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Winter post-droughts amplify extreme nitrate concentrations in German rivers

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Abstract

Hydrological extremes can affect nutrient export from catchments to streams, posing a threat to aquatic ecosystems. In this study, we investigated the effects of hydrological drought on nitrate concentrations in the streamflow of 182 German catchments from 1980 to 2020. We found that across all seasons, 40% and 25% of the catchments showed significantly lower nitrate concentrations during drought and post-droughts, respectively, when compared to non-drought conditions. However, we observed pronounced spatial variability in the responses, particularly during winter droughts and post-droughts, with more catchments exhibiting higher nitrate concentrations. Specifically, nitrate concentrations were significantly higher in 25% of the study catchments during winter droughts, particularly in wetter catchments with low nitrogen retention. During winter post-droughts, nitrate concentrations are significantly higher in 19% of the catchments, especially in wetter catchments with more nitrogen surplus. Moreover, the likelihood of nitrate seasonal extremes increased by 6% during winter post-drought in our study catchments. Considering the projected increase in the frequency of droughts in Germany, the increase in nitrate concentrations during the corresponding post-drought periods poses a potential threat to aquatic ecosystem health.

1. Introduction

Hydrological droughts, characterized by periods with a shortage of surface or subsurface water supply, can alter runoff generation processes and nutrient dynamics at the catchment scale [1, 2]. This is particularly concerning because the frequency of droughts is expected to increase in Germany with advancing climate change [3, 4]. Droughts and post-drought conditions potentially intensify nitrate fluxes from land to streams, threatening aquatic ecosystems and potable water supplies [5, 6].

Anthropogenic pollution is the main trigger of high levels of nitrate contamination in aquatic systems in Europe [7, 8] and worldwide [9, 10]. While point source contamination (e.g. wastewater) is often diluted by discharge into streams, nitrate from diffuse sources such as agriculture is mobilized through fast and shallow hydrological pathways that are activated under wet soil conditions [11]. In addition to transport, interactions between sources and biogeochemical processes in the soil and streams that remove nitrate can lead to diverse concentration–discharge relationships [12]. In German agricultural catchments, out-of-phase seasonal variations of catchment wetness and biogeochemical processes of nitrate removal often result in high nitrate concentrations in winter and low concentrations in summer [13–15].

During hydrological droughts, nitrate dynamics can be altered by changes in both transport and biogeochemical processes [16]. In catchments dominated by point sources, nitrate concentrations generally increase because of the lack of dilution, which can mask in-stream retention processes [1]. However, in agricultural catchments, the responses can vary. Reduced hydrologic connectivity between sources and streams reduces transport [11, 13] and enhances the biogeochemical removal of nitrate owing to longer subsurface residence times in the soil [17, 18] and streams [19], promoting lower nitrate concentrations. Changes in runoff generation processes can also alter nitrate concentrations during drought. Zhou *et al* [11] demonstrated that within a catchment with mixed land use during droughts, enhanced instream removal processes, combined with a more pronounced contribution of runoff from forested upland areas with a lower nitrate influx, led to a decrease in nitrate concentrations at the catchment outlet. Conversely, lower nitrate dilution in catchments with contaminated groundwater during droughts can increase the concentration of nitrate in streams [1, 20, 21]. Dry conditions during drought can also limit denitrification rates and nitrogen consumption by plants, increasing nitrogen storage in the soil [22–24].

The lack of transport from diffuse sources to streams, potential reduction in denitrification, and reduced nitrogen uptake by water-stressed vegetation can lead to the additional accumulation of nitrogen in the soil during dry conditions [25, 26]. During the post-drought period (i.e. the period after the end of a hydrological drought), the excess stored nitrogen can be mineralized and then consumed by plants or mobilized once the moisture levels in the catchments recover from drought [27]. Several studies have reported post-drought flushes of nitrate in individual streams, often with exceptionally high nitrate concentrations [20, 28, 29]. Morecroft *et al* [28] found higher stream nitrate concentrations in agricultural and forest areas in the UK, with only forest areas showing enhanced nitrification and mineralization processes. Jutglar *et al* [30] also observed a post-drought flush in 90% of 41 spring sampling locations in a southwest region of Germany after the severe drought of 2003. However, post-drought nitrate flushes do not always occur. Jarvie *et al* [20] found a post-drought increase in nitrate concentrations only in the upland sites of the Wye catchment in England, and not in the lowlands where agricultural activity is concentrated. In contrast, van Metre *et al* [31] showed that agricultural areas in the Midwest US produced exceptionally high nitrate concentrations after the 2011 drought in zones with high post-drought precipitation. Moreover, Lee *et al* [27] found in their global analysis that 43% of the 118 study catchments exhibited higher post-drought

nitrate transport and this effect mainly occurred in warm regions with anthropogenic modifications of the landscape. Despite these findings, a full understanding of the conditions under which a post-drought flush of nitrate occurs remains challenging.

Contrasting findings from single- or few-site observations and model-based studies indicate a knowledge gap regarding the primary drivers of high nitrate concentrations during and after droughts. In our analysis, we offer a large-scale and large-sample assessment of the impact of hydrological droughts and post-droughts on nitrate concentrations at the outlets of 182 German catchments with diverse land-use, climatic, and topographic features. We aim to (i) quantify the differences in nitrate concentrations under drought, post-drought, and no-drought conditions in our study catchments, and (ii) estimate the likelihood of extremely high nitrate concentrations during these hydrological conditions and their correspondence with nitrate loads. With climate change altering the frequency of droughts in the future, we aim to provide insights for water managers regarding hotspots of post-drought nitrate pollution, helping to mitigate adverse impacts on riverine, lake, and coastal environments.

