



When does nitrate peak in rivers and why? Catchment traits and climate drive synchrony with discharge

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Abstract. Anthropogenic nitrogen loading has disrupted global biogeochemical cycles, degrading water quality and altering ecosystem functions. Rivers mediate nitrogen transport and reactivity, yet at the seasonal scale, the temporal links between peak river nitrate concentrations (N) and water flow (Q) are poorly understood. Here, we used the approach of Weighted Regressions on Time, Discharge, and Season (WRTDS) to reconstruct daily timeseries of N concentrations from routine monitoring data. These were used to assess the long term N-Q synchrony and its variability across 66 river catchments in England (2000–2019), and a Random Forest Model was used to identify the key controls on each synchrony type. This revealed three general behaviours: 1) smaller catchments dominated by agriculture displayed peak N during high flow (QMax-Synced, 28.8% of catchments), 2) larger and/or more urbanised catchments had the highest N concentrations during low flow periods likely due to point-source inputs (QMin-Synced, 25.8% of catchments), and, 3) larger highly mixed land use catchments displayed a decoupling of N and flow conditions, i.e. were asynchronous (Asynced, 46.8% of catchments). The temporal consistency of peak N-Q synchrony was determined by the dominant hydrological processes and their interaction with anthropogenic pressures. In QMax-synced catchments, wetter winters, and steeper slopes promoted more rapid runoff, reinforcing synchrony. In QMin-synced catchments, synchrony reflected the dominance of urban point-source inputs (represented as urban area and population density) but was sustained only under sufficiently extreme low flows. Asynced catchments showed the greatest year-to-year switching in the dominant synchrony year type, with wetter years likely enhanced groundwater recharge and legacy-N delivery, favouring QMin-like behaviour, whereas years dominated by rapid runoff and shallow flow paths promoted QMax-like winter flushing. Our findings reveal that nitrate–discharge synchrony is not fixed but dynamically regulated by hydroclimatic variability, catchment connectivity, and human infrastructure. Framing nitrate export through synchrony exposes a critical temporal dimension of nutrient cycling that a purely spatial analyses of loads or concentrations would overlook, providing new insight into how climatic and anthropogenic forcing interact to shape water-quality responses in human-modified landscapes.



1 Introduction

River networks are critical conduits in the global nitrogen (N) cycle, transporting and transforming nitrogen from terrestrial landscapes to lakes and coasts. However, intensive anthropogenic activities, such as fertilizer application, wastewater discharge, and land drainage, have disrupted this natural nitrogen cycling, leading to widespread water quality degradation and ecological damage (Galloway et al., 2008; Zhang et al., 2015; Diaz and Rosenberg, 2008). While much attention has been given to the magnitude of nitrogen loads, the seasonal dynamics of nitrate delivery and their alignment with hydrological processes remain poorly understood, particularly at broader spatial scales.

River discharge is a dominant control on nitrogen export, particularly in agricultural regions where flow variability can explain up to 75–93% of annual nutrient fluxes (Ezzati et al., 2022). Yet, the timing of peak nitrate concentrations relative to peak or minimum flows remains poorly understood, especially at the interannual scale. These peaks often dominate annual loads and drive the most acute ecological impacts as well as regulatory exceedances. While concentration–discharge (C–Q) relationships offer valuable insights into source–mobilisation dynamics and hydrological controls (Musolff et al., 2015; Bierozza et al., 2018; Knapp and Musolff, 2024), interpreted in isolation they risk emphasising average behaviour and often obscure temporal shifts in nitrate delivery pathways.

The analysis of synchrony, broadly defined as the temporal alignment of two or more processes, was initially developed in ecology to evaluate and interpret ecosystem attributes and processes such as trophic interactions, metapopulation dynamics (Bjørnstad et al., 1999; Hanski, 1998). To better understand interannual hydrological controls on peak nitrate concentrations and their timing, we apply the concept of synchrony, which we describe as the degree to which seasonal nitrate peaks align with seasonal patterns in flow, such as the month of highest or lowest discharge. Thus, synchrony captures the seasonal alignment (or misalignment) of biogeochemical responses with hydrological forcing, offering a dynamic lens on catchment function (Van Meter et al., 2019; Abbott et al., 2018). Despite its potential, few studies have quantified nitrate–discharge synchrony over time, and even fewer have explored how synchrony varies across diverse landscapes and land use types. This peak-based, month-focused metric of synchrony offers a simple categorical classification of catchments, providing insight into management-critical periods. By focusing on the timing of annual peaks, it is also less sensitive to short-term fluctuations and data gaps. Meanwhile, the C–Q slope, quantifying the magnitude and direction of nitrate response to hydrological variation, are often used to explain the spatial distribution and availability of solutes within catchments (Zhi and Li, 2020; Knapp et al., 2022). Combining the synchrony metric and C–Q slope analysis thus clarifies both when seasonal extremes occur and how nitrate is delivered under varying hydrological conditions.

This study addresses our limited understanding of N–Q synchrony, and its variation across different hydrological and anthropogenic conditions, by examining the timing of nitrate concentration peaks relative to seasonal flow patterns in 66 catchments across England. Using long-term datasets and reconstructed concentration time series, we aim to identify distinct synchrony modes and investigate their drivers. The specific objectives of this study are to: 1) identify and characterise catchments based on their dominant synchrony patterns between discharge and nitrate concentration, 2) determine how



catchment properties such as baseflow, slope, and wastewater infrastructure shape synchrony behaviour, and 3) assess how
interannual climate variability and anthropogenic pressures drive synchrony shifts, particularly in catchments with mixed or
competing nitrate sources.

By identifying dominant synchrony behaviours, we seek to reveal how hydrological regimes, land use, and legacy pollution
interact to control seasonal nitrate export, with implications for targeted nutrient management under changing climate and
land use pressures.

2 Data and methods

2.1 Data sources and screening

Water quality data for site across England were obtained from the UK Environment Agency's Water Quality Archive (EA,
2020). The dataset consisted of river water quality measurements collected at irregular intervals from 2000 to 2020. We
focused on nitrate-N concentrations as the dominant form of dissolved N (NO_3^- -N). Initial screening of the data identified
21,049 sampling sites with NO_3^- -N data. Daily mean discharge records were obtained from the National River Flow Archive
(NRFA) which contains daily discharge measurements for over 1500 UK gauging stations.

We applied the following criteria to filter and select nitrate data for our study: (1) the data needed to cover at least 80% of
the months between 2000 and 2019, (2) the time series could not include gaps longer than 3 consecutive months, (3) each
water quality site must be within 1 km of a flow gauge with daily discharge (Q) data and located on the same river, and; (4)
the flow gauge must have at least 90% of the discharge data available over the 20-year period. Application of the criteria
above resulted in 66 catchments (Fig. S1) with nitrate and corresponding discharge time series data. In total, there were
18,947 nitrate concentration observations and 482,130 flow measurements across these 66 sites and the 20 years of study.
All data analyses were based on the water year (from 1st October to 30th September of the subsequent year).

The selected catchments spanned a wide range of hydrological, topographical, land cover, geological, lithology and soil
characteristics and other descriptors (Table 1, (NRFA, 2020)). The Standardized Precipitation Index (SPI) was obtained for
56 out of 66 studied catchments from the UK Centre for Ecology & Hydrology (UKCEH), via the UK Water Resources
Portal (UKCEH, 2024). The standard precipitation index (SPI) expresses precipitation anomalies in units of standard
deviation relative to a long-term baseline (McKee et al., 1993). We adopted the UK gridded SPI data set of (Tanguy et al.,
2017), which used 1961–2010 as its reference period. The SPI can be calculated for different accumulation periods: for
example, SPI1 reflects precipitation anomalies over a 1-month window, while SPI12 reflects anomalies accumulated over 12
months. For each catchment, we defined winter SPI1 as the mean of the monthly SPI1 values for December to February, and
annual SPI12 as the September SPI12 value for each water year. The population density was extracted and calculated from
UK gridded population 2011 based on Census 2011 published by Environmental Information Data Centre (Reis et al., 2017).
The density of Wastewater Treatment Plant (WWTPs) was calculated by dividing the numbers of WWTPs in a catchment by
the catchment area.



Table 1. Key catchment properties calculated and used in subsequent analyses. To aid understanding a more detailed description of each variable is provided.

