Supplement of Hydrol. Earth Syst. Sci., 30, 4001–4018, 2026
https://doi.org/10.5194/hess-30-4001-2026-supplement

Hydrology and Earth System Sciences
Open Access
EGU

Supplement of

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

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S1. Hydrological Variable Definitions and Equations

The mathematical definitions and calculation procedures for all hydrological variables used in the analysis are summarised below. Equations are based on the Flood Estimation Handbook (FEH) Volume 5 (Centre for Ecology & Hydrology, 1999) and values were obtained directly from the National River Flow Archive (NRFA).

S1.1 Baseflow Index (BFI)

BFI quantifies the proportion of streamflow contributed by groundwater and delayed pathways. In this study, BFI values were obtained directly from the National River Flow Archive (NRFA), where they are computed from observed daily discharge using the UKIH smoothed minima baseflow separation method (Gustard et al., 1992).

$$BFI = \frac{Q_{baseflow}}{Q_{total}}$$

where

Q_{baseflow} is the flow component extracted following the UKIH smoothed minima algorithm,

Q_{total} is total annual discharge.

S1.2 Proportion of Time Catchment Soils are Wet (PROPWET)

PROPWET measures how frequently catchment soils are above a wetness threshold.

$$PROPWET = \frac{1}{T}\sum_{t=1}^{T} I(\theta_t > \theta_{wet})$$

where

θ_t= modelled soil moisture at time t,

θ_{wet}= FEH-defined wetness threshold corresponding to near-saturated conditions,

$I(\cdot)$= indicator function.

Values close to 1 indicate persistently wet soils ; lower values indicate predominantly dry soils.

S1.3 Flood Attenuation by Reservoirs and Lakes (FARL) index

FARL quantifies the cumulative attenuation effect of on-line lakes and reservoirs on high flows.

Values near 1 indicate negligible attenuation; smaller values indicate strong attenuation.

$$FARL = \prod_{i=1}^{n}\left(1 - \sqrt{\frac{A_{lake,i}}{A_{subcatch,i}}}\right)^{\frac{A_{subcatch,i}}{A_{catch}}}$$

where

n= number of on-line lakes or reservoirs in the catchment.

$A_{\text{lake},i}$= surface area of lake/reservoir i

$A_{\text{subcatch},i}$= upstream drainage area contributing to lake/reservoir i.

A_{catch}= total catchment area at the outlet.

S1.4 Standard Percentage Runoff (SPR)

SPR (specifically SPRHOST) expresses the standard percentage of rainfall that appears as direct (quick) runoff under average conditions. It is estimated in FEH from the distribution of HOST (Hydrology of Soil Types) soil classes within the catchment.

S1.5 Drainage Path Slope (DPS, m km^{-1})

DPS (specifically DPSBAR) describes the mean slope along the drainage paths defined by the Integrated Hydrological Digital Terrain Model. For each grid cell, the steepest descent direction to a neighbouring cell is used to define a local slope; DPS is then obtained as the catchment-wide mean of these drainage-path slopes. Higher DPS values correspond to steeper, more rapidly draining catchments.