2. Methods

We used stream water nitrate concentration data (NO3.N) obtained from federal state monitoring programs in Germany at the outlets of 182 mesoscale catchments [32] and mean daily discharge measurements from the same locations. Nitrate data were available at biweekly or monthly intervals with a median time span of 21 years (ranging from 5 to 40 years between 1980 and 2020). Catchment sizes varied from 95 to 23 600 km^2, with minimum mean elevations (30 m a.s.l.) in the North German Plain region and the highest elevations in the alpine catchments (1180 m a.s.l.). The predominant land use is agriculture, ranging from 11% to 84% (median 50%) of the catchment area.

2.1. Identification of droughts
We identified hydrological droughts using daily discharge data from 1978 to 2020 and a variable threshold level approach [33]. We computed a variable threshold for each station using the 80th percentile of the flow duration curve (i.e. 80% of the flow values are excluded) of the smoothed discharge time series for each day of the year. We smoothed the discharge time series over a time window of 30 d to reduce the number of dependent events [34]. Drought was defined as a period of 30 or more consecutive days with smoothed discharge values below the threshold. The post-drought period was defined as the 100 d period after the end of the drought. If another drought

occurred during a post-drought period, the corresponding nitrate samples were considered drought samples. We based our selection of 100 d on covering typical response periods [30, 35]. Furthermore, we tested different thresholds for defining droughts (figures S1 and S2) and post-droughts (figures S3(b) and S4) to ensure the suitability of our selections for the diverse catchments in the study area. We found that catchments with a significant difference (p-value $\leqslant 0.05$) in nitrate anomalies between post-drought and drought, and no-drought periods remained consistent across a wide range of possible threshold values.

2.2. Data analysis

Our first goal was to quantify nitrate concentrations during drought and post-drought periods in different seasons. We observed a decreasing trend in nitrate concentrations since the 1990s in many of the studied catchments because of changes in European fertilizer application regulations. To isolate the effect of hydrological droughts from the potential trends and the intrinsic seasonality of the observed nitrate time series, we removed the long-term trend by subtracting a simple moving average method with a 5 year time window (figure S5). We then subtracted the seasonal mean (i.e. the mean value of the samples collected on the day of the year within a 30 d window) from each detrended nitrate sample to obtain nitrate concentration anomalies (Z-NO3.N).

Each identified nitrate anomaly was attributed to drought or post-drought conditions. In the subsequent analyses, we only considered catchments with at least 15 nitrate samples collected during both the drought and the post-drought periods. For each catchment and season, we computed the differences in median anomaly values between drought and post-drought compared to no-drought conditions and tested the significance of these differences using the Kruskal–Wallis nonparametric test with a significance level of 5% [36].

We linked the spatial variability of median nitrate anomalies during the drought and post-drought periods to the spatial variability of catchment descriptors that characterize the main aspects of nitrate export in German catchments. The catchment descriptors were obtained from the QUADICA dataset [32]. We tested the main drivers of nitrate dynamics at the long-term catchment scale using the PLAN framework [37], which incorporates anthropogenic inputs (i.e. the proportion of agricultural land or the number of people, P, weighted by the specific nitrate load, L) and catchment attenuation (artificial and natural attenuation, A and N). For anthropogenic inputs, we analyzed the fraction of agricultural areas in the catchment, which is the primary source of nitrate in our study domain [38]; the total nitrogen input from wastewater treatment plants per
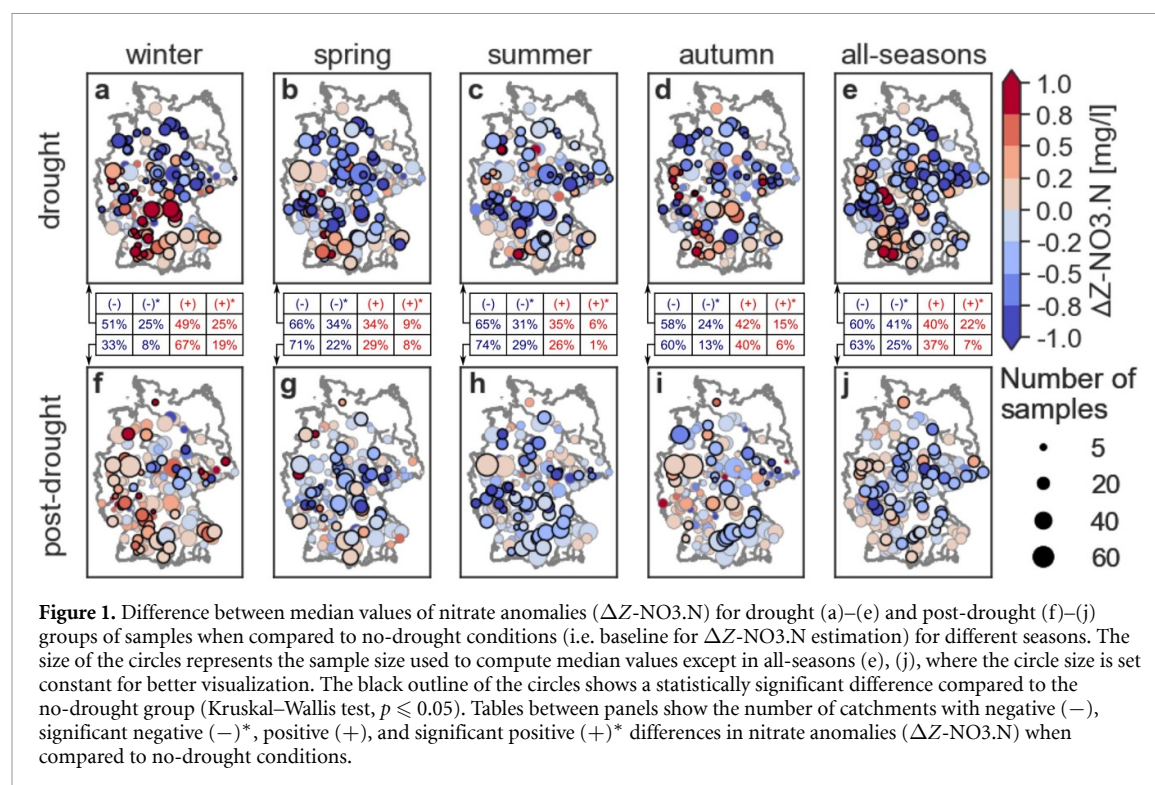
unit of area, which is particularly important during low-flow conditions [1]; and the mean annual nitrate surplus between 1991 and 2015 that includes fertilizer surplus and atmospheric deposition. We characterize the natural attenuation using three proxies: mean annual nitrate retention (i.e. the difference between mean annual nitrogen surplus and mean annual load) that also accounts for a potential biogeochemical removal of nitrate [39], fraction of water-impacted soils (stagnosols, semi-terrestrial, semi-subhydric, subhydric, and moor soils) as a proxy of riparian areas and wetlands where nitrate is often removed [40], and soil thickness which is related to transit times, with thicker soils characterized by longer residence times and hence more biogeochemical retention [41]. In addition to the PLAN framework, we consider climatic descriptors that may affect the temporal variability of nitrate dynamics [42]. We used the mean annual precipitation, mean annual temperature, and mean annual frequency of runoff events, identified using an automatic runoff event identification method as climatic descriptors [43].