Category	Variable	Unit	Description (NRFA,2020)
Topography	Catchment Area	km ²	Area of the catchment at gauging location
	Mean Altitude	m	Mean catchment altitude
Lithology & Soils	High Permeable Bedrock	%	Proportion of highly permeable bedrock
	Moderate Permeable Bedrock	%	Proportion of moderately permeable bedrock
	Low Permeable Bedrock	%	Proportion of low permeability bedrock
	High Permeable Surface	%	Proportion of High-permeability surface deposits
	Low Permeable Surface	%	Proportion of Low-permeability surface deposits
Land Cover	Wood Land	%	Percentage of Woodland cover
	Arable Land	%	Percentage of Arable and horticultural land
	Grass Land	%	Percentage of Grassland cover
	Mountain Heath Bog	%	Percentage of Mountain heath and bog cover
	Urban Land	%	Percentage of Urban land cover
Hydrology	BFI	-	Baseflow Index
	PROPWET	%	The Proportion of Time Soils Are Wet
	FARL	-	The Flood Attenuation by Reservoirs and Lakes index
	SPR	%	Standard Percentage Runoff Coefficient: the percentage of rainfall typically converted to surface runoff
	DPS	m/km	Mean Drainage Path Slope
Climate	Winter SPI1	-	Mean Monthly SPI1 value of the winter months
	SPI12	-	Annual SPI12 value for September of each water year
Anthropogenic	Population Density	Persons/ km ²	Number of people per square km
	WWTPs density	no./km ²	Number of WWTPs per square km



2.2 Modelling daily data and C-Q definitions

100 Daily concentrations were reconstructed using Weighted Regression on Time, Discharge and Season (WRTDS), which was implemented in the R package EGRET (version 3.0.9) (Hirsch, 2023; Hirsch et al., 2010). This approach estimates daily concentrations from irregularly sampled data using a locally weighted regression:

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

where t_i is the time in decimal years, C_i is the concentration on day i , Q_i is the daily discharge, β_0 is the intercept, β_1 captures
 105 long-term concentration trends, β_2 describes the sensitivity of a change in concentration to a change in discharge (i.e. the C-Q slope), and β_3 and β_4 account for seasonal cycles, and ε_i is the residual error term. These coefficients are fitted through regression at each time point, weighting observations by similarity in time, discharge, and season. This dynamic approach allows the concentration–discharge relationship to vary smoothly over time, reduces bias from irregular sampling (especially under-representation of high flows), and handles censored values effectively (Hirsch and De Cicco, 2015). We further used
 110 the locally estimated β_2 coefficients to classify each catchments export regime as dilution ($\beta_2 < 0.1$), chemostasis ($-0.1 \leq \beta_2 \leq 0.1$), and mobilisation ($\beta_2 > 0.1$) following established thresholds (Zhang, 2018; Herndon et al., 2015). The R scripts published by (Zhang et al., 2016) were used to estimate and extract the β_2 coefficients. To support seasonal synchrony analysis, we aggregated the reconstructed daily concentrations This produced a more complete and temporally consistent representation of nitrate dynamics than the observed data alone and enabled robust comparisons across catchments and years
 115 (comparisons of measured and fitted concentrations are shown in Fig. S2-S7).

2.3 Defining Synchrony

We first confirmed that both discharge and nitrate concentration exhibited a distinct unimodal pattern at all sites. We then identified, for each site and each year, the months of maximum and minimum discharge, as well as the month of the maximum nitrate concentration. Based on the consistency between these seasonal timings, we first defined the annual
 120 synchrony status for each year at each site as: 1) *QMax-Synced* when the maximum concentration month coincided with or fell within one month (± 1 month) of the maximum discharge month, 2) *QMin-Synced* using the same criteria as for QMax-Synced, except applied to the minimum discharge month, or 3) *Asynced* for years/catchments that met the criteria for neither category. This one-month coincidence window was chosen because it corresponds to the temporal resolution of seasonal flow regimes in temperate catchments. A narrower window would risk fragmenting the seasonal synchrony into noise,
 125 whereas a broader one would blur seasonality into semi-annual behaviour. We then used these annual synchrony categories in two ways throughout the analysis. First, as a catchment level classification, where each catchment was assigned a dominant category (QMax-synced, QMin-synced) based on the majority ($>50\%$) of its annual classifications while all others were grouped as the Asynced. Second, we assessed the consistency of synchrony within each catchment across years, using the proportion of years in which it exhibited QMax- or QMin-synchrony as a measure of interannual variability. This dual



130 approach allowed us to characterise both the dominant synchrony pattern at each site and its temporal stability (or lack of)
 over two decades of record.

2.4 Statistical analysis with catchment characteristics

To analyse the spatial variability of nitrate concentrations in rivers, the mean discharge and nitrate concentration for each
 catchment were calculated. The ratio of the coefficients of variation (CV) of discharge (CV_q) and concentrations (CV_c) was
 135 also calculated for each site across years to understand the hydrological impact on nitrate concentrations in each catchment.

To understand the catchment controls on the two synchrony patterns, a series of catchment descriptors (Table 1) were
 selected for the next step, where Random Forest (RF) modelling was applied to examine the relationship between the spatial
 patterns in synchrony and catchment characteristics. RF analysis was chosen for its robustness and ability to handle complex
 interactions within the data (Breiman, 2001). It is a non-parametric machine learning model composed of multiple decision
 140 trees, which builds each decision tree by randomly selecting attributes and optimally splitting the data. In our analysis, a
 random forest classification model was trained for the two significant synchrony patterns (QMax-Synced and QMin-Synced)
 to recognise the factors controlling the different synchrony patterns. Asynced Catchments were excluded as this group
 represents catchments with no dominant synchrony pattern and high variability, which would reduce the clarity and
 interpretability of the results. A Random Forest classifier implemented via the efficient and scalable ranger package in R
 145 was chosen for its robustness to small sample sizes and its ability to handle complex, nonlinear relationships between
 features (Wright and Ziegler, 2017). A three repeated 10-fold cross-validation approach was employed to evaluate model
 performance and ensure generalizability. The model was configured to compute permutation-based variable importance,
 allowing identification of the most influential descriptors for classification ($p < 0.05$), which has proved useful in previous
 study (Altmann et al., 2010). The number of trees was set to 500. The random forest (RF) model was implemented using the
 150 mlr3 (Version 0.22.1) in R (Lang et al., 2019) and the importance was ranked using the ranger (Version 0.16.0) package in R
 (Wright and Ziegler, 2017). Then, the important variables identified by RF model were tested for significant differences
 between synchrony types using the non-parametric Wilcoxon rank-sum test (R Core Team, 2024). In this way, we used the
 RF to explore which catchment and climatic variables most strongly distinguish QMax- and QMin-synced sites. Given the
 modest sample size and uneven class distribution, our aim was to use the RF primarily for variable importance ranking rather
 155 than formal prediction.

In addition, we assessed whether climatic variability and catchment properties influenced the frequency with which a
 catchment exhibits QMax, QMin, or Asynced behaviour from year to year. Initially we tested whether climate anomalies,
 represented by winter SPI1 and annual SPI12, differed between Synchronous and Asynced years within each synchrony
 pattern using paired Wilcoxon signed-rank tests. Second, we assessed the climate–discharge linkage by correlating SPI
 160 metrics with the annual maximum and minimum of the monthly mean discharge (hereafter MaxQ and MinQ). Then, to test
 whether discharge extremes were directly associated with synchrony outcomes, we converted annual MaxQ and MinQ to
 percentile ranks relative to each site’s full distribution of monthly discharges. We then compared MaxQ percentiles between