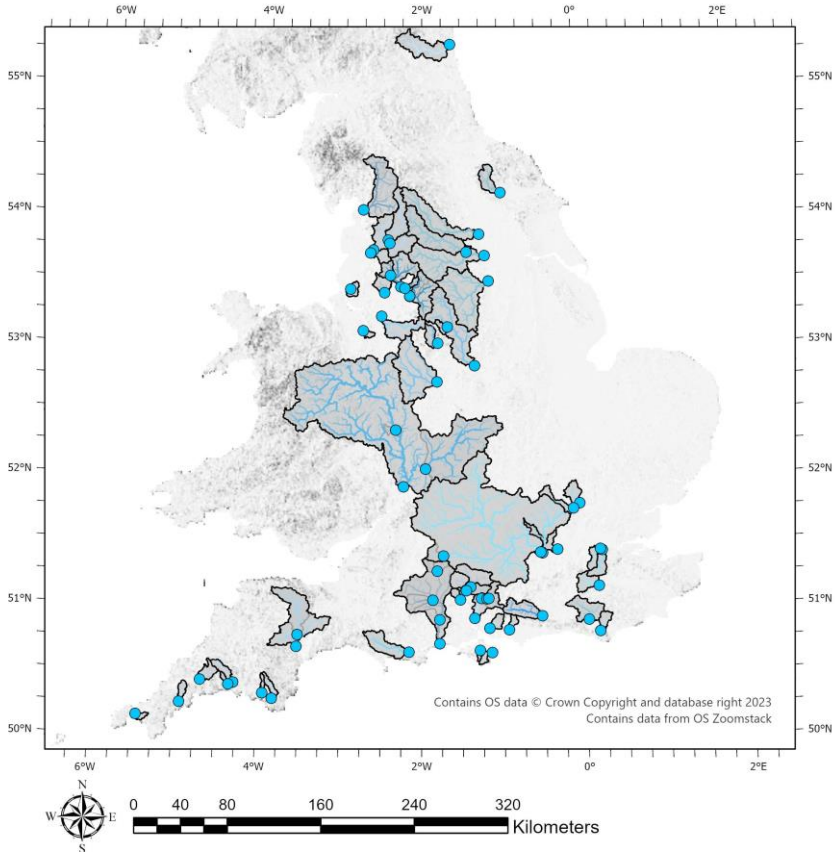

Figure S1: Map of the sampling stations (blue points) and study catchments. River networks (blue lines) were obtained from the UK Atlas Rivers (ECRINS) dataset (Esri ArcGIS FeatureServer, ArcGIS Online)

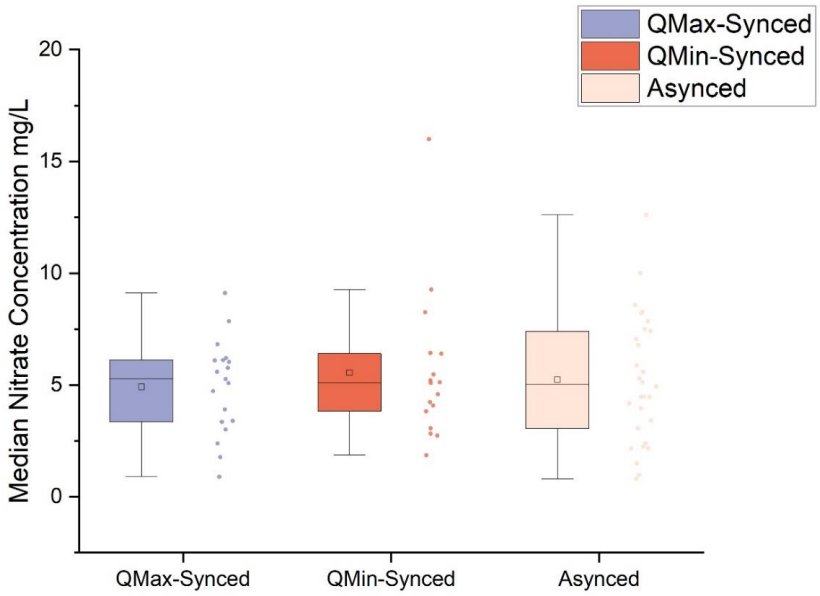

Figure S2: Boxplots of concentrations in synchronous patterns; Note: The central line in each box indicates the median nitrate concentration; the square marker represents the mean. Boxes span the interquartile range (IQR, 25th-75th percentiles), and whiskers show the range excluding outliers (beyond 1.5IQR) . No statistically significant differences in median nitrate concentrations were observed among the synchrony groups (Kruskal-Wallis test, $p > 0.05$).