Finally, we define seasonal extremes as nitrate anomalies that exceeded the 85th percentile of all anomalies in a given catchment and season (i.e. calendar winter, spring, summer, and autumn). We further computed the frequency of occurrence of these seasonal extremes during drought and post-drought conditions (figure S6) and compared this occurrence frequency to the expected frequency, assuming a uniform distribution of seasonal extremes for each hydrological condition (i.e. 15%). We quantified the effect of selecting different thresholds to define seasonal extremes on their likelihoods by comparing them with the corresponding expected frequencies (figure S7).

3. Results

3.1. Drought and post-drought nitrate anomalies

The observed median nitrate anomalies during drought and post-drought exhibited varied responses compared to the no-drought conditions (figures 1(e) and (j)). During droughts in any season, 60% of the catchments exhibited lower and 40% significantly lower nitrate anomalies (median difference of -0.59 mg l^{-1} of NO3.N, p-value $\leqslant 0.05$) compared to no-drought conditions (figure 1(e)). However, this was reversed in winter, the most critical season of nitrate export from catchments (figures 1(a), (e), table S1 and figure S8). During winter droughts, we observed higher nitrate concentrations compared to no-drought conditions in 49% of the catchments, with 25% of the catchments showing a positive significant difference (median difference of 0.57 mg l^{-1} of NO3.N, p-value $\leqslant 0.05$) regardless of the drought definition (figures S1 and S2), primarily in Southern Germany (figure 1(a)).

Figure 1. Difference between median values of nitrate anomalies (ΔZ-NO3.N) for drought (a)–(e) and post-drought (f)–(j) groups of samples when compared to no-drought conditions (i.e. baseline for ΔZ-NO3.N estimation) for different seasons. The size of the circles represents the sample size used to compute median values except in all-seasons (e), (j), where the circle size is set constant for better visualization. The black outline of the circles shows a statistically significant difference compared to the no-drought group (Kruskal–Wallis test, $p \leqslant 0.05$). Tables between panels show the number of catchments with negative ($-$), significant negative ($-$)*, positive ($+$), and significant positive ($+$)* differences in nitrate anomalies (ΔZ-NO3.N) when compared to no-drought conditions.