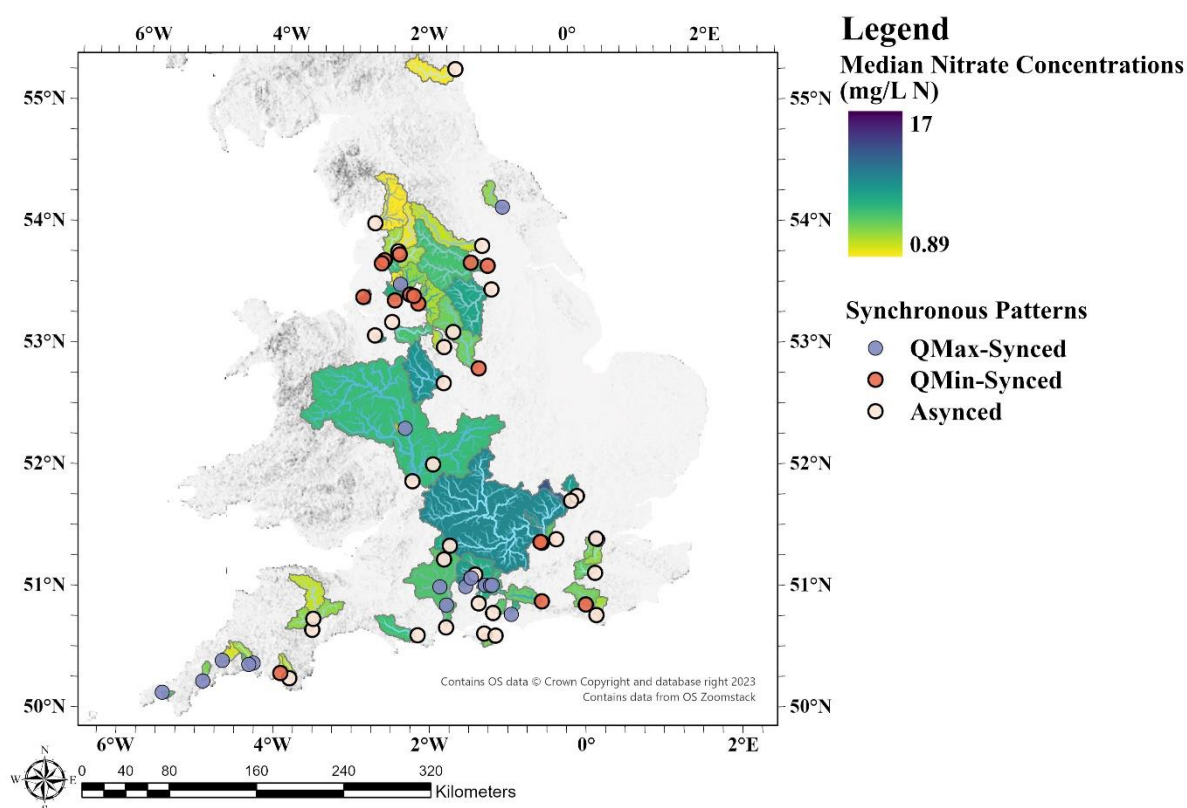
165 QMax- and non-QMax years in catchments where QMax-synchrony was more frequent and compared MinQ percentiles between QMin- and non-QMin years in catchments where QMin-synchrony was more frequent. Last, we used Spearman rank correlations and non-parametric Wilcoxon rank-sum tests to assess the relationship between synchrony variability and potential influential factors, calculated and visualised using the numpy, pandas, seaborn, matplotlib and scipy packages in Python (Virtanen et al., 2020; Reback et al., 2020; Harris et al., 2020; Waskom, 2021; Hunter, 2007).

3 Results

170 To ensure the reliability of modelled nitrate concentrations, we assessed the goodness-of-fit of the WRTDS models for each catchment. Across all sites, the median R^2 value was 0.59 ranging from 0.11 to 0.82, and the median RMSE was 0.60 mg/L, ranging from 0.20 to 4.12 mg/L. Monthly comparisons of observed and modelled concentrations for each site are provided in the Supplementary Information (Figures S2–S7).

3.1 Spatial patterns across and temporal variability within catchments

175 Catchment synchrony classifications and their temporal stability differed across the 66 catchments (Fig. 1 & 2). QMax-synced catchments (28.8%) were primarily located in southern and southwestern England, where nitrate peaks typically aligned with winter high flows. QMin-synced catchments (25.8%) were concentrated in the northwest, showing peak nitrate concentrations during or near summer low flows. The Asynced catchments (46.8%) were more broadly distributed across the country and did not exhibit a consistent seasonal alignment between nitrate and discharge.



180 **Figure 1: Spatial Distribution of Synchrony Patterns across England.** Sites classified as QMax-Synced show consistent alignment between peak nitrate (N) and discharge (Q) timing (± 1 month) in over 50% years. QMin-Synced sites represent those where over 50% of years align with minimum discharge months. Asynced sites represent all other cases.

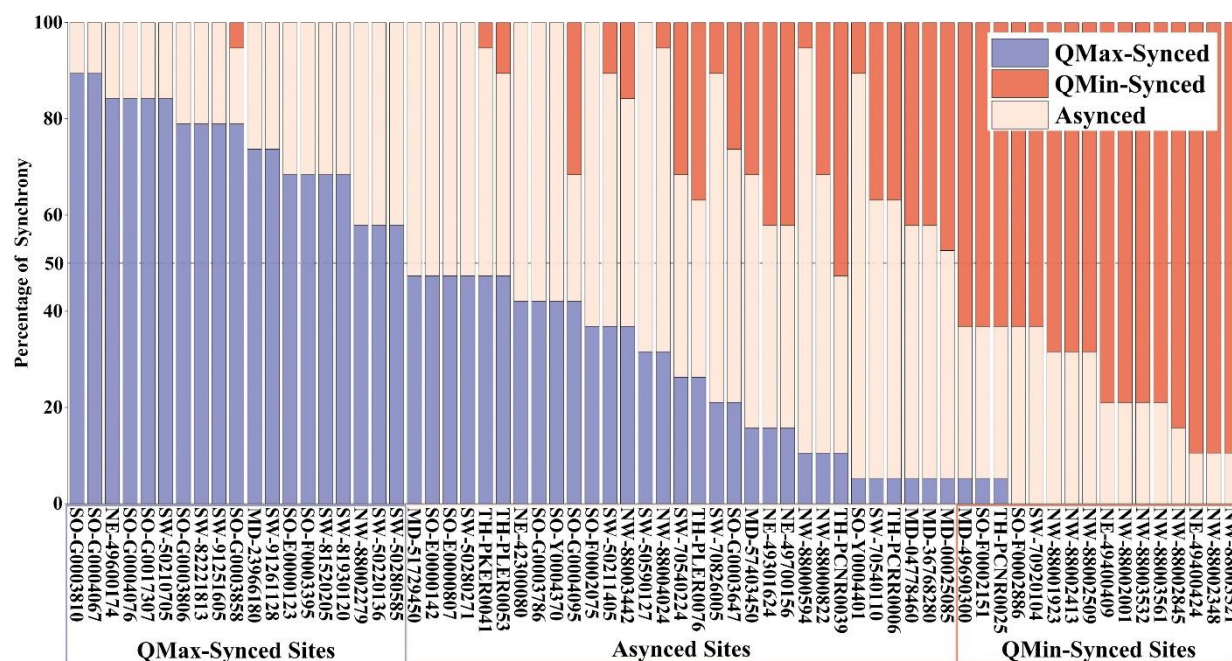


Figure 2: Interannual Consistency of Synchrony Patterns. The QMax-Synced segments represent the percentage of years where the peak nitrate concentration and peak discharge occur around the same time of year (± 1 month). The QMin-Synced segments indicate the percentage of years where the peak nitrate concentration coincides with the time of minimum discharge (± 1 month). The Async segments represent the percentage of years in between (i.e., neither QMax- nor QMin synced years).

QMax-synced sites exhibited clear winter nitrate peaks (Fig. 3a), with highest median concentrations in February (6.45 mg L^{-1} , IQR: $4.19 - 6.95 \text{ mg/L}$) and lowest in September (4.39 mg L^{-1} , IQR: $2.80 - 5.70 \text{ mg/L}$). In contrast, QMin-synced catchments typically showed a reversed seasonal pattern, with lowest concentrations during winter high flow (January: 4.40 mg/L , IQR: $3.12 - 4.95 \text{ mg/L}$) and peak concentrations during summer low flow (July: 6.15 mg/L , IQR: $4.15 - 8.02 \text{ mg/L}$; Fig. 3b). Async sites displayed flatter, more spatially variable nitrate regimes, without a dominant seasonal signal. While individual sites may have distinct seasonal patterns, the lack of alignment in their timing and magnitude resulted in the group-average curve appearing flat. Despite these marked seasonal differences, median nitrate concentrations did not differ significantly among the three synchrony types (Fig. S8). Overall, interannual variability in nitrate concentrations was substantially lower than variability in discharge (median $\text{CVc}/\text{CVq} = 0.19$, IQR: $0.14 - 0.32$). However, QMin-synced catchments showed significantly higher CVc/CVq ratios compared to the other two synchrony types (Fig. S9), suggesting stronger hydrological modulation of nitrate variability in these catchments. Descriptive statistics for discharge, nitrate concentration, and other related variables across all catchments are summarised in Table S1.

