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

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Abstract. Anthropogenic nitrogen loading has disrupted riverine~~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 reconstructed daily nitrate concentrations from routine monitoring data using Weighted Regressions on Time, Discharge, and Season (WRTDS).~~we used the approach of Weighted Regressions on Time, Discharge, and Season (WRTDS) to reconstruct daily timeseries of N concentrations from routine monitoring data.~~ We assessed long-term N–Q synchrony and its variability across 66 English catchments (2000–2019) and used a Random Forest model to help identify climatic, hydrological, and anthropogenic controls.~~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 consistent with~~likely due to~~ point-source dominance~~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, reflecting sensitivity to hydroclimatic variability that intermittently favoured QMin- or QMax-like behaviour. ~~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; Bieroza et al., 2018; Knapp and Musolff, 2024), they primarily describe magnitude-based responses. When interpreted alone, they may not resolve whether the timing of concentration peaks aligns with hydrological extremes, thereby obscuring temporal shifts in nitrate delivery pathways.~~interpreted in isolation they risk emphasising average behaviour and often obscure temporal shifts in nitrate delivery pathways.~~

Beyond flow control, riverine nitrate concentrations are also influenced by multiple interacting factors. Nitrogen inputs from fertiliser, manures and wastewater largely determine baseline nitrate levels, while landscape and hydrogeological properties, such as soil permeability, groundwater pathways and denitrification capacity, govern N retention and subsurface delivery (Ehrhardt et al., 2021; Jiajia et al., 2021). Meteorological controls like moisture conditions, drought–rewetting cycles, and recharge pulses further modulate mineralisation, leaching, and dilution, generating substantial temporal variability even under similar land-use pressures (Mcaleer et al., 2022). These controls describe why nitrate levels rise or fall, but not when peak nitrate delivery occurs, a key dimension for management. Our synchrony analysis explicitly targets this temporal gap.

The analysis of synchrony, broadly defined as the temporal alignment of two or more processes, ~~was initially developed~~originated in ecology to evaluate and interpret ecosystem attributes and processes such as trophic interactions, metapopulation dynamics (Bjørnstad et al., 1999; Hanski, 1998). Here, we apply synchrony to quantify the degree to which seasonal nitrate concentration peaks align with seasonal discharge extremes, specifically the months of highest or lowest flow.~~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). These studies demonstrate that the degree of seasonal alignment reflects how source availability, connectivity, and hydrological forcing interact to shape nutrient export. However, because they rely on multi-year average seasonal regimes, they may not further explore whether the timing of nitrate and discharge peaks remains aligned from year to year and how this alignment responds to climatic variability. ~~Despite its potential, f~~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, the synchrony metric does not depend on short-term fluctuations or event-scale variability, making it suitable for low-frequency and irregularly sampled datasets. It only requires sufficient monthly coverage to identify peak timing.~~it is also less sensitive to short-term fluctuations and data gaps.~~ Meanwhile, the C-Q slopes, 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 for river sites 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. Short missing segments of daily discharges were filled using simple linear interpolation to produce the continuous daily series, but these gaps were rare and short relative to the full record. 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). A complete description of the hydrological variables now appears in Supplement S1. ~~(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. Winter SPI1 was used because winter precipitation is the main driver of hydrological connectivity in UK catchments, when soils approach saturation and both surface and subsurface pathways become activated (Muchan et al., 2015). In contrast, summer flows are controlled largely by evapotranspiration and accumulated soil-moisture deficits (Kilsby et al., 2019), making SPI12 a more appropriate indicator of antecedent conditions relevant to low-flow behaviour. ~~The p~~Population density was derived ~~extracted and calculated~~ from the 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 number~~s~~ of WWTPs in a catchment by the catchment area (Environment Agency, 2024).

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)	Source
Topography	Catchment Area	km^2	Area of the catchment at gauging location	(NRFA,2020)
	Mean Altitude	m	Mean catchment altitude	

Lithology & Soils	High Permeable Bedrock	%	Proportion of highly permeable bedrock	(NRFA,2020)
	Moderate Permeable Bedrock	%	Proportion of moderately permeable bedrock	(NRFA,2020)
	Low Permeable Bedrock	%	Proportion of low permeability bedrock	(NRFA,2020)
	High Permeable Surface	%	Proportion of High-permeability surface deposits	(NRFA,2020)
	Low Permeable Surface	%	Proportion of Low-permeability surface deposits	(NRFA,2020)
Land Cover	Wood Land	%	Percentage of Woodland cover	(NRFA,2020)
	Arable Land	%	Percentage of Arable and horticultural land	(NRFA,2020)
	Grass Land	%	Percentage of Grassland cover	(NRFA,2020)
	Mountain Heath Bog	%	Percentage of Mountain heath and bog cover	(NRFA,2020)
	Urban Land	%	Percentage of Urban land cover	(NRFA,2020)
Hydrology	BFI	-	BFIHOST (Baseflow index derived from the 29-class HOST (Hydrology of Soil Types) classification)~~Baseflow Index~~	(NRFA,2020)
	PROPWET	%	The Proportion of Time Soils Are Wet	(NRFA,2020)
	FARL	-	The Flood Attenuation by Reservoirs and Lakes index	(NRFA,2020)
	SPR	%	Standard Percentage Runoff Coefficient: the percentage of rainfall typically converted to surface runoff	(NRFA,2020)
	DPS	m/km	Mean Drainage Path Slope	(NRFA,2020)
Climate	Winter SPI1	-	Mean Monthly SPI1 value of the winter months	(Tanguy et al., 2017)
	SPI12	-	Annual SPI12 value for September of each water year	(Tanguy et al., 2017)
Anthropogenic	Population Density	Persons/km^2	Number of people per square km	(Reis et al., 2017)
	WWTPs density	no./km^2	Number of WWTPs per square km	(DEFRA, 2023)

2.2 Modelling daily data and C-Q definitions

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 long-term concentration trends, β_2 represents the local C-Q slope~~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. The WRTDS method estimates a smooth concentration surface in time–discharge–season space by performing a locally weighted regression for every modelled day, producing thousands of smoothly varying coefficient vectors for each catchment rather than a single global fit. The local weighting is defined by three half-window widths: 7 years in time, 0.5 years in season, and 2 natural-log units in discharge. 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 the locally estimated β_2 coefficients to classify each catchment's export regime as dilution (β_2<0.1), chemostasis (-0.1≤β_2≤0.1), and mobilisation (β_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~~β2~~ coefficients. To support seasonal synchrony analysis, reconstructed daily concentrations were aggregated to monthly mean values.~~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. For the synchrony analysis, both reconstructed concentrations and observed discharge were subsequently aggregated to monthly mean values, and all synchrony classifications were determined at the monthly scale based on the timing of monthly maxima and minima. To assess the adequacy of WRTDS-estimated concentrations for identifying monthly peaks, we computed the temporal Spearman correlation between observed and modelled monthly concentrations to assess agreement in temporal patterns relevant to the synchrony analysis. Across sites, spearman correlations were calculated showing a median ρ of 0.72 (IQR = 0.134). No sites were excluded based on model performance.