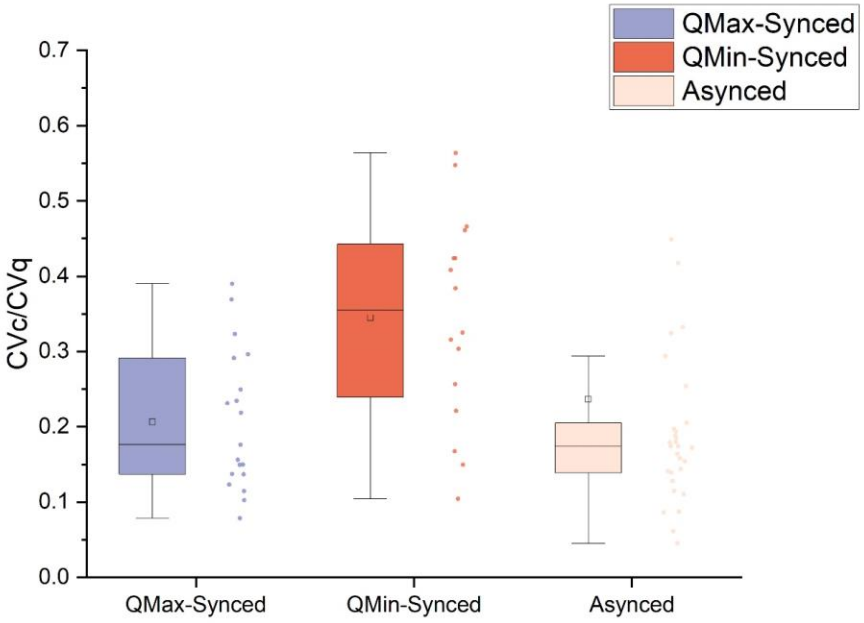

Figure S3: CV_c/CV_q in synchrony patterns; Note: The central line in each box indicates the median CV_c/CV_q Values; the square marker represents the mean. Boxes span the interquartile range (IQR, 25th-75th percentiles), and whiskers show the range excluding outliers (beyond 1.5IQR). The QMin-Synced group

exhibits significantly higher CV_c/CV_q values than both the QMax-Synced and Asynced groups (Wilcoxon rank-sum test, $p < 0.05$).