Although our classification groups catchments based on their dominant synchrony type, catchments also exhibited varying degrees of interannual variation in their synchrony status (Fig. 2). Among QMax-synced sites, the proportion of QMax-

aligned years ranged from 58% to 90%; similar ranges were found for QMin-synced sites. Asyncd catchments showed
 205 greater fluctuation between synchrony types.

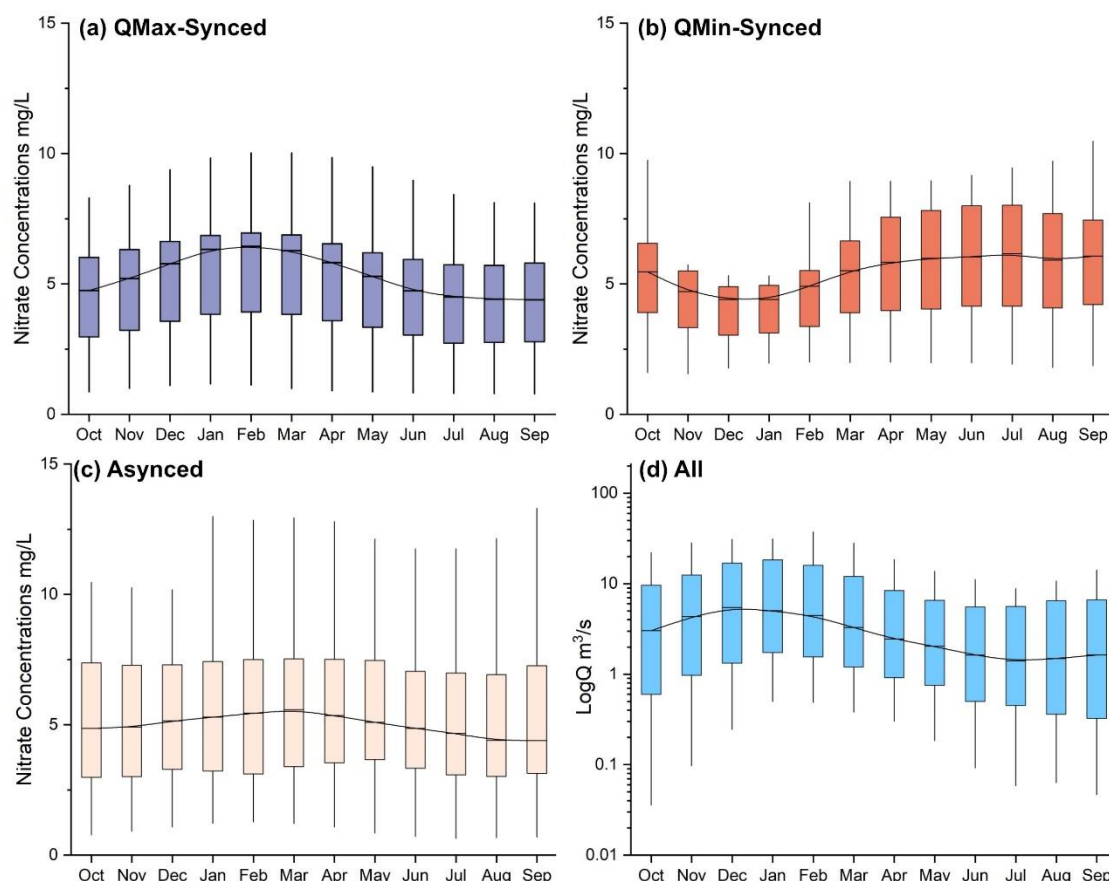


Figure 3: Annual Regimes of Nitrate Concentrations in (a) QMax-Synced, (b) QMin-Synced Sites (c) Asyncd, and (d) Discharge (Q) of all sites. The boxes represent the interquartile range (IQR; 25th-75th percentiles), and whiskers extend to the furthest values within $1.5 \times$ IQR from the box. The central line in each box indicates the median and the smooth connecting curve was generated using B-spline interpolation of the medians.

3.2 C-Q relationship and Variability in Synchrony Patterns

Catchments within each synchrony classification exhibited contrasting nitrate export behaviours, as reflected in the relationship between discharge and peak nitrate concentrations. Here, the interannual slope refers to the regression slope between annual peak nitrate concentrations and their corresponding discharge (in log units) for each catchment (Fig. 4a–c).

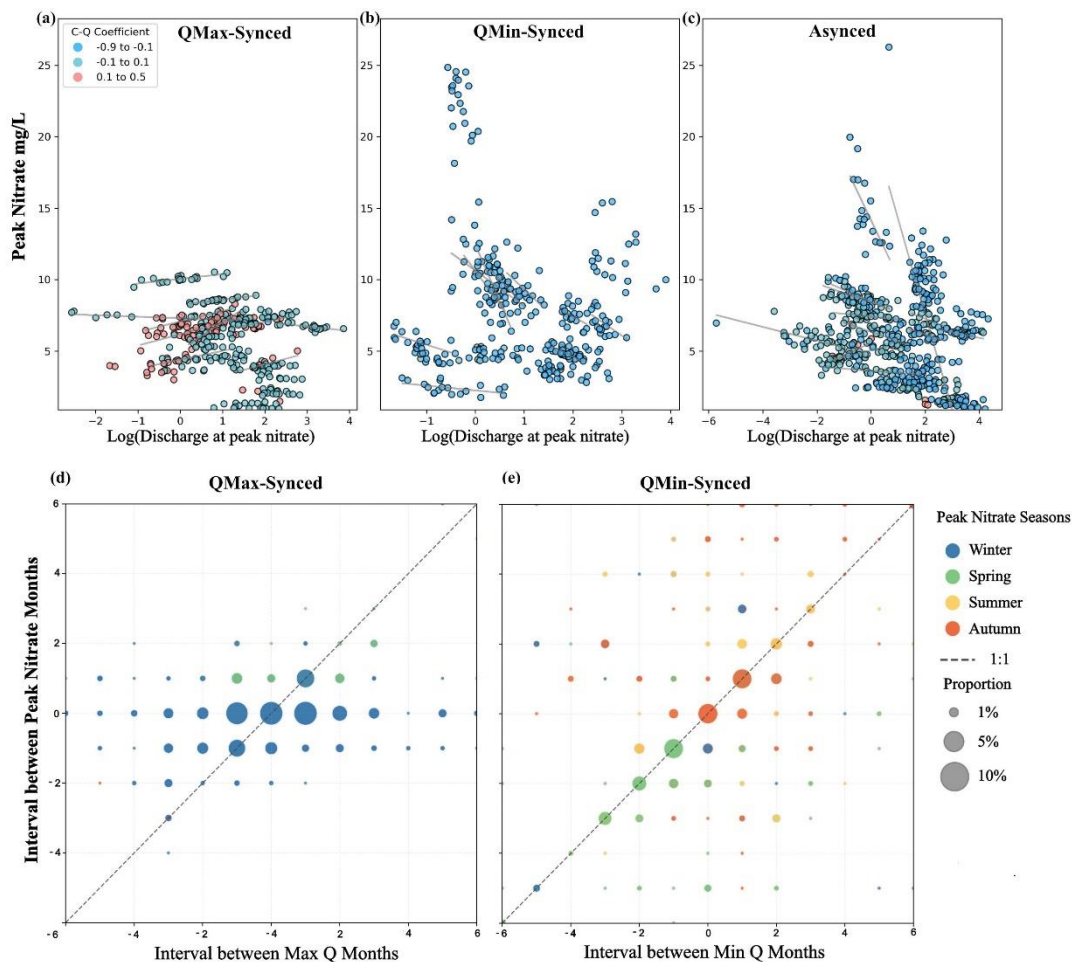
QMax-synced catchments showed shallower and more variable interannual slopes that were typically weakly positive or near-zero. Almost 42.1% of catchments had a positive and 10.5% exhibited a negative slope. β_2 values (i.e. C-Q slopes



estimated from the WRTDS model) of QMax-synced catchments fell mostly in the chemostasis to mobilisation range (Mean β_2 : 0.07 ± 0.10).