~~(comparisons of measured and fitted concentrations are shown in Fig. S2-S7).~~

2.3 Defining Synchrony

We confirmed that both discharge and nitrate concentration exhibit a clear seasonal peak–trough structure at all sites, based on their long-term monthly means. ~~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 synchrony status for each year at each site as: 1) *QMax-Synced* when the month of 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, 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 type~~category~~ (QMax-synced, QMin-synced) if that category occurred in more than 50% of years, and all remaining catchments were classified as Asynced. ~~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 synchrony variability. This dual 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. One catchment (NW-88003442) exhibited a clear structural change in the early 2000s. As a robustness check, we recalculated its synchrony using only post-2004 data; the dominant synchrony category remained unchanged, so the full record was retained for consistency across sites.

2.4 Statistical analysis with catchment characteristics

To analyse the spatial variability of nitrate nitrate-discharge synchrony and its controls~~ concentrations in rivers~~, the mean discharge and nitrate concentration for each catchment were calculated. The ratio of the coefficients of variation ~~(CV) ~~of discharge (CVq) and concentrations (CVc) was also calculated quantify the relative hydrological modulation of nitrate variability~~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, and a Random Forest (RF) model was applied to relate dominant synchrony type (QMax-Synced vs QMin-Synced) to catchment characteristics. RF analysis was chosen for its robustness and ability to handle complex interactions within the data (Breiman, 2001). Asynced catchments were excluded from this analysis because they do not exhibit a dominant synchrony pattern, as such including them would reduce interpretability of contrasts between the two synchronous modes. A Random Forest classifier was implemented using the ranger (Version 0.16.0) engine via mlr3 (Version 0.22.1) in R (Lang et al., 2019; Wright and Ziegler, 2017). No hyperparameter tuning was performed; ranger default settings were used except that the number of trees was set to 500. A three-repeated 10-fold cross-validation procedure was used to evaluate model performance and its generalizability. Following cross-validation, a final RF model was trained on the full dataset, and permutation-based variable importance values were extracted from the underlying ranger model, following Altmann et al. (2010). Empirical permutation p-values (<0.05) were obtained from 1000 random permutations of the response variable to identify descriptors whose importance exceeded the null distribution. ~~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 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 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 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~~ Variables identified by the 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 than formal prediction. To test the possible internal heterogeneity of QMin-Synced catchments, we also calculated Spearman correlations among land-use variables and two nitrate metrics (median concentrations and CVc/CVq) to assess whether different nitrate metrics respond differently to land use within QMin-Synced catchments.

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 (QMax- or QMin-Synced) and Asynced years within each synchrony pattern using paired Wilcoxon signed-rank tests. Second, we assessed the climate–discharge linkage by correlating SPI 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 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. Finally, we assessed relationships between spatial synchrony variability, defined as differences among catchments in their long-term tendency toward QMax-, QMin-, or Asynced behaviour, and potential controlling factors using Spearman rank correlations and Wilcoxon rank-sum tests. Analyses were conducted in Python using d 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).~~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

~~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

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, in these catchments~~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.

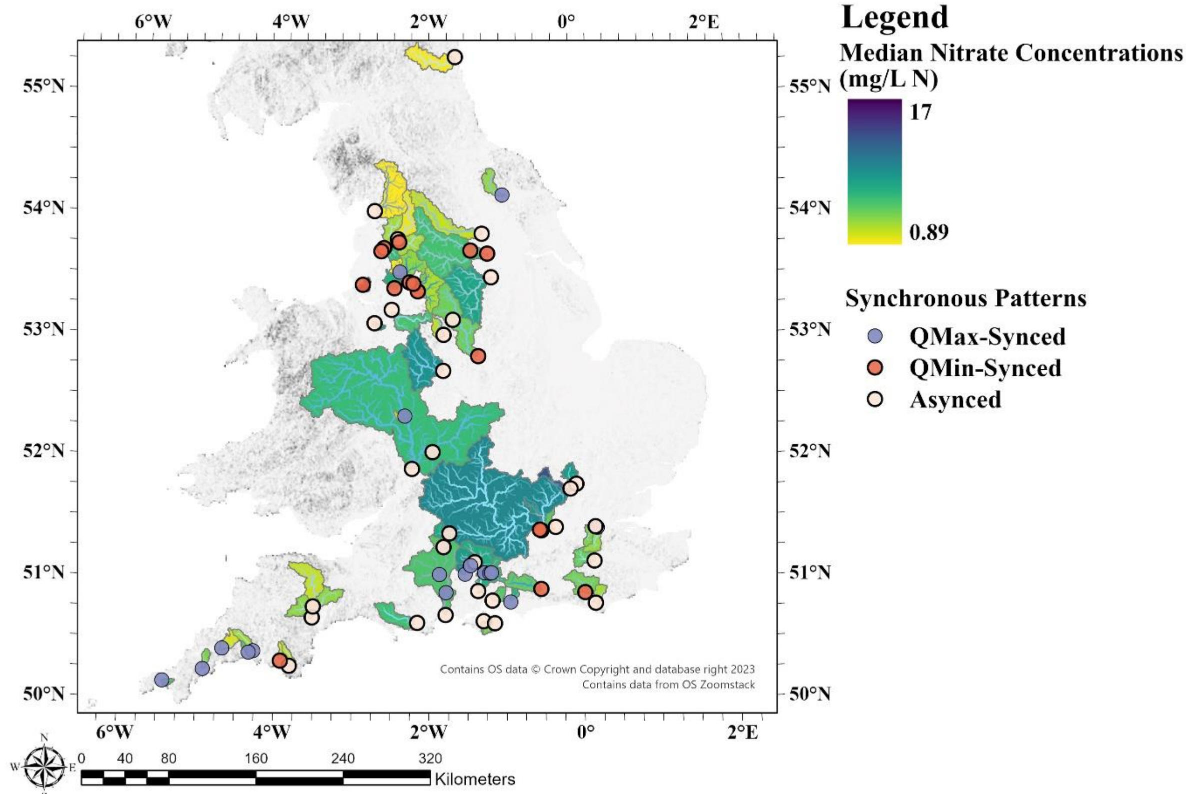


Figure 1: Spatial Distribution of Synchrony Patterns across England. Sites classified as QMax-Synced show consistent alignment between peak nitrate (N) and discharge (Q) timing (± 1 month) in over 50% years. QMin-Synced sites represent those where over 50% of years align with minimum discharge months.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

