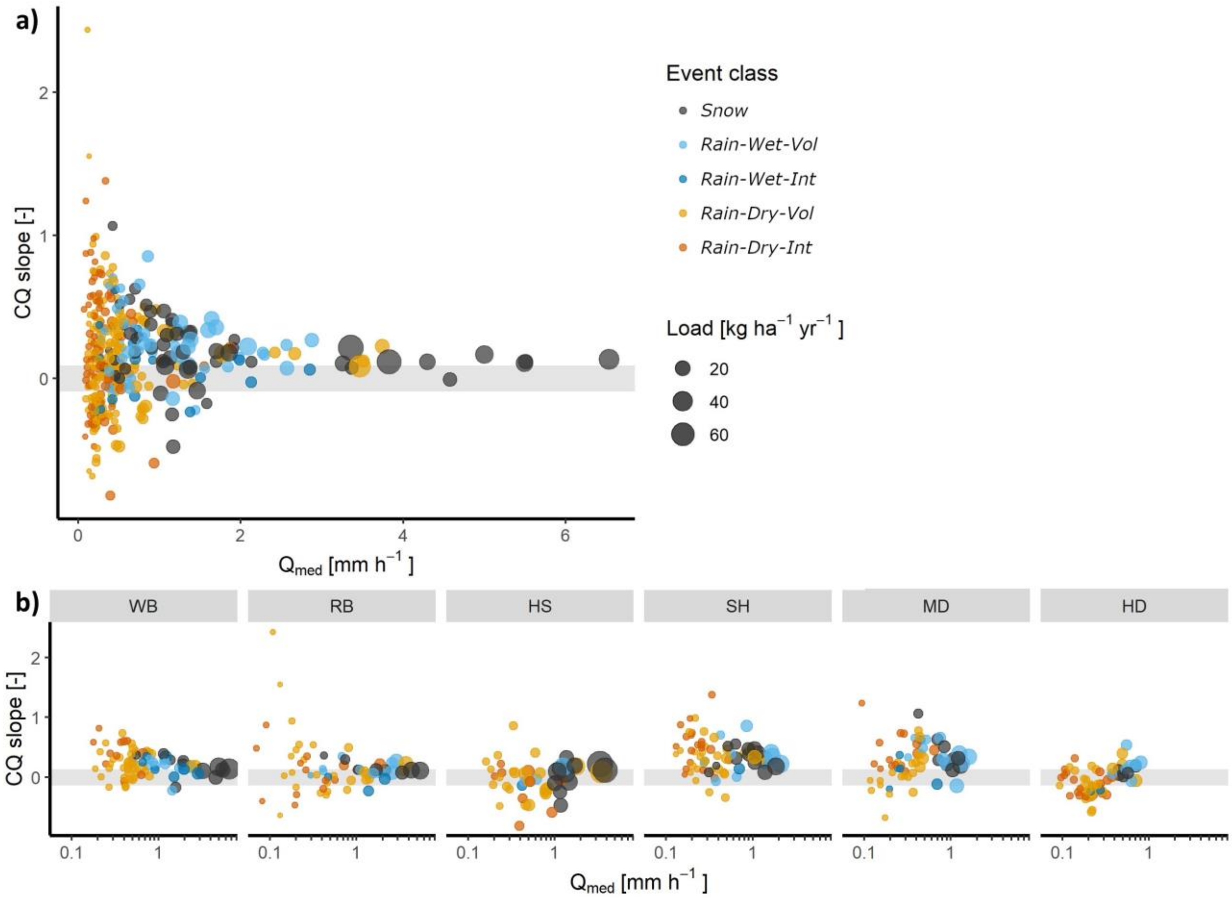

Figure 6. Event-specific CQ slopes (slope of nitrate concentrations and discharge in the log-log space) against the specific median discharge (Q_{med}) of each event shown for all catchments in one plot (a) and with logarithmic x-axis and separated by catchments to visualize differences in events with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

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 organization of the inducing rainfall, being either *intensity*- or *volume-dominated*. To assess whether the difference in temporal organization of rainfall events explains any additional variability in event-specific CQ slopes of small 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). Moreover, the median of event-specific CQ slopes from *Rain-Dry-Int* events was higher compared to *Rain-Dry-Vol* events in all six catchments. In contrast, no significant difference in C_{med} and Q_{med} between *Rain-Dry-Int* and *Rain-Dry-Vol* events could be detected (Figure S12), except for the SH catchment, where C_{med} and Q_{med} were significantly higher during *Rain-Dry-Vol* events.