Similarly, during post-droughts at any season, 63% of all catchments showed lower and 25% significantly lower nitrate anomalies (median difference of $-0.34\,\mathrm{mg\,l^{-1}}$ of NO3.N, p-value $\leqslant 0.05$) compared to no-drought conditions (figure 1(i)). However, during winter post-drought conditions, we observed higher nitrate concentrations compared to no-drought conditions in 67% of the catchments, with 19% of the catchments showing significantly higher concentrations (median difference of $0.41\,\mathrm{mg\,l^{-1}}$ of NO3.N, p-value $\leqslant 0.05$) irrespective of the post-drought definition (figure S14), particularly in Western Germany (figure 1(e)).
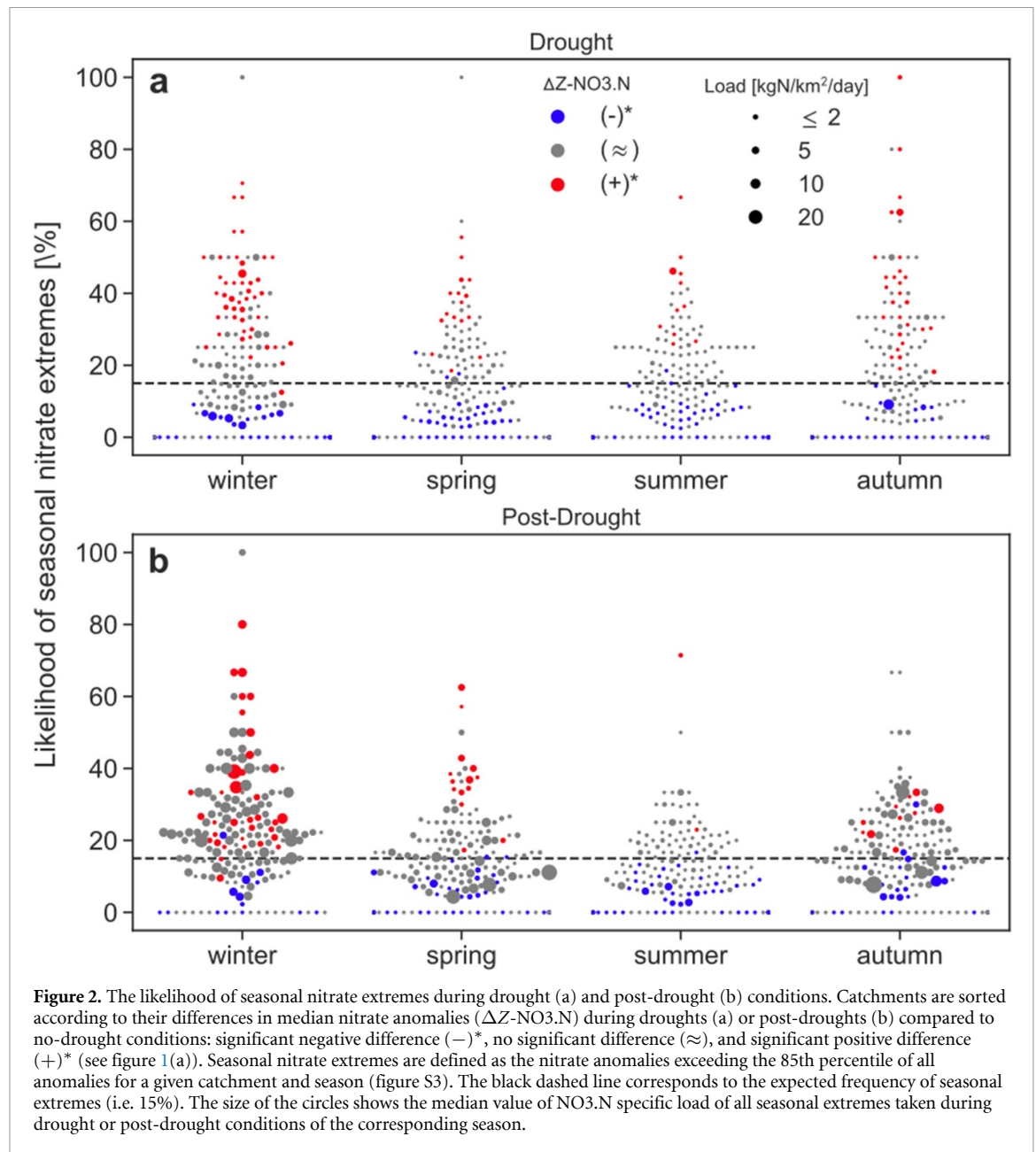
In spring, summer, and autumn, nitrate concentrations were lower during drought and post-drought periods than under non-drought conditions. In fact, we found lower nitrate anomalies in 65% of the catchments in spring (figure 1(b), 31% of which decrease significantly, p-value $\leqslant 0.05$), 66% of the catchments in summer (figure 1(c), 31% of the catchments show a significant decrease, p-value $\leqslant 0.05$), and 58% of the catchments in autumn (figure 1(d), 24% of the catchments show a significant decrease, p-value $\leqslant 0.05$). The median magnitude of nitrate reduction during droughts in the catchments with significantly lower nitrate anomalies varies from 0.55 to $0.73\,\mathrm{mg\,l^{-1}}$ of NO3.N in these seasons (table S1). Furthermore, during post-droughts, nitrate concentrations are lower compared to no-drought conditions in 71% of the catchments in spring (figure 1(f), 22% of the catchments show a significant decrease, p-value $\leqslant 0.05$, 74% of the catchments in summer

(figure 1(g), 29% of the catchments show a significant decrease, p-value $\leqslant 0.05$), and 60% of the catchments in autumn (figure 1(h), 13% of the catchments show a significant decrease, p-value $\leqslant 0.05$). The median magnitude of reduction in nitrate anomalies during spring, summer and autumn in catchments with significantly lower nitrate anomalies ranges between 0.4 and $0.45\,\mathrm{mg\,l^{-1}}$ of NO3.N (table S1).