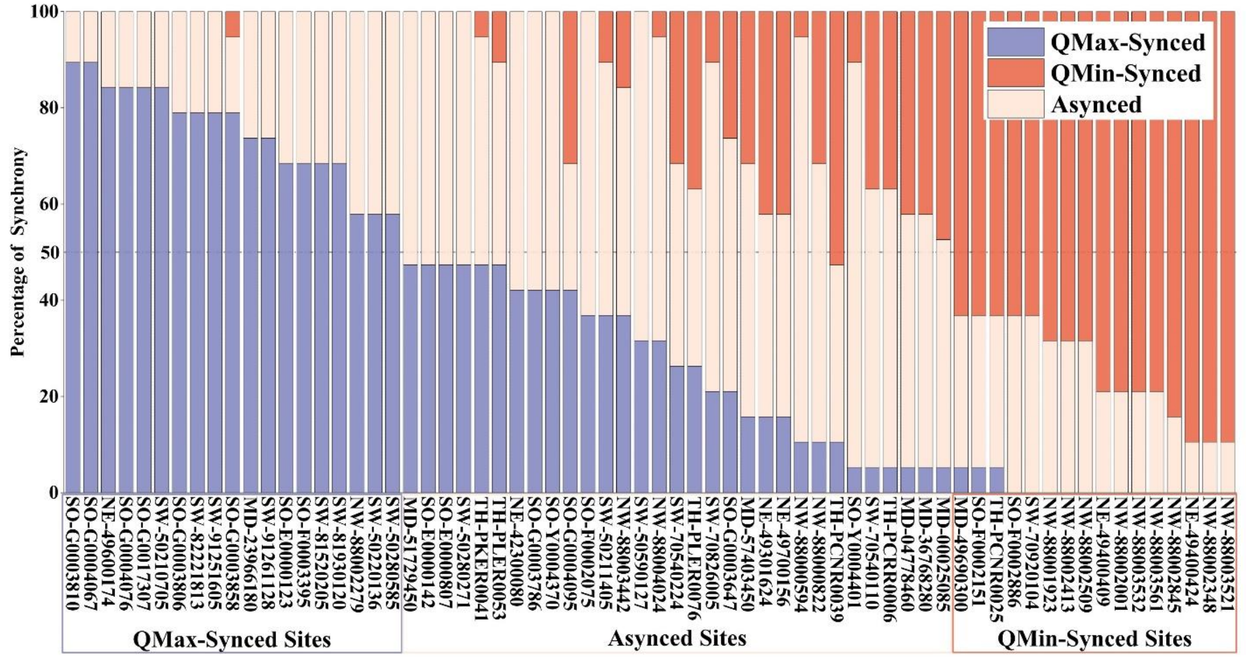


Figure 2: Interannual Consistency of Synchrony Patterns. The QMax-Synced segments represent the percentage of years where the peak nitrate concentration and peak discharge occur around the same time of year (±1 month). The QMin-Synced segments indicate the percentage of years where the peak nitrate concentration coincides with the time of minimum discharge (±1 month). The Asynced 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~~mg L^{-1}~~, IQR: 4.19 – 6.95 mg/L) and lowest in September (4.39 mg/L~~mg L^{-1}~~, IQR: 2.80 – 5.70 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 mg/L) and peak concentrations during summer low flow (July: 6.15 mg/L, IQR: 4.15–8.02 mg/L; Fig. 3b). Asynced 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 CVc/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), indicating~~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. Asynced catchments showed greater fluctuation between synchrony types. Asynced catchments showed greater fluctuation between synchrony types. Consistent with this interannual variability, synchronous or asynced years are sparsely distributed through time (Fig. S4), with no indication of a long-term trend.

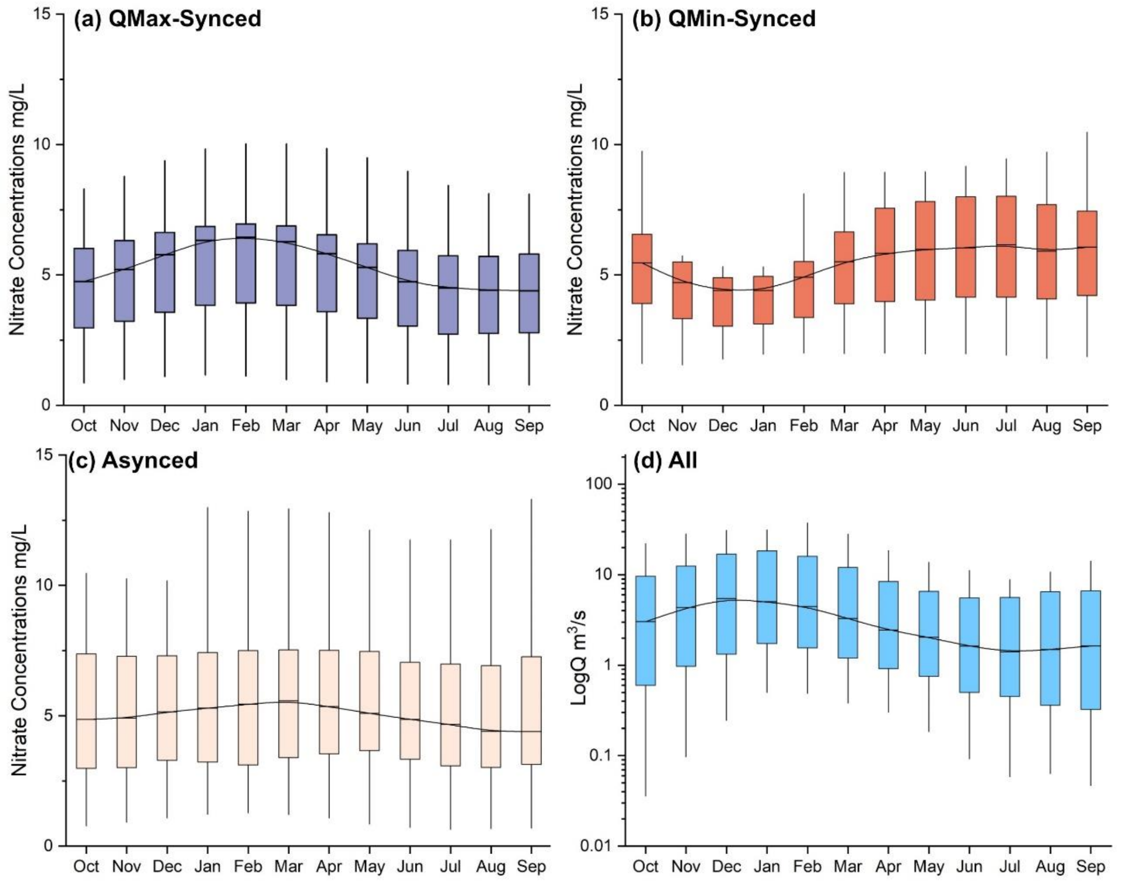


Figure 3: Annual (monthly) r~~R~~egimes of n~~N~~itrate c~~C~~oncentrations in (a) QMax-Synced, (b) QMin-Synced Sites (c)Asynced, and (d) Discharge (*Q*) of all sites. The boxes represent the interquartile range (IQR; 25th-75th percentiles), and whiskers extend to the furthest values within 1.5 x IQR 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 Variablity in Synchrony Patterns