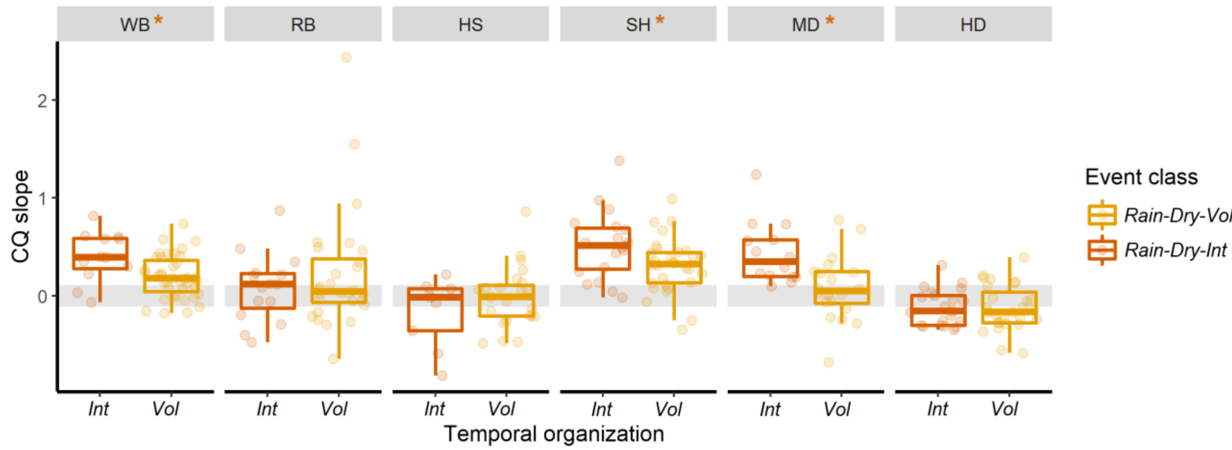

Figure 7. Event-specific CQ slopes (slope between nitrate concentrations and discharge in the log-log space) for all six study catchments and the two event classes *Rain-Dry-Int* and *Rain-Dry-Vol*, representing rain-induced runoff events that occurred under dry antecedent soil moisture conditions with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

4 Discussion

4.1 Impact of runoff event characteristics on nitrate export

The main aim of this study was to understand if and how runoff event characteristics, as characterized in the typology of events, relate to nitrate export during and across runoff events. Our results show that in general nitrate export across events is strongly driven by event size (in regard to runoff) with a pronounced seasonality. Large events in winter and spring exported highest nitrate concentrations and loads and small events during summer and autumn exported lowest concentrations and loads. The variability of event-specific CQ slopes decreased with increasing event size, indicating differences in the dominant drivers for nutrient export between low and high-flow seasons. In the following, we discuss the impact of runoff event characteristics on nitrate export during these different conditions in more detail. Further, we discuss how well the analyzed runoff event characteristics from the high frequency period (2013 - 2017) represent the long-term runoff event characteristics and implications of trends in the long-term runoff event characteristics.

4.1.1 Small runoff events

Small 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 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 active flow paths) with lower antecedent soil moisture during summer and autumn, compared to winter and spring. As a result, 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 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., 2020; Ehrhardt et al., 2019; Kumar et al., 2020; Nguyen et al., 2021). Moreover, with higher temperatures during summer and autumn, nitrate uptake and removal increases, especially in streams and in the riparian zones (Baird et al., 1995; Lutz et al., 2020; Rode et al., 2016b). Due to lower discharge during summer and autumn, also the relative role of those processes increases (Knapp et al., 2020).

The 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 small events, reflecting a high variability of mobilization and transport processes. We explain this high variability by an increased relevance of different environmental factors such as i) catchment characteristics and the spatial distribution and connectivity of N sources within a catchment, ii) riparian and in-stream biogeochemical processes and iii) the spatial and temporal organization 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 small 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, small events 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 role for nitrate export during small events (e.g., Knapp et al., 2020; Marinos et al., 2020; Moatar et al., 2017). Hence, variability in these processes through, for example, varying instream temperature (Rode, et al., 2016a) 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 & Bieroza (2021), who found that nutrient export dynamics during small 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 organization of precipitation can explain another part of the variability in mobilization patterns during small runoff 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 (Figure 1, Figure 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 small runoff 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 larger runoff events under wet antecedent conditions (see section 4.1.2).

4.1.2 Large runoff events

In contrast to small runoff events in summer and autumn, runoff events in winter and spring were either snow-influenced (*Snow*) or rain-induced (< 5% snowmelt) and generated by *volume-dominated* precipitation under wet antecedent conditions (*Rain-Wet-Vol*, Figure 2, Figure 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 (Figure 4, Figure 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 (Figure 5d-f). 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 large runoff 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., 2015, 2017; J. Yang 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 et al., 2018). Together with a reduced N demand of ecosystems in winter and spring compared to summer (Baird et al., 1995; Rode et al., 2016b), this flow path activation in a highly saturated catchment can explain the high nitrate concentrations and loads observed in the studied catchments (Figure 4, Figure 5). Moreover, it can explain the low variability in event specific-CQ slopes (Figure 6), because if all flow paths are activated, no changes in nitrate mobilization through bypassing or activation of additional N sources can occur.