In contrast, QMin-synced catchments showed the strongest coupling to flow control with consistently steep negative slopes between discharge and peak nitrate, and correspondingly negative β_2 values (Mean β_2 : -0.42 ± 0.19). Almost 58.8% of catchments had a negative slope between peak nitrate concentrations and corresponding log(discharge). Asynced catchments also exhibited predominantly negative Q–C slopes (Mean: -0.12 ± 0.12), but with greater scatter and a broader mix of β_2 values spanning dilution and chemostasis regimes. Nevertheless, many catchments exhibited negative β_2 values, implying that their nitrate peaks are often shaped by dilution-like behaviour despite lacking a consistent seasonal alignment with flow. Despite these differences in export dynamics, peak nitrate concentrations did not differ significantly among synchrony types (Kruskal-Wallis’s test: $H = 3.62$, $df = 2$, $p = 0.16$).

Secondly, we analysed the stability of the timing of nitrate and discharge peaks from year to year. For each synchrony type, we analysed the annual change in the month of peak nitrate concentration and compared it to the change in the month of maximum or minimum discharge (Figs. 4 d&e). In QMax-synced catchments (Fig. 4d), both nitrate and discharge peak timing intervals were mostly stable around the 1:1 line. This temporal coherence is consistent with more reliable nitrate delivery governed by winter flow mobilisation. In QMin-synced catchments (Fig.4e), the timing of minimum discharge varied more substantially between years, yet nitrate peaks generally tracked these changes closely.

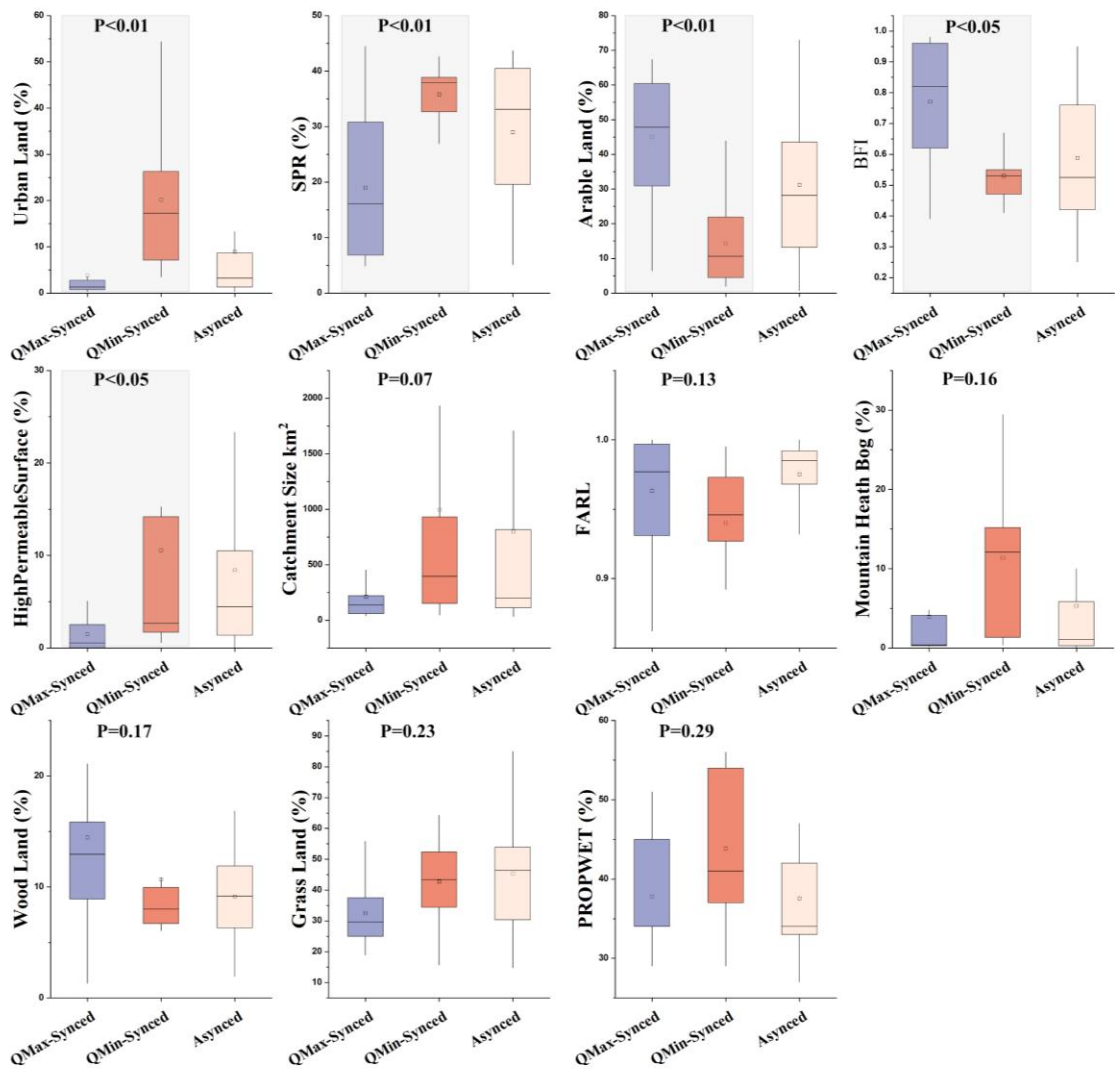


235 **Figure 4: Patterns of discharge and nitrate concentrations during peak nitrate months across synchrony types. (a-c)**
Regression lines are only shown for catchments where the annual regression has $R^2 > 0.3$. (d-e) Bubble plots showing
the relationship between the interval of peak nitrate months and the interval of maximum or minimum discharge
months.

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245 **3.3 Catchment Characteristics controlling Synchrony patterns**



250 **Figure 5: Controls of Synchrony Patterns Following the Order of Importance. Boxplots show the distribution of key catchment descriptors ordered by importance from a RF classification model. P values (Wilcoxon rank-sum test) compare QMax- and QMin-Synced Catchment. See Table 1 for descriptions of all variables**

To understand which catchment attributes best explain the dominant synchrony behaviour identified in Section 3.2, we used a Random Forest classification model to relate land use, hydrology, and landscape properties to synchrony type (QMax-Synced, QMin-Synced). The random forest classification model achieved a classification error of 12.2%, corresponding to



255 an overall accuracy of 87.8%. This indicates that the model was able to distinguish between the synchronous patterns based on the selected predictors. Post permutation method (i.e after removal of non-significant variables), only a small increase in classification error was apparent 12.5% (+0.3%).

The most influential catchment descriptors identified by the RF model align with known hydrological and land use controls on nitrate dynamics (Fig. 5). Urban Land area is ranked as the most important factor for the Synchrony patterns classification, followed by the Standard Percentage Runoff (SPR), Arable Land, Baseflow Index (BFI) and the percentage of High Permeable Surface. QMax-Synced catchments had the smallest percentage of urban areas while QMin-Synced catchments had the highest ($p < 0.01$). In contrast, the percentage of arable land was significantly higher in QMax-Synced catchments compared to QMin-Synced ones. Regarding the hydrological characteristics, linear regression analysis indicated a strong inverse relationship between SPR and BFI, with an R^2 value of 0.71. The strong linear relationship between SPR and BFI indicated that they essentially represent similar catchment hydrological characteristics. The Lowest SPR and Highest BFI are observed in QMax-Synced catchments. The predictor of High Permeable Surface, reflecting the infiltration capacity and groundwater recharge potential of the catchment, is lowest in QMax-Synced Catchments. Although catchment area did not reach statistical significance ($p = 0.07$), QMax-synced catchments tended to have smaller catchment areas than QMin-synced catchments.

270 3.4 The Drivers of Synchrony Variability

While Section 3.3 identified catchment characteristics that explain dominant synchrony types across space, here we examine what controls interannual variability in synchrony within catchments. For QMax-Synced catchments wetter winters (higher SPI1) were apparent during QMax-Synced years than Asynced years (mean SPI1 difference, $\Delta = 0.27 \pm 0.32$, $p < 0.01$, Table 2). SPI did not impact QMin-Synced catchment behaviour ($p > 0.05$). In catchments classified as Asynced overall, the years identified as QMin-Synced were significantly wetter, both in terms of winter SPI1 and annual SPI12, than years identified as either QMax-Synced or Asynced ($p < 0.01$ for both comparisons). Across the 56 sites, both winter SPI1 and SPI12 showed strong positive correlations with the annual maximum of monthly mean discharge (MaxQ), with median ρ values of 0.78 and 0.78, respectively, and 49 and 56 sites showing statistically significant relationships. In addition, SPI12 was also positively correlated with the annual minimum of monthly mean discharge (MinQ) (median $\rho = 0.51$; 35 sites significant).