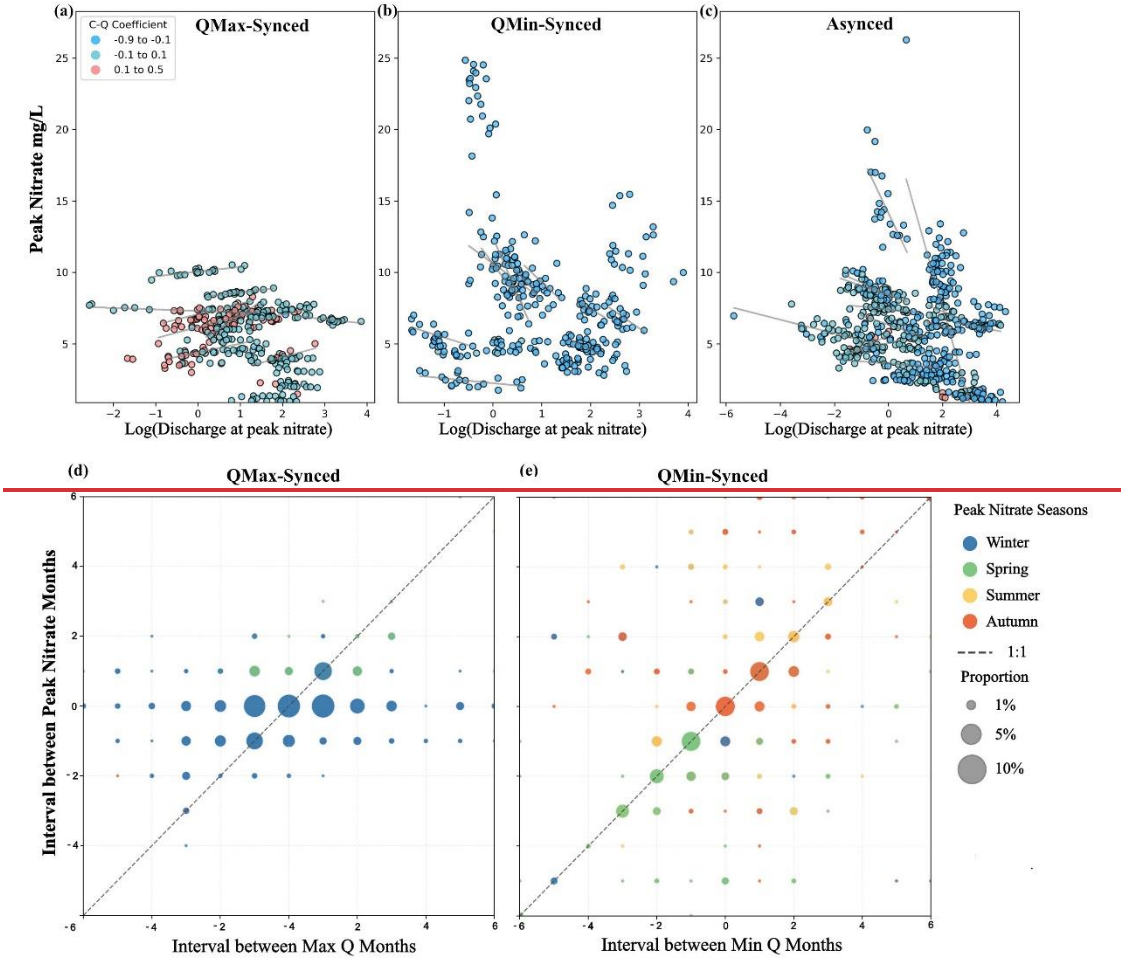
Catchments within each synchrony classification exhibited contrasting nitrate export behaviours, as reflected in the relationship between discharge and annual peak nitrate concentrations. Here, the interannual slope refers to the regression slope between annual peak nitrate concentrations and the discharge during the month of peak concentration~~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. Within this group,~~Almost~~ 42.1% of catchments exhibited~~had a~~ positive slopes and 10.5% exhibited ~~a~~ negative slopes.~~-~~ β_2 values (i.e. C-Q slopes estimated from the WRTDS model) ~~of~~ for 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 inverse coupling to discharge ~~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). Within this group,~~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, suggesting~~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 examined the interannual ~~analysed the~~ stability of the timing of nitrate and discharge peaks from year to year. For each synchrony type, we analysed the consecutive-year change in the month of peak nitrate concentration and compared it with the corresponding change in the month of maximum or minimum discharge (Fig. 4 d&e). In QMax-synced catchments (Fig. 4d), both nitrate and discharge peak timing intervals were mostly stable around the 1:1 line, with most intervals confined within ±1 month. This temporal coherence is consistent with relatively stable winter-dominated nitrate delivery. In QMin-synced catchments (Fig.4e), the interval between minimum-flow months varied more widely across years and seasons, yet the corresponding intervals between nitrate peaks tracked these changes closely.

~~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.~~



(a)
QMax-Synced
C-Q Coefficient
-0.9 to -0.1
-0.1 to 0.1
0.1 to 0.5
(b)
QMin-Synced
(c)
Asynced
Peak Nitrate mg/L
Log(Discharge at peak nitrate)
Log(Discharge at peak nitrate)
Log(Discharge at peak nitrate)
(d)
QMax-Synced
(e)
QMin-Synced
Interval between Peak Nitrate Months
Interval between Max Q Months
Interval between Min Q Months
Peak Nitrate Seasons
Winter
Spring
Summer
Autumn
1:1
Proportion
1%
5%
10%