3.2. Seasonal nitrate extremes during droughts and post-droughts

We extend our analysis to explore the impact of hydrological droughts on the likelihood of extremely high nitrate anomalies in each season. Differences in the likelihood of observed seasonal extremes during droughts compared to the expected likelihood (i.e. 15%) were consistent with median differences in nitrate anomalies during droughts compared with non-drought conditions (figures 1(a)–(d)). In catchments where nitrate anomalies were significantly higher during droughts (red dots figure 2(a)), the likelihood of seasonal extremes was the highest, with a median increase in the likelihood of seasonal extremes of 23% (table S2). Nevertheless, the nitrate load during these events was lower than the median values of winter loads (point sizes figures 2(a) and S9) owing to low discharges during droughts.
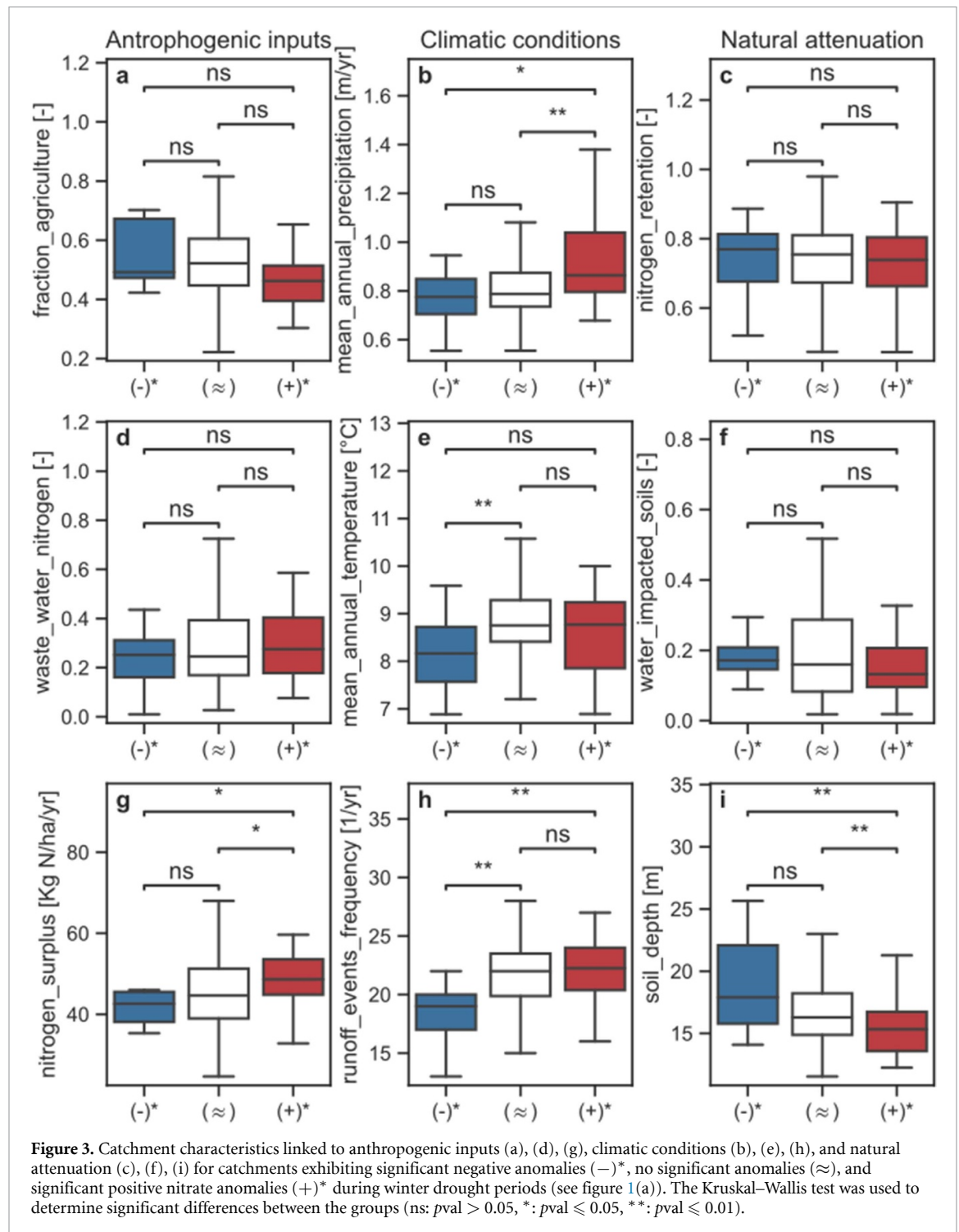
Seasonal extremes during winter post-drought were generally more likely to occur than the expected value (median increase of 6% in the likelihood). In

Figure 2. The likelihood of seasonal nitrate extremes during drought (a) and post-drought (b) conditions. Catchments are sorted according to their differences in median nitrate anomalies (ΔZ-NO3.N) during droughts (a) or post-droughts (b) compared to no-drought conditions: significant negative difference $(-)^*$, no significant difference $(\approx)$, and significant positive difference $(+)^*$ (see figure 1(a)). Seasonal nitrate extremes are defined as the nitrate anomalies exceeding the 85th percentile of all anomalies for a given catchment and season (figure S3). The black dashed line corresponds to the expected frequency of seasonal extremes (i.e. 15%). The size of the circles shows the median value of NO3.N specific load of all seasonal extremes taken during drought or post-drought conditions of the corresponding season.

particular, catchments with higher median nitrate anomalies (red dots figure 2(b)) have a median increase in the likelihood of extremes of 11% (table S2), and catchments with no significant differences in median nitrate anomalies compared to non-drought conditions (gray dots figure 2(b)) in winter, have a median increase in the likelihood of seasonal extremes of 5%. In both groups of catchments, the combined effect of seasonal extremes of nitrate anomalies and recovered winter levels of streamflow (which were the highest in winter in the majority of the study catchments) led to higher specific loads than the median winter specific loads, amplifying the hazard of extreme nitrate concentrations and nitrate loads (figure S9(c)).