280 The ternary plots (Fig. 6) showed that no catchment sits at a single vertex; instead, most exhibited a mix of synchrony types, with Asynced catchments spanning a particularly wide range. There was a clear absence of catchments located near the extremes of both QMax- and QMin-synchrony, with no site exhibiting huge switching just between these two patterns. In catchments where QMax-synchrony occurred more frequently (36 sites), QMax years did not show significantly higher percentiles of maximum monthly discharge than non-QMax years (median 0.897 vs 0.910, $p = 0.30$). In contrast, in catchments where QMin-synchrony was more frequent (30 sites), non-QMin years exhibited significantly higher percentiles of the driest month than QMin years (median 0.086 vs 0.068, $p = 0.007$).

Table 2. Mean differences in Winter SPI1 ($\Delta \pm \text{SD}$) and SPI12 ($\Delta \pm \text{SD}$) among hydrological year types, based on paired Wilcoxon signed-rank tests within each site. Δ represents the mean difference in SPI between synchronous and asynched years at each site.

Catchment Synchrony Patterns	Difference in (a)synchronous years	n	Winter SPI1 ($\Delta \pm \text{SD}$)	p	SPI12 ($\Delta \pm \text{SD}$)	p
QMax-Synched	QMax-Synched vs Asynched	16	0.27 ± 0.32	<0.01	-0.00 ± 0.53	>0.05
QMin-Synched	QMin-Synched vs Asynched	14	-0.10 ± 0.32	>0.05	-0.07 ± 0.41	>0.05
Asynched	QMax-Synched vs QMin-Synched	18	-0.45 ± 0.42	<0.01	-0.64 ± 0.62	<0.01
Asynched	QMax-Synched vs Asynched	18	-0.09 ± 0.33	>0.05	-0.23 ± 0.56	>0.05
Asynched	QMin-Synched vs Asynched	18	0.36 ± 0.36	<0.01	0.41 ± 0.39	<0.01

QMax-synched catchments were characterised by high arable land cover and low Drainage Path Slope (DPS). Spearman Rank correlation showed that the arable fraction correlated positively with the share of QMax-Synched years ($\rho = 0.58$, $p < 0.05$), while DPS showed the opposite trend ($\rho = -0.50$, $p < 0.05$). In contrast, in QMin-synched catchments, urban land cover ($\rho = 0.53$, $p < 0.05$), population density ($\rho = 0.58$, $p < 0.05$), as well as higher CVc/CVq and The Proportion of Time Soils Are Wet (PROPWET) (both $\rho = 0.58$, $p < 0.05$), were all positively associated with the frequency of low-flow synchrony. Asynched catchments behaved as transitional systems with a higher density of WWTPs shifting the year mix towards QMin-Synched years ($\rho = 0.36$, $p < 0.05$) and away from QMax-Synched years ($\rho = -0.50$, $p < 0.05$). A higher baseflow index (BFI) tended to support QMax-Synched years ($\rho = 0.38$, $p < 0.05$), while larger catchment area ($\rho = 0.39$, $p < 0.05$), and lower SPR ($\rho = -0.38$, $p < 0.05$) were linked to a greater prevalence of QMin-Synched years. A full summary of additional correlations is provided in Fig. S11.

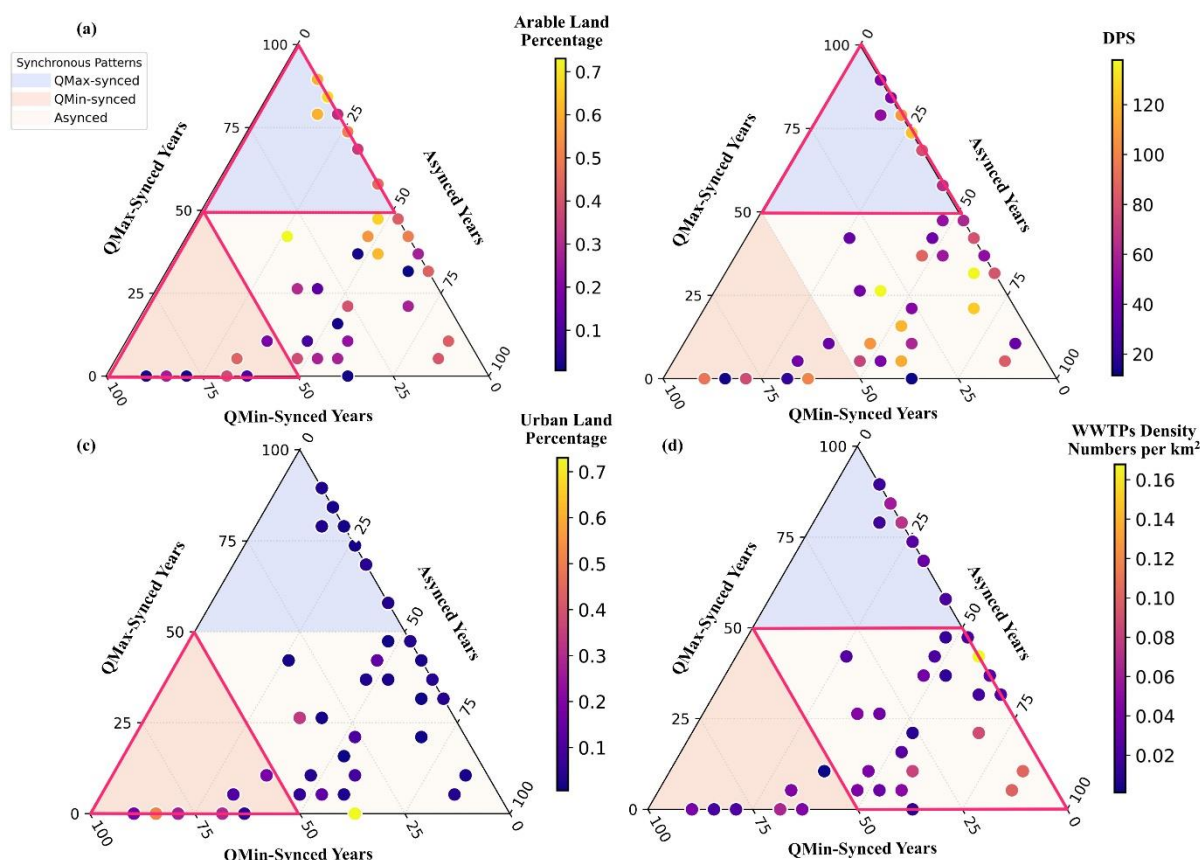


Figure 6: Ternary plots of percentage of synchronous years and key drivers for each catchment, coloured by (a) Arable land percentage, (b) DPS, (c) Urban land percentage, and (d) Population density Density of WWTPs. Coloured: The pink polygon highlights the subset of catchments for which the percentage of the synchronous years was significantly correlated with the corresponding driver (Spearman ρ , $p < 0.05$).

4 Discussion

4.1 Spatial Synchrony and Controls of Nitrate and Discharge

The emergence of three synchrony regimes demonstrates that space and time imprint differently on peak nitrate export. Each regime reflects a distinct organisation of sources, pathways, and hydrological connectivity that together determine when nitrate and flow peaks coincide or diverge. Spatially fixed contrasts, driven by land use, geology, and drainage infrastructure, give rise to the relatively stable QMax- and QMin-synchrony types, while temporal reorganisation of those same controls produces the mixed and shifting behaviour of Asynced catchments. In this sense, synchrony is not a static property but an emergent expression of how catchment structure interacts with climatic forcing. The following sections examine each



synchrony type in turn, tracing how characteristic source–pathway–connectivity configurations lead to QMax, QMin, or Asynched behaviour.

4.1.1 Agriculture-dominated QMax-Synched Catchments

Catchments in which peak flow and peak nitrate concentrations occurred simultaneously (QMax-Synched catchments) exhibited a spatially consistent, agriculture-driven coupling reflecting hydrological mobilisation of ample nitrogen stocks from arable land during periods of higher winter flow and connectivity. These catchments were predominantly distributed in southern and southwestern England accounting for 28.8% of all catchments.