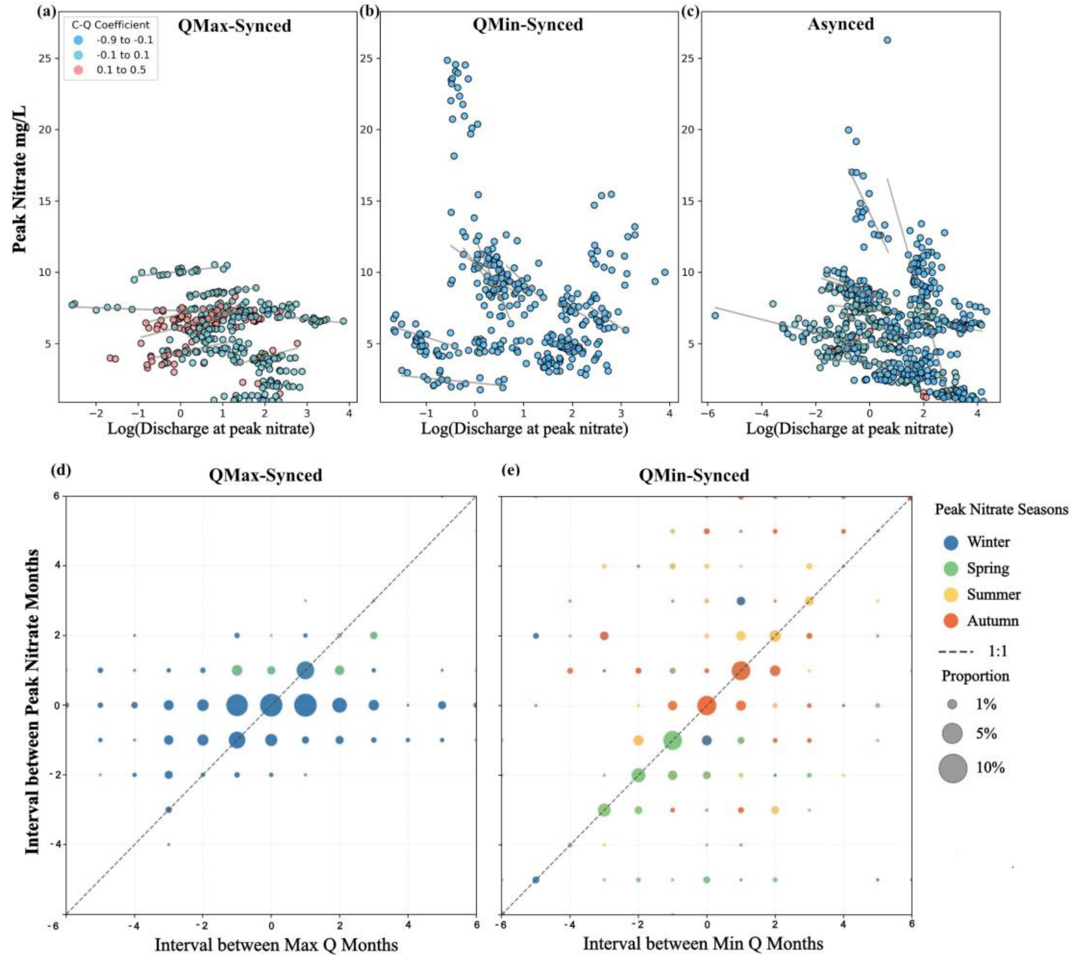


Figure 4: Patterns of discharge and nitrate concentrations during ~~peak nitrate~~ months of peak nitrate across synchrony types. (a-c) Regression lines are only shown for catchments where the annual regression has $R^2 > 0.3$. (d-e) Bubble plots showing the relationship between ~~the~~ consecutive year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

3.3 Catchment Characteristics controlling Synchrony patterns

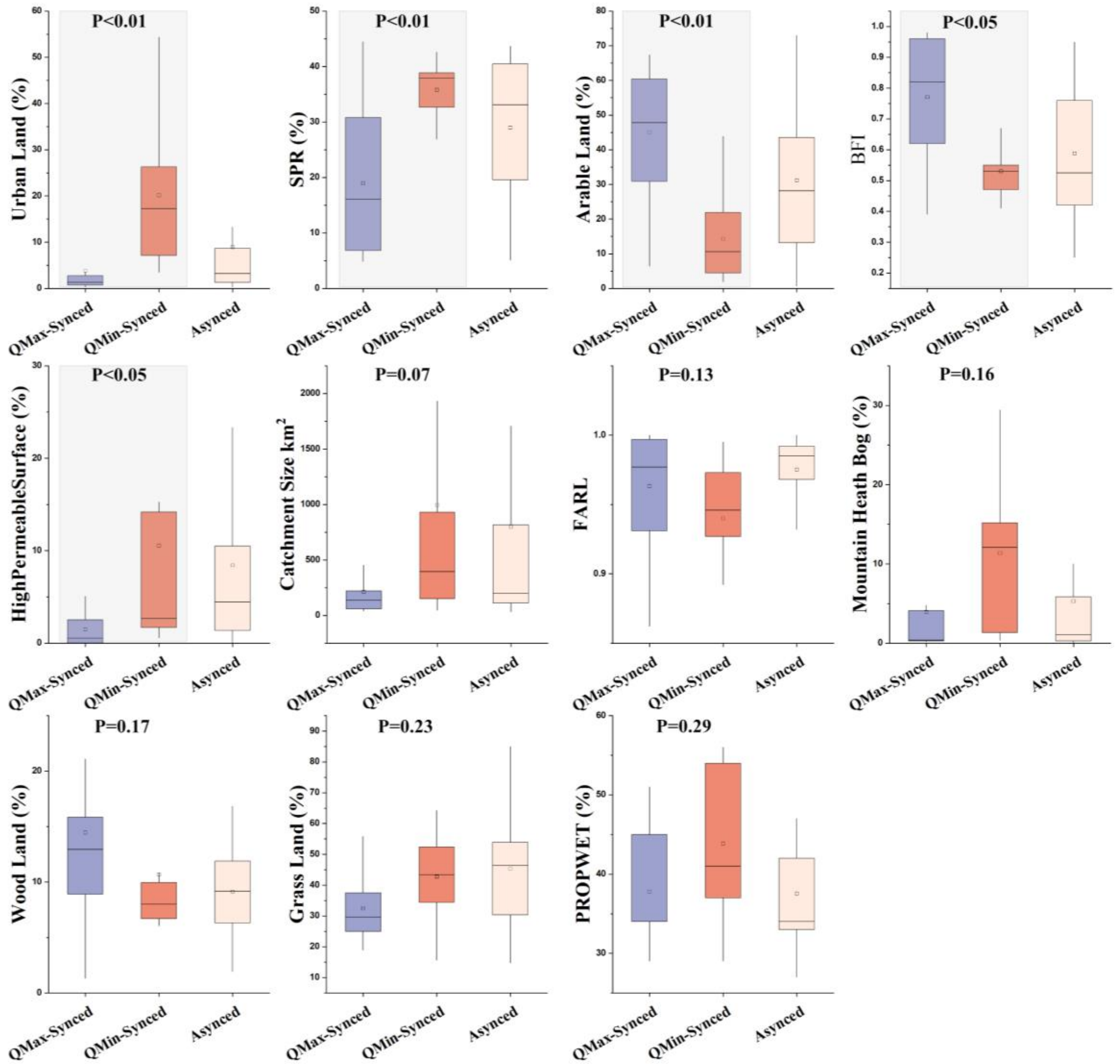


Figure 5: Catchment descriptors associated with dominant synchrony type, ordered by Random Forest importance. ~~Controls of Synchrony Patterns Following the Order of Importance.~~ Boxplots show the distribution of key catchment descriptors ordered by importance from ~~a~~ the RF classification model. 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 differences in 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 an overall accuracy of 87.8%, indicating strong separability between the two synchrony types given the selected descriptors. This indicates that the model was able to distinguish between the synchronous patterns based on the selected predictors. After removing descriptors whose importance was not statistically significant, the classification error increased only marginally to 12.5% ~~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 are consistent with~~align with~~ known hydrological and land use controls on nitrate dynamics (Fig. 5). Urban Land cover~~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 a significantly smaller ~~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 indicating, not surprisingly, that these variables capture overlapping aspects of catchment hydrological behaviour. QMax-Synced catchments exhibited lower SPR values and higher BFI.~~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 proportion of highly permeable surface deposits, reflecting infiltration capacity and groundwater recharge potential, was lowest 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. Within QMin-Synced catchments, median nitrate concentrations showed positive (though non-significant) associations with arable and urban land cover, and a significant negative association with grassland cover ($\rho = -0.50$, $p = 0.04$). In contrast, CVc/CVq was most strongly correlated with urban land ($\rho = 0.55$, $p < 0.05$), population density ($\rho = 0.52$, $p < 0.05$), arable land ($\rho = -0.59$, $p < 0.05$) and woodland cover ($\rho = -0.61$, $p < 0.01$). All the other correlation results are shown in Fig. S6.

3.4 The Drivers of Synchrony Variability

While Section 3.3 identified catchment characteristics that explain dominant synchrony types across space, here we examine (i) what controls interannual variability in synchrony within catchments, and (ii) how long-term variability in synchrony composition relates to catchment attributes. ~~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, winters were significantly wetter~~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). No significant differences in SPI were observed between QMin-Synced and Asynced years in QMin-Synced catchments ~~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 ρ = 0.51; 35 sites significant).