Remarkably, the event-specific CQ slopes during large 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 large 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 lower concentrated water from newly activated zones (Fovet et al., 2018; Rose et al., 2018). Here, we reported consistently 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 large events ($Q_{med} > 1$ mm h^{-1}). These patterns provide strong evidence for a transport rather than a source limitation of N in all six catchments (Basu et al., 2010), even in the forest dominated catchments, which is alarming in terms of water quality. While fertilization in the agricultural catchments (HS and HD) is likely the main N source (Ehrhardt et al., 2019; Winter et al., 2021), there is reported evidence for high atmospheric N deposition over the Harz Mountains (Kuhr et al., 2014; Winter et al., 2021) that could explain part of those non-depleting N sources in the more forested catchments. 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. Nevertheless, the strikingly similar nitrate export patterns during *Snow* and *Rain-Wet-Vol* events with comparable event size hints at similar N sources for both event classes and thus not at the melting snowpack as key source. Hence, we hypothesize that a large part of those N sources stem from legacy N stores in the soils, either from the previous summer or from N accumulation over longer time periods (Dupas et al., 2020; Van Meter et al., 2016).

4.2 Long-term trends of event characteristics and their implications for nutrient export patterns

We analyzed nitrate export patterns for a 5-year period of high-frequency nitrate concentration data (2013 - 2017), which is not sufficient to estimate any long-term trends. The analyzed long-term runoff event characteristics from daily data, however, allowed us to detect those trends and 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 smaller event size (in regard to runoff), proportionally lower nitrate concentrations and loads and a higher variability in 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. Additionally, rewetting after especially dry summer periods was often reported to cause disproportionally high nitrate export peaks, which can cause severe water quality deteriorations and 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 a decrease of large 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 decrease of *Snow* events and trigger similarly high event runoff and nitrate export, as observed in the SH, MD and HD catchments (Figure 5d-f). As such, nitrate export peaks would not be restricted to the melting period but to the entire high flow season in winter and early spring. 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 large 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?

Classification of long-term series of runoff events 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 composition. 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 nitrate export in the future. Furthermore, 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 - 2002, runoff events in these clusters were typically dominated by *Rain-Dry* events, while approximately 15% – 25% were snow-influenced events (*Snow*) and *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 *volume-dominated* rainfall prevailing over *intensity-dominated* rainfall. Basesd 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. Nevertheless, 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 and its spatial distribution (Dupas et al., 2019; Musolff et al., 2017) among other things. However, by analyzing the impact of these representative runoff event characteristics on nitrate export 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.

Including an extended set of hydro-meteorological variables into our analysis enabled us to disentangle a large part of the variability in nitrate export patterns and to create results that are better transferable to other catchments and time periods. A hydrological classification can thus be seen as one prerequisite for creating transferrable results in both space and time 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 processes that shape nitrate export dynamics.

5 Conclusions

In this study, we analyzed the impact of runoff event characteristics on high-frequency nitrate export in 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 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 size 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 i.e., projected changes in temperatures and other hydro-meteorological conditions.

Lowest nitrate concentrations and loads were transported during small 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 residence times, and higher nitrate 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 horizontal and vertical 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 large 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 homogenous among large events across all catchments, showing a relatively small increase of nitrate concentrations compared to discharge (approximately chemostatic), which we explain by the activation of all relevant flow path within a catchment that facilitate the land-to-stream connection of all relevant N sources. As classes for large events, i.e., *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 and catchment saturation are the main drivers of nitrate export during large 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, 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, e.g., dominantly forested versus mainly agricultural land cover, allowed us to analyse 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 to analyze event-driven nitrate export also in catchments from other areas, ideally in larger-scale comparisons across a wide range of catchment characteristics, N input histories and climatic conditions. Establishing robust relationships between runoff event characteristics and nitrate export, and relating them to long-term trends in runoff event characteristics would be an informative tool for understanding possible directions of future changes in water quality.

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Data availability

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 ftp://opendata.dwd.de/climate_environment/CDC/grids_germany/daily/regnie/ (daily precipitation) and ftp://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 archieved in the TERENO data base and are available upon request through the TERENO-Portal (www.tereno.net/ddp). All runoff event characterisics from the long-term and from the high-frequency data will be available in hydroshare upon acceptance of the manuscript.

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