A high percentage of agriculture, specifically arable land cover, was one of the most important factors identified in QMax-Synched catchment. Our analysis also revealed that QMax-Synched catchments were typically smaller headwater catchments with intensive arable land cover. The agricultural area provided sufficient and diffuse nitrogen sources readily mobilised by high flow and younger water, as periods of higher flow enhance catchment connectivity by activating shallow subsurface and surface flow paths that link agricultural areas to the river channel (Yang et al., 2018). This could also be supported by the predominance of chemostasis to mobilisation C-Q relationship in these catchments, which were commonly observed in the previous studies (Zhang, 2018; Moatar et al., 2017) and suggests a uniform distribution of nitrate with depth (Dupas et al., 2016). As highlighted by Worrall et al. (2014), annual maximum nitrate concentrations were sensitive to shifts in nutrient sources such as land use change, fertiliser application. The generally positive or weakly correlated regression slopes observed between annual peak nitrate concentrations and corresponding peak discharges support the ample or non-limiting nitrate pools played an important role in the dominating QMax-synchrony.

The hydrological connectivity also contributed to the synchrony in winter. These agriculturally dominated catchments contained less extensive high-permeability superficial deposits (mainly sands and gravels) and exhibited relatively high Baseflow Index (BFI) and low Standard Percentage Runoff (SPR). This pattern likely reflects the widespread use of artificial subsurface drainage in agricultural areas. After World War II, the UK initiated a major program of land drainage on poorly drained land, which resulted in the delivery of leached nitrate to groundwater and rapidly transported nitrate to streams during rainfall (Green, 1979; Burt et al., 2011). Piped systems were used to drain around 6.4 million hectares of agricultural land in England and Wales (Hill et al., 2018). Such drainage networks could enhance hydrological connectivity and shorten the discharge pathways, promoting the delivery of diffuse nitrogen to streams (Hirt et al., 2005). Tile drains have also been proved to increase the peak flows (Wesström et al., 2001). Thus, the combination of increased hydrological connectivity and sufficient nitrogen supply favoured the occurrence of QMax-Synched catchments. This perspective reframes diffuse agricultural pollution as a timing problem as much as a loading problem. Where increased hydrological connectivity locks nitrate release into the wet (winter) season, management interventions aimed solely at reducing inputs may have limited effect on seasonal synchrony unless they also alter flow–path activation or storage dynamics.



4.1.2 Urban-dominated QMin-Synced Catchments

QMin-Synced catchments (24.4 % of the total) exhibited an inverse seasonal regime between nitrate concentrations and discharge and were mainly located in the north-western and southern UK in urban areas. A QMin-Synced pattern has also
 350 been reported in some catchments in western France (Guillemot et al., 2021) and the Great Lakes region (Van Meter et al., 2019). This phenomenon can result from strong dilution of stable or legacy nitrate sources (such as groundwater or urban point sources) during high flows (Minaudo et al., 2015), or from the spatial separation between flow-generating areas and nitrogen sources in the catchment (Abbott et al., 2018).

In our study, random forest analysis identified urban area as the strongest explanatory variable in these catchments. Strong
 355 dilution patterns were observed and most catchments showed negative regression slopes between peak nitrate concentrations and discharge, suggesting stable urban point sources and lack of large or spatially distributed N stores. Meanwhile, higher SPR and lower BFI, opposite to QMax-Synced catchments, suggest that surface runoff dominated over groundwater contributions, resulting in rapid transport and efficient dilution of nitrate during high-flow periods. Nitrate delivery was tightly coupled to the timing of low flows, i.e. rather than occurring during a fixed month, peak concentrations consistently
 360 follow the annual flow minimum.

A legacy-nitrogen explanation for QMin-synchrony, whereby slower drainage of stored soil or groundwater nitrate could elevate concentrations during low-flow periods, would be consistent with the large literature on this topic (Johnson and Stets, 2020). However, our results do not support this mechanism. The strong link to urbanisation with steeply negative C–Q slopes, indicates instead the dominance of stable point inputs rather than gradual legacy release for QMin-synched
 365 catchments. Moreover, if both diffuse and point sources were active, we would likely expect dual peaks, one during winter flushing (as with QMax-Synched catchments) and another at low flow, yet only a single low-flow maximum is observed. This pattern further implies that urban infrastructure associated inputs have largely displaced the diffuse, winter-mobilisation behaviour typical of QMax-Synched catchments, creating an engineered inversion where nitrate concentrations peak only under low-flow conditions and are otherwise easily diluted (Kaushal and Belt, 2012; Kaushal et al., 2011).

370 4.2 Synchrony Variability and Drivers

Our peak-based analysis showed that, although both nitrate concentration and discharge follow a consistent seasonal cycle on average, the timing of their annual peaks varies substantially among years and catchments. Earlier studies have shown that riverine nitrate concentrations generally track discharge seasonality (Ebeling et al., 2021; Van Meter et al., 2019). Our results extend this understanding by showing that synchrony itself fluctuates through time and space. The strength and
 375 timing of nitrate and flow coupling vary with hydro-climatic conditions and catchment characteristics. This variability reveals how climate sets the potential for synchrony, while local land use and hydrological structure determine whether that potential is realised.



4.2.1 Winter precipitation and Drainage Path Slope Regulate QMax-Synced Variability

Our results indicated that in QMax-synced catchments, synchrony variability was primarily governed by winter precipitation, nitrogen source availability, and catchment topography. The proportion of QMax years was positively correlated with the fraction of arable land, implying that catchments with larger diffuse N inputs were more likely to exhibit synchronous winter peaks, as nitrate stores in agricultural catchments could be easily mobilised during winter high flow (Jordan et al., 1997; Musolff et al., 2015). Moreover, QMax-Synced catchments experienced significantly wetter winters during synchronous years, as indicated by elevated winter SPI1 values. These wetter winters not only elevated peak discharges in winter but likely also saturating soils and enhancing runoff, thereby increasing the hydrologic connectivity within the catchments. This increased wetness results in shorter hydrological travel times and consequently the co-occurrence of discharge and nitrate peaks (Winter et al., 2022; Blaen et al., 2017). Importantly, the MaxQ percentiles did not differ significantly between QMax and non-QMax years, suggesting that synchrony was not simply driven by more extreme high flows but rather by enhanced connectivity that facilitated nitrogen mobilisation.

While the availability of diffuse nitrogen sources, together with wet winters, sets the stage for synchrony, the efficiency of nitrate flushing was governed by topographic controls. Catchments with lower Drainage Path Slopes (DPS), reflecting flatter topographic gradients and longer flow paths, tended to show weaker and less consistent synchrony between nitrate and discharge peaks. In such settings, slower runoff and longer residence times increase opportunities for nitrate retention, reducing the likelihood that discharge and nitrate peaks coincide. Similar findings have been reported for three German rivers, where flatter topography was associated with reduced N export efficiency (Ehrhardt et al., 2019). In contrast, catchments with steeper drainage paths and rapid runoff generation can facilitate efficient flushing of nitrate from shallow soils during high flow events (Schiff et al., 2002; Harms and Jones, 2012). Overall, our findings extend this previous understanding by showing that, at the seasonal scale, synchrony variability depends less on the magnitude of high flows than on the efficiency with which catchment wetness and structure translate those flows into connectivity. This highlights that nitrate–flow coupling strengthens when climatic wetness aligns with source availability and topographic facilitation of transport, rather than simply when seasonal flow is higher.

4.2.2 Low Flow Dilution and Anthropogenic Pressure Drives QMin-Synced Variability

In contrast to QMax-Synced catchments, the synchrony variability in the QMin-Synced were largely shaped by the intensity of anthropogenic loading and the configuration of urban water infrastructure and the temporal variability of discharge in low-flow period. Our analysis showed that more urbanised and densely populated catchments were more likely to exhibit nitrate concentration peaks coinciding with periods of minimum flow. In urban dominated catchments, greater extent of impervious surfaces and engineered drainage systems likely disrupts the natural connection and limit the mobilisation of diffuse sources, especially during wet periods (Duncan et al., 2017). Consequently, during low-flow conditions, persistent point sources like wastewater effluent and sewer leakage can dominate riverine nitrate sources, leading to a stronger



410 sensitivity of nitrate concentration to dilution effects (Zhao et al., 2023). Meanwhile, The CVc/CVq ratio (generally < 0.5) showed a positive correlation with the proportion of QMin-Synced years. Higher CVc/CVq indicated more variable nitrate concentrations, potentially signalling stronger and more dynamic anthropogenic pressures. Thus, increased urbanisation and population density are likely the main drivers of QMin-Synchrony, reflecting the dominance of continuous anthropogenic nitrate inputs.