The ternary plots (Fig. 6) summarise the long-term synchrony composition at each site by showing the relative proportion of QMax-, QMin- and Asynced years. In these diagrams, each vertex represents 100% dominance of one synchrony type, with positions along the edges indicating a mixture of two types; and points near the centre represent a balanced mixture of all three. The colour scale applied to each point represents values for a selected catchment descriptor (e.g., Arable land percentage, Drainage Path Slope), and visualise how synchrony composition varies along environmental gradients. These colour gradients are consistent with the spatial correlations shown in Fig. S7. No catchment sites were located at a single vertex, instead, most exhibited a mix of synchrony types, with Asynced catchments spanning a particularly wide range. No sites are located near both the QMax and QMin vertices simultaneously, indicating that switching occurs mainly between a dominant mode and Asynced behaviour rather than directly between the two synchronous modes. ~~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 showed slightly higher percentiles of the minimum-flow month than QMin years (median 0.086 vs 0.068). Although the difference is modest, it is statistically distinguishable ($p = 0.007$).~~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).~~

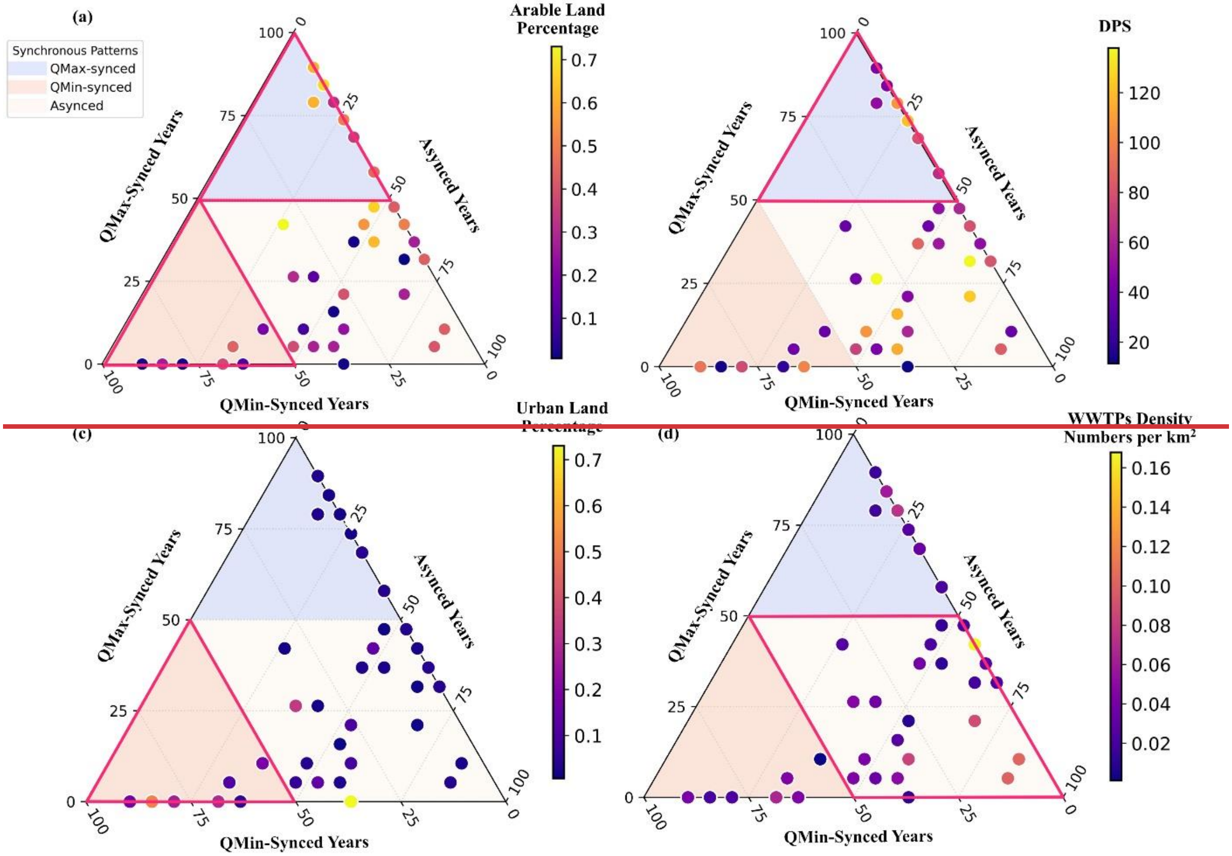
Table 2. Mean differences in Winter SPI1 (Δ ± SD) and SPI12 (Δ ± SD) among hydrological year types within catchments, based on paired Wilcoxon signed-rank tests within each site. Δ represents the mean difference in SPI between synchronous and asynced years at each site.

Catchment Synchrony Patterns	Difference in (a)synchronous years	n	Winter SPI1 (Δ ± SD)	p	SPI12 (Δ ± SD)	p
QMax-Synced	QMax-Synced vs Asynced	16	**0.27 ± 0.32**	**<0.01**	-0.00 ± 0.53	>0.05

QMin-Synced	QMin-Synced vs Asynced	14	-0.10 ± 0.32	>0.05	-0.07 ± 0.41	>0.05
Asynced	QMax-Synced vs QMin-Synced	18	**-0.45 ± 0.42**	**<0.01**	**-0.64 ± 0.62**	**<0.01**
Asynced	QMax-Synced vs Asynced	18	-0.09 ± 0.33	>0.05	-0.23 ± 0.56	>0.05
Asynced	QMin-Synced vs Asynced	18	**0.36 ± 0.36**	**<0.01**	**0.41 ± 0.39**	**<0.01**

In addition to the interannual variability, we also considered spatial variability in synchrony composition captured as long-term differences in the relative occurrence of QMax-, QMin- and Asynced years across catchments. These catchment-level synchrony metrics were then related to catchment attributes to identify the key controls on the dominant synchrony state (i.e. providing insight into why certain catchments display QMax-, QMin- or mixed synchrony). Within QMax-synced catchments, a higher share of QMax years was associated with greater arable land cover ($\rho = 0.58$, $p < 0.05$), lower Drainage Path Slope (DPS; $\rho = -0.50$, $p < 0.05$) and low standard percentage runoff (SPR, $\rho = -0.53$, $p < 0.05$). In contrast, in QMin-synced 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 proportion of QMin-synced years. Asynced catchments behaved as transitional systems with a higher density of WWTPs shifting the year mix towards QMin-Synced years ($\rho = 0.36$, $p < 0.05$) and away from QMax-Synced years ($\rho = -0.50$, $p < 0.05$). A higher baseflow index (BFI) tended to support QMax-Synced 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-Synced years. A full summary of additional correlations is provided in Fig. S7.