4. Discussion

Nitrate anomalies displayed pronounced spatial heterogeneity, particularly in winter during drought and post-drought periods (figure 1). Winter was the most critical season for delivering nitrate downstream at our study sites. In winter, we observed a higher mean nitrate concentration and discharge, and hence higher loads, compared with the other seasons (figure S8). Additionally, we observed that extreme nitrate concentrations (i.e. the 15th highest 15th) mainly occur in this season. Consequently, the following analyses attempt to disentangle the spatial variability of nitrate concentrations, particularly during winter droughts and post-droughts, by

Figure 3. Catchment characteristics linked to anthropogenic inputs (a), (d), (g), climatic conditions (b), (e), (h), and natural attenuation (c), (f), (i) for catchments exhibiting significant negative anomalies (−)*, no significant anomalies (≈), and significant positive nitrate anomalies (+)* during winter drought periods (see figure 1(a)). The Kruskal–Wallis test was used to determine significant differences between the groups (ns: $p$val > 0.05, *: $p$val $\leqslant 0.05$, **: $p$val $\leqslant 0.01$).

exploring and discussing the differences in catchment descriptors following the PLAN framework by characterizing anthropogenic nitrogen inputs (PL), catchment natural attenuation (N), and climatic conditions for catchments with contrasting directions of nitrate anomalies.

4.1. Spatial variability of nitrate export during winter droughts

We found that the groups of catchments that exported significantly higher (25% of the catchments, figure 1,

table S1 (+)*) and significantly lower (25% of the catchments, figure 1, table S1 (−)*) nitrate concentrations in streams compared with non-drought conditions did not differ in their anthropogenic inputs (PL, figures 3(a), (d) and (g)). Although we found differences in the proportion of agricultural land between catchments with different nitrate concentrations during winter droughts, the mean annual nitrogen surplus, which is a more precise indicator of diffuse nitrogen sources, did not show any significant differences between these catchments. Moreover,

the fraction of wastewater nitrogen contribution to annual nitrogen sources was not significantly different between catchments with significantly higher and lower nitrate concentrations during winter droughts, indicating that anthropogenic sources were not the main drivers of spatial variability. During spring and autumn droughts, when runoff rates were lower than during winter droughts, catchments with more wastewater contribution showed significantly higher nitrate anomalies (figures S10 and S11), which is in agreement with previous studies reporting high nitrate concentrations from point sources during drought conditions due to a lack of dilution [1, 20]. However, the fraction of wastewater input did not affect summer droughts (figure S12). During the warm summer months, biogeochemical removal in the soil and streams increases, which might obscure the effects of wastewater sources [11].

Natural attenuation (N) is a main driver of spatial variability in nitrate responses during winter droughts. Catchments with increasing nitrate concentrations during winter droughts had lower mean annual nitrogen retention and a reduced abundance of water-impacted soils (figure 3(c)), illustrating the importance of natural retention and transformation in the catchment, specifically in riparian wetlands during winter droughts compared to non-drought conditions. Furthermore, catchments with shallower soils correspond to smaller subsurface storage and are potentially associated with shorter transit times, which might lead to less efficient nitrogen removal from soils [41].

Catchments with significantly higher nitrate concentrations during winter droughts had higher mean annual precipitation and lower mean annual temperatures. Diffuse sources may be less disconnected in wetter catchments than in drier catchments, even during winter droughts. Therefore, the expected reduction in nitrate transport due to source-stream disconnection might be less pronounced. In contrast, warmer and drier catchments with higher annual nitrogen retention exhibit lower nitrate concentrations during winter droughts than during non-drought periods, suggesting that climatic conditions and natural nitrogen attenuation are the primary drivers of spatial variability in nitrate export during winter droughts.

Additionally, we examined all descriptors available from the QUADICA dataset relevant for our study period (i.e. 1978–2020) and normalized per unit area (i.e. descriptors that are applicable for comparing a set of catchments of diverse sizes) to complement our analysis and uncover any potential drivers beyond the PLAN framework (table S3). Catchments with relatively higher nitrogen abundance in the groundwater than in the topsoil (lower vertical nitrogen heterogeneity, het_v in table S3) also showed increased nitrate concentrations during winter droughts, possibly due to the contribution of

contaminated groundwater [44]. These catchments often have a higher fraction of fissured aquifers, which are known for their low nitrogen retention (table S3) [45], highlighting the importance of natural retention in aquifers. Although instream processes can increase nitrogen removal, especially during low flows [19], we did not identify descriptors that specifically pinpointed these processes (e.g. drainage density) as primary drivers of the spatial variability of nitrate responses during winter droughts, possibly because of lower instream removal during winter [11].

We checked the overlap of catchments with significantly higher nitrate anomalies during winter drought and post-drought compared to non-drought conditions (figure S13). We found that only 9% of the catchments showed significantly higher nitrate anomalies during winter drought and post-drought. This suggests that the observed spatial heterogeneity during winter droughts and post-droughts was driven by different processes.