415 At the same time, antecedent wetness still modulated its strength. Synchrony tended to be more pronounced following wetter conditions (high PROPWET), consistent with greater baseflow contributions or sustained connectivity between subsurface pathways and receiving waters. If low-flow nitrate peaks were primarily driven by legacy agricultural or groundwater stores, we would expect stronger QMin signals in arable catchments. However, this is not observed in our data, instead, those catchments exhibited QMax behaviour linked to winter mobilisation. The absence of a low-flow legacy signal in more
 420 agricultural catchments suggests that any remaining legacy nitrate stores either become hydrologically disconnected during dry periods or are depleted earlier in the hydrological year. In urban catchments, by contrast, continuous wastewater and leakage inputs maintain elevated nitrate during low flows, fixing the timing of concentration peaks to the discharge minimum, which itself can vary substantially. These patterns indicate that while antecedent wetness can modulate synchrony expression, QMin behaviour likely reflects a structural shift from diffuse to persistent anthropogenic loading rather than
 425 delayed release of legacy nitrate under low flow.

Finally, our results highlighted the critical role of low flow extremes in shaping QMin-synchrony. Years with less severe low flows tended to shift toward asynchrony, consistent with the idea that higher baseflows quickly dilute the dominance of persistent urban inputs. These findings suggest that while urban effluents and legacy nitrate inputs establish the conditions for QMin-synchrony, its occurrence is ultimately constrained by how extreme this low flow period becomes.

430 4.3 Asynched Catchments with Mixed Sources and Complex Controls

Asynched behaviour was characterised by a lack of consistent alignment between peak nitrate concentrations and discharge. These asynched catchments are common (46.8% of study basins), broadly distributed across England and displayed weak seasonal patterns in monthly nitrate concentrations. They occupied a continuum shaped by the interplay of sources and flow pathways. Mean β_2 values in the peak N months were intermediate between chemostasis QMax-Synced and dilution-
 435 dominated QMin-Synced types, and most year-to-year regressions showed negative slopes, likely reflecting limited nitrogen stores. And their catchment characteristics generally fell between those of the two synchronous patterns. Similar Asynched N patterns have also been reported in western France, where large legacy nitrogen stores in groundwater, bottom-loaded nitrate profiles, and spatially variable hydrological connectivity together maintained persistently high but weakly seasonal concentrations (Guillemot et al., 2021; Abbott et al., 2018). Moreover, anthropogenic activities (e.g., tile drainage,
 440 groundwater extraction, and land use changes) have also been found to amplify chemical contrasts between shallow and deep flow paths, further decoupling nitrate responses from surface hydrology and promoting asynchrony (Zhi and Li, 2020).



In most Asynced catchments, all three synchrony states were observed across years, highlighting their mixed and shifting controls. This instability likely reflects the absence of persistent hydrological forcing. As we discussed above, QMax-synchrony arose primarily from enhanced hydrologic connectivity during wet winters rather than from the extremity of peak flows, whereas QMin-synchrony depended on sufficient low-flow conditions to emerge. Asynced catchments, likely lacking either consistent high-flow connectivity or prolonged low-flow extremes, are therefore highly prone to switching between synchrony states. Unlike consistently QMin-synced catchments, where continuous anthropogenic loading and extreme low flows dominated and SPI showed little influence, Asynced catchments were more sensitive to climatic anomalies. Wetter winters (higher SPI1) and wetter years (high SPI12) occasionally promoted QMin-like behaviour, though not through urban effluents but likely because increased recharge temporarily reconnected shallow groundwater or legacy nitrate stores to the stream network. It is interesting that these transient connections can mimic the timing of QMin behaviour, nitrate peaks during low-flow periods, but likely arise from hydroclimatic modulation of connectivity rather than from persistent point-source dominance, as they represent the only context in which our analysis indicates a likely contribution from legacy or groundwater-derived nitrate.

Beyond hydroclimatic influences, nitrate export regimes in Asynced catchments were further shaped by catchment size and anthropogenic pressures. Larger catchments tended to dilute diffuse inputs, favouring QMin- like behaviour, while denser wastewater infrastructure reinforced nitrate peaks during low flow periods. Year-to-year differences were also likely influenced by broader environmental variability, such as air temperature, extreme rainfall, or antecedent soil moisture, that can alter uptake and denitrification efficiency and thus accentuate asynchrony (Van Meter et al., 2019). Importantly, because none of these controls acts consistently across years, correlations with individual drivers remain modest. These results indicate that Asynced catchments are not characterised by greater climatic or hydrological variability per se, but by greater sensitivity to it. With weaker structural constraints than the spatially organised QMax and QMin regimes, their synchrony state shifts readily in response to interannual changes in wetness, storage, or loading. This heightened sensitivity may arise because Asynced catchments lack a single dominant source–pathway, as diffuse, groundwater, and urban inputs likely all contribute, but their relative influence depends on hydrological thresholds that vary from year to year. When those thresholds are reached, even modest climatic anomalies can switch the dominant transport pathway, altering whether export resembles QMax- or QMin-like behaviour. The fact that Asynced catchments constitute the most common catchment type in our dataset underscores the importance of this temporally responsive regime, one that is easily overlooked in analyses focused solely on spatial contrasts in land use or source dominance. Together, these results show that the synchrony framework adds a critical temporal dimension to understanding nitrate–flow coupling, revealing how small climatic or infrastructural perturbations can reorganise export dynamics across seasons and years.



5 Conclusion

We analysed long-term nitrate–discharge seasonality for 66 English catchments to characterise N-Q synchrony patterns and identify the climatic, hydrological, and anthropogenic factors governing this. Three synchrony regimes emerged, QMax-Synced (28.8%), QMin-Synced (25.8%), and Asynced (46.8%) catchments.

QMax-Synced catchments, typically small, agricultural with high base-flow index and low surface permeability, exhibited chemostatic behaviour under high nitrate supply. Synchrony in these catchments was maintained not by the extremity of peak flows but by enhanced hydrologic connectivity during wetter winters, as reflected in high SPI1 values, and especially in catchments with steeper slopes that further promote efficient flushing.

In contrast, QMin-Synced catchments were characterised by higher urban land cover and urban-related point sources, with nitrate peaks predominantly occurring during low-flow periods. Interannual variability in QMin-synchrony was modulated by the interaction between anthropogenic loading, antecedent wetness, and the severity of the low flow extremes. Asynced catchments, the most widespread regime, exhibited frequent interannual switching between synchrony types. This transitional behaviour reflects sensitivity to hydroclimatic anomalies and the interplay between diffuse and point sources, with wetter years or increased effluent inputs favoured QMin-like synchrony, whereas stronger hydrological flushing promoted QMax-like responses.

Overall, our findings demonstrate that peak nitrate–discharge synchrony in catchments is not static but is dynamically regulated by climatic variability, anthropogenic activity and by how these pressures are mediated and expressed through catchment properties. By framing nitrate export in terms of synchrony rather than mean concentration or load, this approach reveals the temporal dimension of catchment response, where the timing and efficiency of connectivity, not just source strength, determine when and how nitrate reaches streams.

Data availability

Water quality data were available online at Open Water Quality Archive Datasets (WIMS) <https://environment.data.gov.uk/water-quality/view/download>. Daily discharge records were available from the National River Flow Archive <https://nrfa.ceh.ac.uk/>. The catchment characteristics were available from <https://nrfa.ceh.ac.uk/feh-catchment-descriptors>. The Standardized Precipitation Index (SPI) was available from <https://ukwrp.ceh.ac.uk/>.

Author contributions

LY, JL, KK and JK conceptualised the research project. LY conducted the formal analysis and prepared the manuscript with contributions from all co-authors.



500 Competing interests

At least one of the (co-)authors is a member of the editorial board of Hydrology and Earth System Sciences. The authors have no other competing interests to declare.

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