~~QMax-synced 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-Synced years ($\rho = 0.58$, $p < 0.05$), while DPS showed the opposite trend ($\rho = -0.50$, $p < 0.05$). In contrast, in QMin-synced 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. Asynced catchments behaved as transitional systems with a higher density of WWTPs shifting the year mix towards QMin-Synced years ($\rho = 0.36$, $p < 0.05$) and away from QMax-Synced years ($\rho = -0.50$, $p < 0.05$). A higher baseflow index (BFI) tended to support QMax-Synced 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-Synced years. A full summary of additional correlations is provided in Fig. S11.~~


(a)
Synchronous Patterns
QMax-synced
QMin-synced
Asynced
Arable Land Percentage
QMax-Synced Years
Asynced Years
QMin-Synced Years
DPS
(c)
Urban Land Percentage
(d)
WWTPs Density Numbers per km²

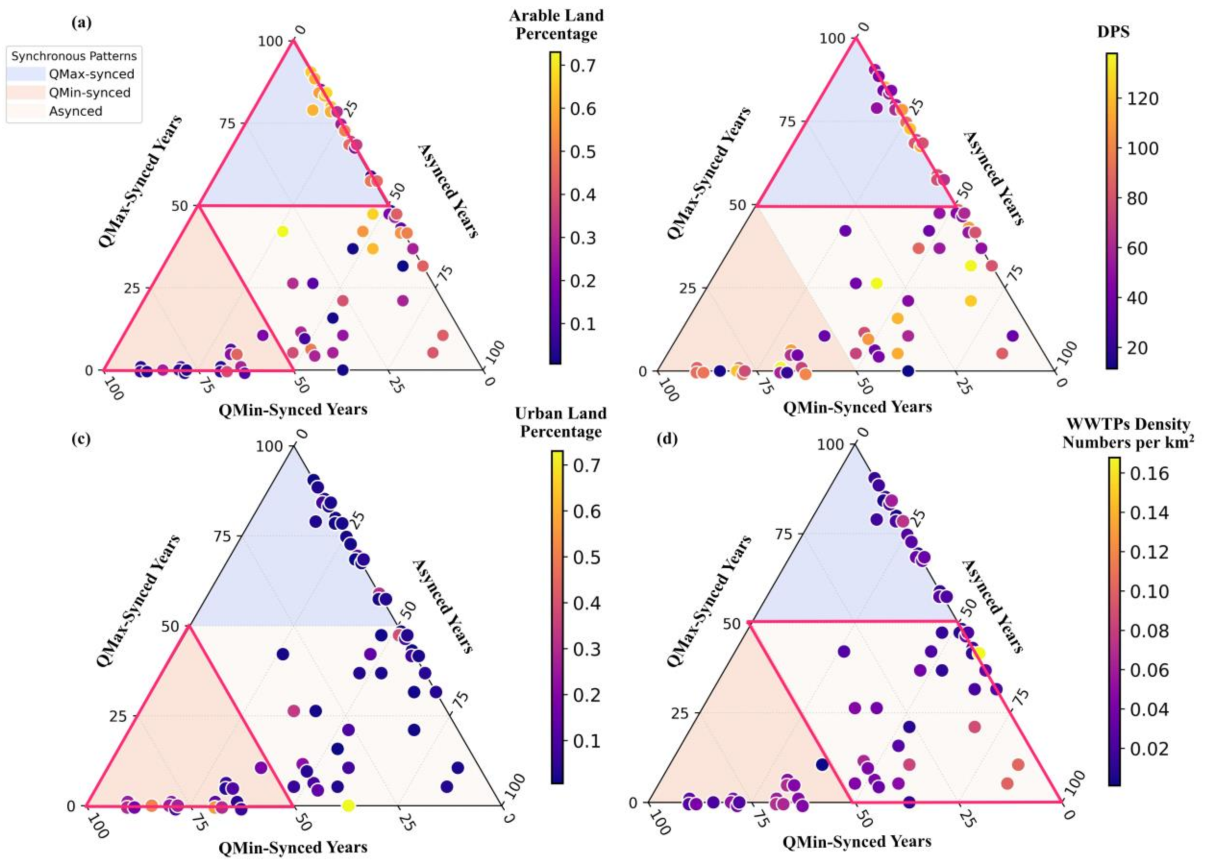


Figure 6: Ternary plots of percentage of synchronous years and key drivers for each catchment, coloured by (a) Arable land percentage, (b) DPS, (c) Urban land percentage, and (d) ~~Population density~~ Density of WWTPs. Coloured: The pink polygon highlights the subset of catchments for which the percentage 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, provide a first order control~~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. Asynced catchments, in contrast, lack a single dominant source–pathway configuration, resulting in a mixed synchrony signature. 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 Asynced behaviour.

4.1.1 Agriculture-dominated QMax-Synced Catchments

Catchments in which peak flow and peak nitrate concentrations occurred simultaneously (QMax-Synced ~~QMax-Synched~~ catchments) exhibited a spatially consistent, agriculture-driven coupling. This behaviour ~~reflecting~~ reflects hydrological mobilisation of diffuse nitrogen stored in arable soils ~~ample nitrogen stocks from arable land~~ during periods of ~~higher~~ enhanced 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, particularly~~specifically~~ arable land ~~cover~~, was one of the most influential attributes associated with ~~important factors identified~~ in QMax-Synced catchment. Our analysis also revealed that QMax-Synced catchments were typically smaller headwater catchments with intensive arable land cover. These agricultural areas provide~~d~~ sufficient and diffuse nitrogen sources that are readily mobilised during high flow conditions~~by high flow and younger water, as~~. P~~p~~eriods 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 interpretation is consistent with the predominance of chemostatic to mobilisation-type C–Q relationships observed in these catchments, as reported in previous studies~~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) This behaviour has been linked to relatively uniform nitrate availability with depth in agricultural soils~~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 between annual peak nitrate concentrations and corresponding peak discharges indicate that nitrate availability was not strongly limiting, supporting the dominance of QMax-synchrony in these catchments.~~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.~~ Although agricultural catchments receive larger nitrogen inputs, winter high-flow conditions, groundwater mixing and subsurface denitrification can suppress concentration peaks (Bowes et al., 2014; Hiscock et al., 2023). In contrast, urban catchments experience amplified nitrate concentrations during summer low-flow conditions due to continuous wastewater and urban drainage inputs (Cooper et al., 2022); As a result, QMin-Synced catchments may exhibit peak nitrate concentrations comparable to those in QMax-Synced systems.

Hydrological connectivity further reinforces winter synchrony in these catchments. ~~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, at least in part, 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 drain~~s~~age ~~have~~ has also been ~~proved~~ shown to increase the peak flows (Wesström et al., 2001). Thus, ~~the~~ this combination of increased hydrological connectivity and sufficient nitrogen supply ~~favoured~~ favours the ~~occurrence~~ generation of QMax-Synced catchments. This perspective reframes diffuse agricultural pollution as a timing problem as much as it is 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 urbanised regions of the north-western and southern UK. A QMin-Synced pattern has also been reported in some catchments in western France (Guillemot et al., 2021) and the Great Lakes region (Van Meter et al., 2019).

~~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 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 land cover as the most influential descriptor for distinguishing QMin- from QMax-synced catchments, with Wilcoxon tests confirming significant differences between the two groups. ~~In our study, random forest analysis identified urban area as the strongest explanatory variable in these catchments.~~ Strong dilution patterns were observed, ~~and~~ with most catchments ~~showed~~ showing negative regression slopes between peak nitrate concentrations and discharge~~,~~. This behaviour is consistent with a dominant influence of relatively~~suggesting~~ stable urban point sources rather than mobilisation of large or spatially distributed N stores~~and lack of large or spatially distributed N stores~~. Meanwhile, higher SPR and lower BFI, opposite to QMax-Synced catchments, suggest that ~~surface~~ shallow runoff generation plays a greater role ~~dominated over groundwater~~than 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 follow the annual flow minimum.