4.2. Spatial variability of nitrate export during winter post-droughts

During winter post-droughts, we found that catchments exhibiting higher nitrate anomalies compared to non-drought conditions (19% of the catchments, figure 1(f), (+)*) were mainly located in the West and Southeast Germany. Catchments with a higher nitrogen surplus exhibited significantly higher stream nitrate concentrations during winter post-droughts than during non-drought periods (figure 4(g)). Catchments with higher fertilizer applications, represented by a higher nitrogen surplus [46], are prone to nitrogen accumulation in the soil during droughts because of reduced plant uptake and less nitrate export from the soils during dry periods. Thus, after the drought ends, these catchments can export anomalously high nitrate concentrations [31]. Instead, the natural attenuation of nitrate in catchments does not considerably affect the spatial patterns of winter post-drought export of nitrate to streams (figure 4(c), (f) and (i)), which is in line with Jutglar *et al* [30], who did not find a relationship between soil types associated with different denitrification potential, and the magnitude of the post-drought flush [47].

We found that catchments with significantly higher nitrate concentrations during post-drought winter had higher mean annual precipitation and a higher frequency of runoff events (figure 4(b) and (h)). Wetter conditions can enhance the transport of accumulated nitrogen from the soil to streams, leading to higher nitrate concentrations. In addition, in catchments with a higher frequency of runoff events (figure 3(h)), faster pathways from sources to streams are more likely to be activated, thereby mobilizing the stored nitrogen in the soil under dry conditions [48, 49]. Conversely, the post-drought nitrate anomalies in winter were lower than those in
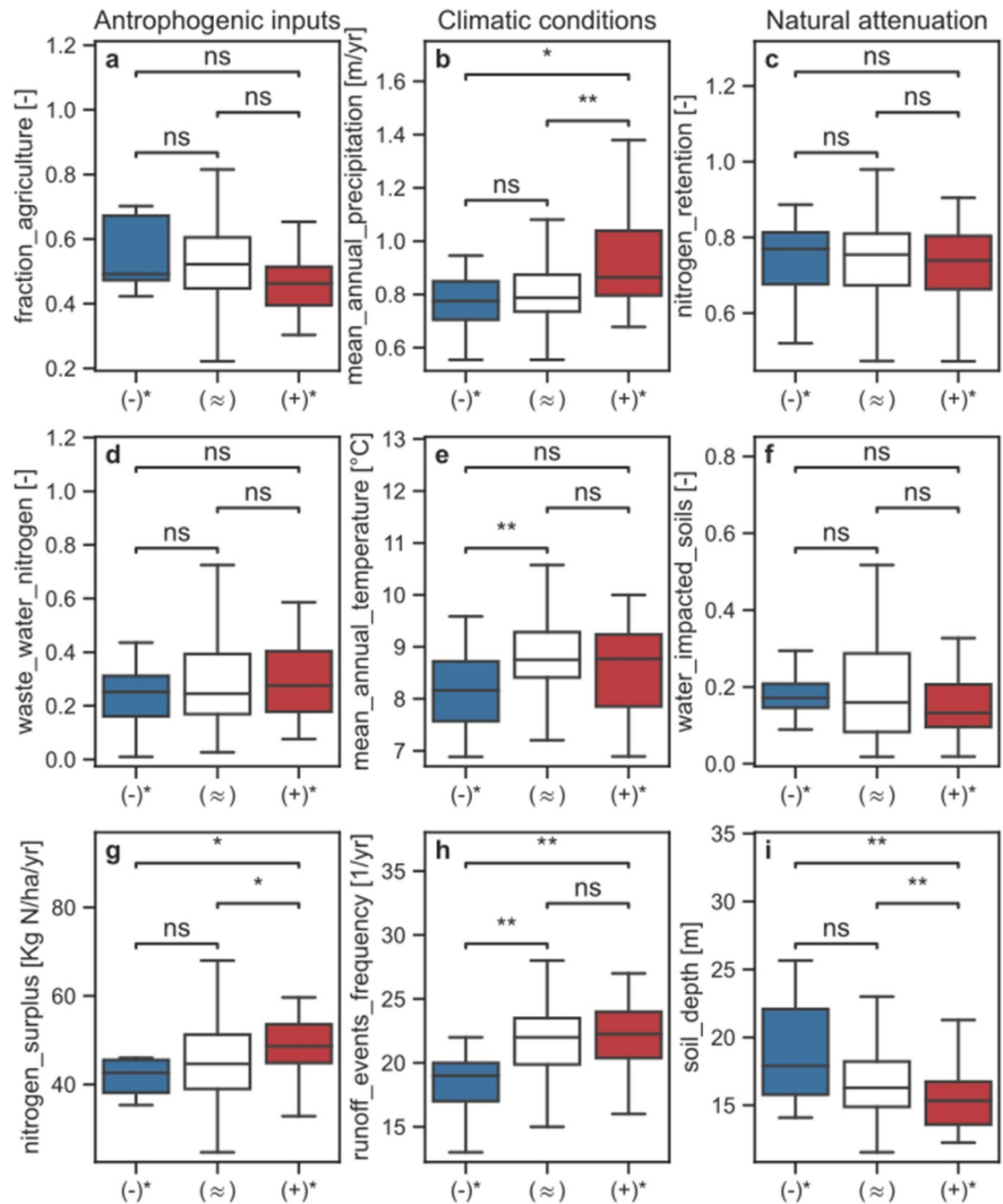
Figure 4. Catchment characteristics linked to anthropogenic inputs, climatic conditions, and natural attenuation for catchments exhibiting significant negative anomalies $(-)^*$, no significant anomalies $(\approx)$, and significant positive anomalies $(+)^*$ during winter post-drought periods (see figure 1(b)). The Kruskal–Wallis test was used to determine significant differences between the groups (ns: $p$val > 0.05, *: $p$val $\leqslant 0.05$, **: $p$val $\leqslant 0.01$).