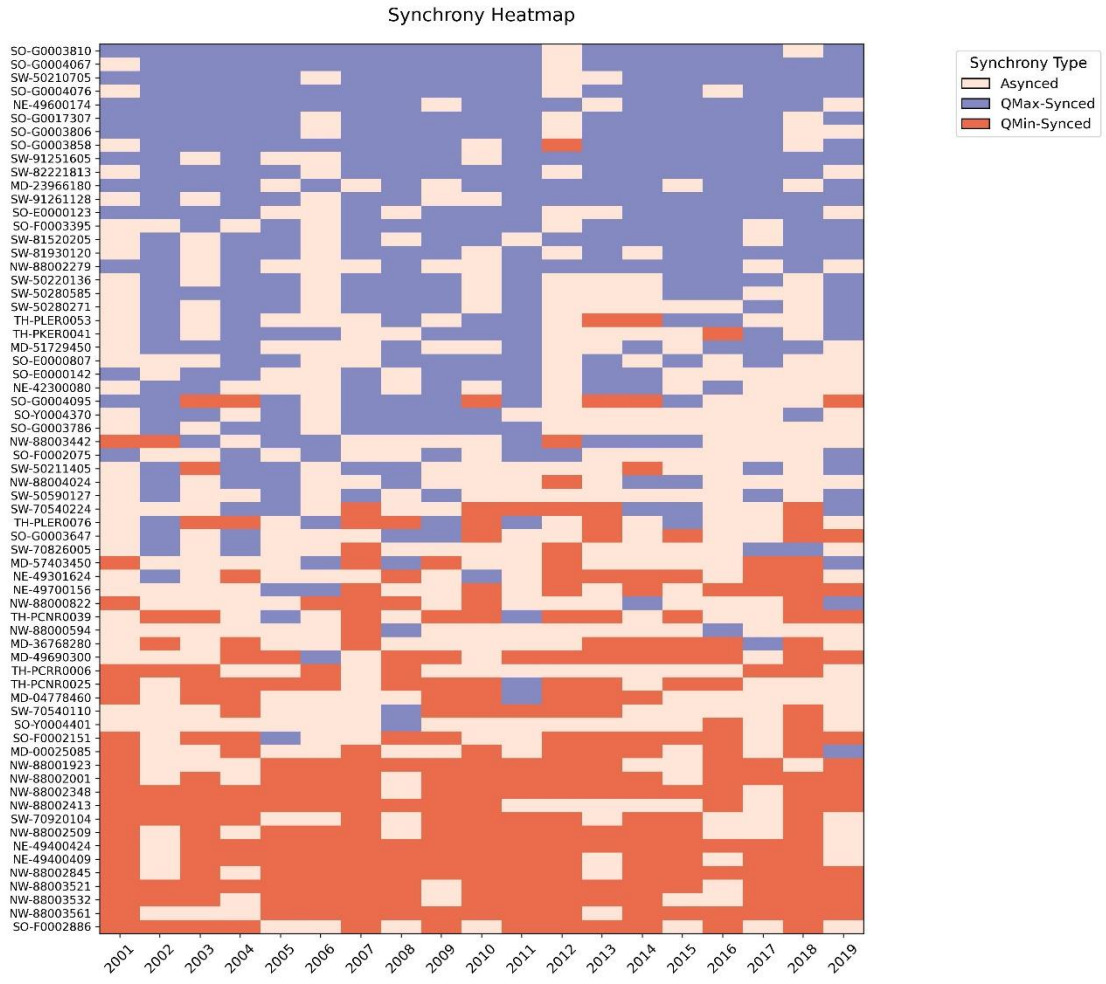

Figure S4: Heatmap of annual synchrony types (2001–2019) across 66 catchments

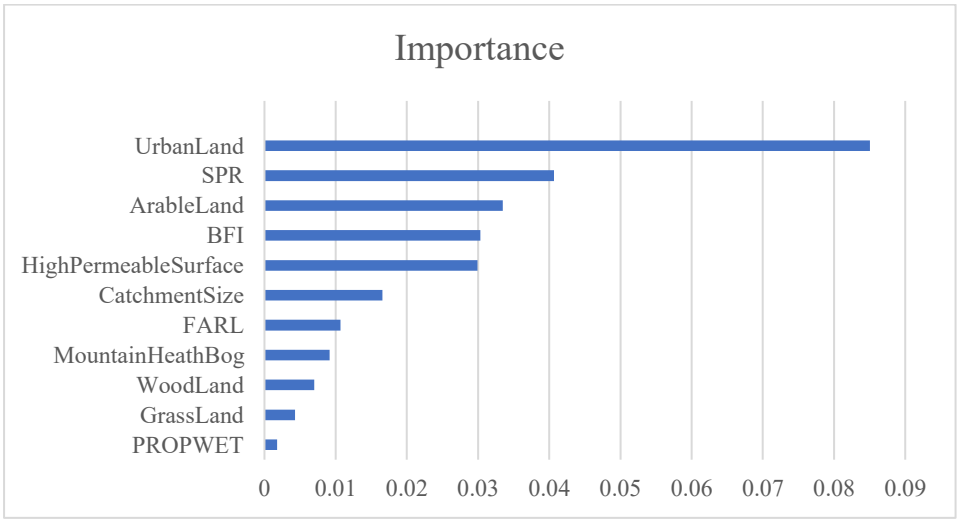

Figure S5: Feature importance from random forest classification model for QMax-Synced and QMin-Synced catchment