One possible explanation for QMin-synchrony is the influence of legacy nitrogen, whereby slow release of stored soil or groundwater nitrate elevates concentrations during low-flow periods, as widely documented in the literature (Johnson and

Stets, 2020). Our Spearman correlations suggest that agricultural legacy may indeed contribute to background nitrate levels in some QMin-Synced catchments. Legacy-dominated agricultural systems typically show weak or chemostatic C–Q behaviour and comparatively low temporal variability because nitrate is released gradually from subsurface stores (Winter et al., 2021).

At the same time, several characteristics of our QMin-Synced catchments point to a stronger influence of continuous urban inputs on the synchrony pattern. These catchments feature steeply negative C–Q slopes, consistent with hydrological dilution of relatively stable urban point sources. Moreover, if both diffuse and point sources were active, we would likely expect dual peaks, one during winter flushing (as with QMax-Synced catchments) and another at low flow, yet only a single low-flow maximum is observed.

This pattern further implies that urban land and population density associated inputs have reduced the expression of diffuse, winter-mobilisation behaviour typical of QMax-Synced 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). Our correlation analyses further support the interpretation that interannual nitrate variability relative to discharge variability (CVc/CVq) increases with urbanisation, whereas arable land is associated with reduced variability, suggesting a more stable, weakly flow-responsive behaviour typical of systems influenced by legacy nitrogen contributions. In combination, this means that while legacy nitrate may contribute to background concentration levels in some QMin-Synced catchments, the observed QMin-synchrony is likely to be primarily shaped by flow-dependent dilution of continuous urban inputs.

~~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 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).~~

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 among 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 across~~through~~ time and space. The strength and 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 wetness and the expression of interannual variability in QMax-synchrony~~Winter precipitation and Drainage Path Slope Regulate QMax-Synced Variability~~

Our results indicated that in QMax-synced catchments, temporal synchrony variability was primarily governed by winter precipitation. Synchronous years were characterised by wetter winters as indicated by elevated winter SPI1 values. These wetter winters not only elevated winter peak discharges but also likely expanded saturated soils and increasing the hydrologic connectivity within the catchments (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.

Spatial attributes such as arable land cover and topographic gradients set the stage for synchrony, modulating catchment sensitivity to interannual climate variations. Catchments with greater diffuse nitrogen availability tended to exhibit stronger synchrony during wetter winters, as accumulated soil nitrate can be readily mobilised when winter flows increase (Jordan et al., 1997; Musolff et al., 2015). Flatter catchments with lower DPS were less responsive to interannual fluctuations in winter wetness, because longer residence times enhance nitrate retention and weaken the translation of increased winter SPI1 into catchment-wide connectivity (Ehrhardt et al., 2019).Conversely, steeper drainage paths facilitate rapid runoff generation, allowing even modest increases in winter wetness to produce efficient mobilisation of shallow nitrogen stores (Schiff et al., 2002; Harms and Jones, 2012). Thus, structural characteristics modulate how effectively winter hydro-climatic conditions are converted into flushing efficiency and nitrate–flow synchrony.

~~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

Interannual variability in QMin-synchrony was primarily governed by the severity of the annual minimum-flow period. Years with more extreme low flows expressed clearer QMin-synchrony because reduced dilution capacity allowed persistent nitrate inputs to dominate the concentration peak (Spill et al., 2024). In contrast, when low flows were less severe, higher baseflows dilute these inputs more effectively and catchments more frequently shifted toward asynchrony.

Beyond low-flow severity, some specific spatial attributes modulated the sensitivity of catchments to interannual variability in QMin-synchrony. Urban land cover increased the sensitivity of nitrate dynamics to low-flow extremes because impervious surfaces and engineered drainage reduce the mobilisation of diffuse sources during wetter periods (Duncan et al., 2017). Under such constrained mobilisation, persistent wastewater effluent and sewer leakage dominate the nitrate signal once dilution capacity diminishes (Zhao et al., 2023). More urbanised catchments exhibited stronger interannual hydrological modulation of nitrate concentrations during severe low-flow conditions, as reflected in the positive association between CVc/CVq and the proportion of QMin-synchrony years. Meanwhile, Wetter antecedent conditions in catchments (high PROPWET) likely amplify the probability of QMin-Synchrony by sustaining subsurface contributions and create more stable hydrological conditions leading into the minimum-flow period. This allows persistent urban inputs to become more apparent as dilution capacity declines.

~~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 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.~~

~~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 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 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.~~

4.3 Asynced Catchments with Mixed Sources and Complex Controls

Asynced behaviour was characterised by a lack of consistent alignment between peak nitrate concentrations and discharge. These asynced catchments are common (46.8% of study basins), broadly distributed across England and display~~ed~~ weak seasonal patterns in monthly nitrate concentrations. They occupy~~ied~~ a continuum shaped by the interplay of multiple nitrate sources and flow pathways. Their intermediate export behaviour reflects neither persistent mobilisation nor strong dilution dominance, indicating mixed source contributions rather than a single controlling process. ~~Mean β_2 values in the peak N months were intermediate between chemostasis QMax-Synced and dilution-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 Asynced N patterns in western France have been attributed to legacy nitrogen stores in groundwater, bottom-loaded nitrate in soil profiles, and spatially variable hydrological connectivity together maintained persistently high but weakly seasonal concentrations~~Similar Asynced 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, 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. Whereas QMax-synchrony requires enhanced winter connectivity and QMin-synchrony requires sufficiently severe low-flow conditions, Asynced catchments often experience neither consistently.~~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 where 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~~ These transient connections can mimic the timing of QMin behaviour, producing nitrate peaks during low-flow periods~~,~~. However, they~~but~~ likely arise from hydroclimatic modulation of connectivity rather than from persistent point-source dominance, ~~as~~ and they represent the ~~only~~ primary context in which legacy nitrate appears to contribute to synchrony~~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 configuration, 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~~ across 66 English catchments to identify recurring patterns in N-Q~~characterise N-Q synchrony patterns~~, and ~~identify~~ the climatic, hydrological, and anthropogenic conditions under which they form~~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~~,~~ and agricultural dominated, ~~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, which effectively mobilised diffuse agricultural nitrate.~~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 reflected~~was modulated by~~ the interaction between persistent anthropogenic loading, antecedent wetness, and the severity of the low flow conditions~~extremes~~. Asynced catchments, the most widespread regime, exhibited frequent interannual switching between synchrony types. This transitional behaviour reflects heightened sensitivity to hydroclimatic anomalies and shifting dominance among~~the interplay between~~ diffuse and point sources, different forcing conditions temporarily favouring QMin or Qmax–like responses.~~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 a static but a dynamic outcome of how climatic variability~~is dynamically regulated by climatic variability,~~and anthropogenic pressures interact with catchment structure.~~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 a critical ~~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.

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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