drier catchments, with a generally low frequency of runoff events and a low nitrogen surplus. In drier catchments, we expect a slower reconnection of hydrological pathways after droughts and therefore reduced nitrate transport from diffuse sources during the post-drought period [50]. Similarly, we found lower nitrate anomalies during drier seasons under post-drought conditions in most catchments, suggesting that during these periods, though discharge levels are recovered, nitrate transport between diffuse sources and streams is lower than that under normal hydrological conditions [35]. Although there is evidence that post-drought nitrate flashes are related to episodes of fast rewetting conditions [51], we found no consistent relationship between the magnitude of post-drought flashes and the runoff magnitude or rewetting speed during the post-drought period (figures S14(d) and (e)). Similarly, we found no consistent relationship between the post-drought nitrate responses and drought characteristics (duration, severity, and intensity, figures S14(a)–(c)).

4.3. Implications

Our results revealed that the winter season exhibited the most distinct disparities between drought, post-drought, and no-drought conditions. Winter is the most critical season for high nitrate concentrations and loads in the streams (figure S8). Notably, winter nitrate contamination can be particularly impactful on water bodies, such as lakes and estuaries, exacerbating the risk of eutrophication in subsequent periods [5, 52]. Moreover, more frequent drought events are likely to occur in the future due to climate change [3, 4], potentially increasing the threat of harmful episodes of high nitrate concentrations in streams.

Our analysis indicates that wetter catchments generally display higher nitrate concentrations during winter droughts and post-droughts than under non-drought conditions. In addition, during winter droughts, natural attenuation is a major driver of spatial variability in nitrate responses. These findings indicate that during winter droughts, the interplay between transport and biogeochemical retention processes at the catchment scale becomes particularly sensitive, which highlights the importance of protecting and expanding nitrate retention zones, such as riparian wetlands, to mitigate the environmental challenges associated with high nitrate concentrations during winter droughts [53, 54]. Furthermore, climatic characteristics and anthropogenic inputs of the catchments shaped the spatial variability of nitrate responses during winter post-droughts. We observed that catchments limiting fertilizer application in recent decades were less prone to experience winter post-drought flushes of nitrate (negative relationship with reduction in nitrogen surplus in the last few decades, table S4), evidencing that at large scale it is important to curtail fertilizer application [55]. Additional measures, such as tile drain management, might also be beneficial at the local scale to limit rapid nitrate transport from agricultural land to streams [56].

The likelihood of seasonal extreme nitrate concentrations was 24% higher during winter droughts compared to the expected levels in catchments with significantly higher nitrate anomalies than during non-drought conditions (i.e. catchments with wetter conditions and low nitrogen retention capacity). Regardless of the load levels, elevated nitrate concentrations in streams can alter nutrient stoichiometry and affect aquatic ecosystems that are sensitive to variations in nutrient ratios [57]. Moreover, the frequency of seasonal extremes was 11% higher during winter post-drought in catchments exhibiting significantly higher nitrate concentrations compared to no-drought conditions, leading to high levels of loads (figure 2(b)). More frequent seasonal nitrate extremes during winter post-drought can have adverse ecological effects on downstream estuaries and lakes. Nitrates can persist for extended periods in water bodies, increasing the risk of eutrophication [5, 58, 59]. Moreover, the excessive transport of nitrate from diffuse sources during post-drought periods affects groundwater even for longer periods, which could jeopardize current attempts to improve groundwater quality [7, 30].

5. Conclusions

In this study, we conducted a large-scale analysis to examine the effects of hydrological drought and post-drought conditions on the nitrate concentrations in streams across a diverse set of catchments in Germany. Generally, we found that 40% and 25% of the catchments during seasonal droughts and post-droughts, respectively, show significantly lower nitrate anomalies. However, during winter, the most critical season for nitrate concentrations and loads, nitrate anomalies showed more pronounced spatial variations, with more catchments showing higher nitrate anomalies, particularly during the post-drought period. Specifically, we find that 25% of the catchments exhibited significantly higher median nitrate concentrations during winter droughts than during non-drought periods. On average, these catchments are characterized by wetter conditions and higher nitrogen retention capacities. During winter post-droughts, 20% of the study catchments exported significantly higher nitrate concentrations than during non-drought conditions. Catchments with significantly higher nitrate concentrations during the winter post-drought had wetter conditions and higher nitrogen surpluses. During the winter post-droughts period, we observed an increase in the frequency of seasonal nitrate extremes in our study catchments, which, combined with high winter discharge levels, can result in exceptionally high nitrate loads. Our study highlights the diverse responses of nitrate concentrations to drought and post-drought conditions across catchments and seasons, indicating that most catchments are likely to exhibit higher nitrate concentrations during extreme hydrological events. As the frequency of droughts is expected to increase under climate change conditions, these insights are crucial for targeted adaptation in the future.

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