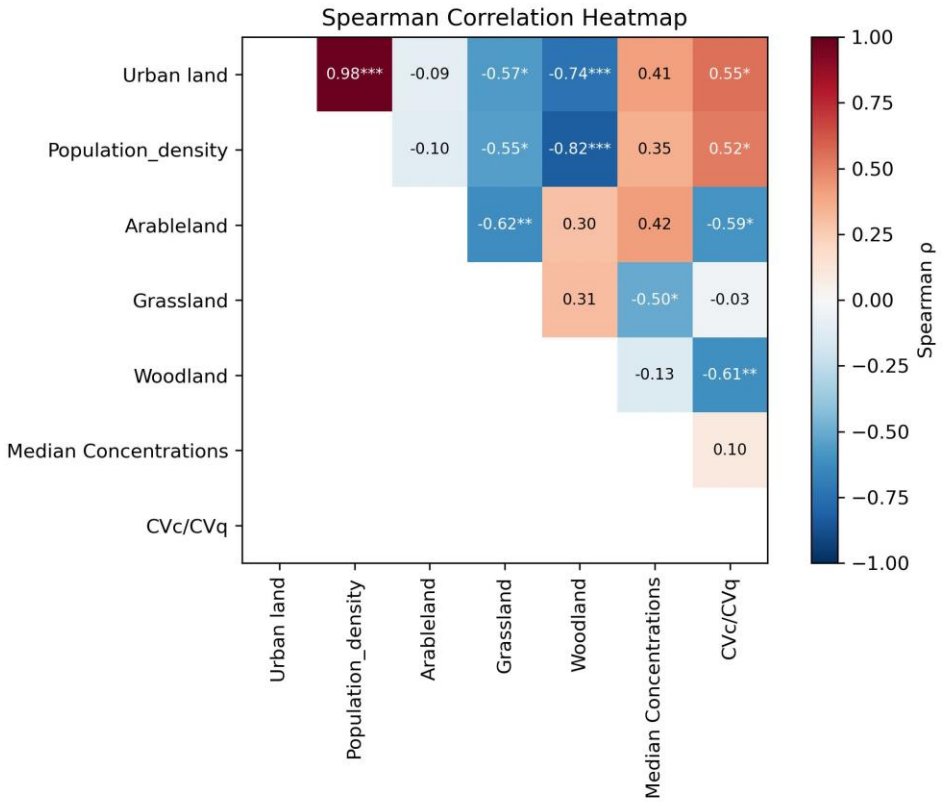

Figure S6: Spearman Correlation matrix for land-use variables and nitrate metrics in QMin-Synced catchments; Colours indicate correlation strength and direction. Asterisks denote significance: $p < 0.05$ (*), $p < 0.01$ (**), $p < 0.001$ (***).

Figure S7: Heatmaps showing Spearman correlations between catchment descriptors and the proportion of years classified as QMax-Synced, QMin-Synced, or Asynced within three groups of catchments. Coloured cells indicate the direction and strength of correlation (ρ), with warm colours denoting positive and cool colours denoting negative correlations. Asterisks mark statistically significant correlations ($p < 0.05$).

Table S1. Summary Statistics of Calculated Metrics in All Catchments (n=66) from Observations and the WRTDS Models

	Mean Discharge m^3/s	CV_q	Mean NO_3-N mg/L	CV_c	CV_c/CV_q	C-Q Coefficient β_2
Max	114.66	1.37	16.62	1.26	1.65	0.27
Min	0.36	0.33	0.89	0.04	0.04	-0.61
Median	3.52	0.71	5.11	0.15	0.19	-0.12
IQR (25%-75%)	11.6	0.20	3.48	0.10	0.18	0.27
Standard Deviation	17.04	0.21	2.75	0.16	0.21	0.19

Reference:

Bayliss, A.C.: Flood Estimation Handbook, Volume 5: Catchment Descriptors, Centre for Ecology & Hydrology, Wallingford, UK, 1999.

Gustard, A., Bullock, A., and Dixon, J. M.: Low Flow Estimation in the United Kingdom, Institute of Hydrology Report No. 108, Wallingford, UK, 1992.

National River Flow Archive (NRFA): FEH catchment statistics, UK Centre for Ecology & Hydrology, [dataset], available at: https://nrfa.ceh.ac.uk/feh-catchment-descriptors, last access: 12 July 2023, 2020.