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Granger, S. J., Upadhayay, H. and Collins, A. L. 2023. Hydro-chemical responses at different scales in a rural catchment, UK, and implications for managing the unintended consequences of agriculture. *Environmental Research.* https://doi.org/https://doi.org/10.1016/j.envres.2023.115826

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PII: S0013-9351(23)00618-7

DOI: https://doi.org/10.1016/j.envres.2023.115826

Reference: YENRS 115826

To appear in: *Environmental Research*

Received Date: 6 December 2022

Revised Date: 6 March 2023

Accepted Date: 31 March 2023

Please cite this article as: Granger, S.J., Upadhayay, H.R., Collins, A.L., Hydro-chemical responses at different scales in a rural catchment, UK, and implications for managing the unintended consequences of agriculture, *Environmental Research* (2023), doi: https://doi.org/10.1016/j.envres.2023.115826.

Hydro-chemical responses at different scales in a rural catchment, UK, and implications for managing the unintended consequences of agriculture

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Abstract:

Diffuse pollutant transfers from agricultural land often constitute the bulk of annual loads in catchments and storm events dominate these fluxes. There remains a lack of understanding of how pollutants move through catchments at different scales. This is critical if the mismatch between the scales used to implement on-farm management strategies, compared to those used for assessment of environmental quality, is to be addressed. The aim of this study was to understand how the mechanisms of pollutant export may change when assessed at different scales and the corresponding implications for on-farm management strategies.

A study was conducted within a 41 km^2 catchment containing 3 nested sub-catchments, instrumented to monitor discharge and various water quality parameters. Storm data over a 24-month period were analysed and hysteresis (HI) and flushing (FI) indices calculated for two water quality variables that are typically of environmental significance; NO_3-N and suspended sediment (SSC). For SSC, increasing spatial scale had little effect on the mechanistic interpretation of mobilisation and the associated on-farm management strategies. At the three smallest scales NO_3-N was chemodynamic with the interpretation of dominant mechanisms changing seasonally. At these scales, the same on-farm management strategies would be recommended. However, at the largest scale, NO_3-N appeared unaffected by season and chemostatic. This would lead to a potentially very different interpretation and subsequent on-farm measures.

The results presented here underscore the benefits of nested monitoring for extracting mechanistic understanding of agricultural impacts on water quality. The application of HI and FI indicates that monitoring at smaller scales is crucial. At large scales, the complexity of the catchment hydrochemical response means that mechanisms become obscured. Smaller catchments more likely represent critical areas within larger catchments where mechanistic understanding can be extracted from water quality monitoring and used to underpin the selection of on-farm mitigation measures.

Keywords: chemo-dynamic; chemostatic; water quality; nutrients; sediment

1. Introduction

Intensive agricultural, and other human, activities have elevated nutrient inputs to the environment (Haygarth et al., 1998; Vitousek et al., 1997) and have also altered hydrological pathways and connectivity (Alaoui et al., 2018; Chen and Chang, 2019; Kennedy et al., 2012). While these activities are often necessary to deliver increased agricultural productivity and profitability, they can frequently lead to the degradation of aquatic ecosystems (Conley et al., 2009; Toggweiler, 1999). This can occur because of the movement of eroded particulate materials (Celeri et al., 2005; Heywood and Walling, 2007), through the loss of dissolved nutrients such as nitrogen (N) and phosphorus (P) (Conley et al., 2009), and often through complex interactions of both particulate and dissolved phases (Carignan and Kalff, 1980; Shaughnessy et al., 2019).

Diffuse pollutant transfers from agricultural land often constitute the bulk of annual loads in river catchments (Smith et al., 2005), and storm events are dominant in the downstream transfer of both soluble and particulate material (e.g. Kronvang et al., 1997; Pionke et al., 1996; Vaughan et al., 2017). Such periods of high flow can, for example, contribute >50% of annual nitrate (Royer et al., 2006) and >66% of annual sediment (Smith et al., 2003) loads in agricultural catchments. Long term meteorological observation data in the UK suggests a warming trend with increasing winter precipitation (Kendon et al., 2020). Recent climate projections for the UK in the 21st century reported in the United Kingdom Climate Projections (2018) suggest a continued warming trend with warmer, wetter winters and hotter, drier summers, accompanied by an increase in the frequency and intensity of weather extremes (Met Office, 2021). Agricultural watersheds are potentially susceptible to changes in precipitation patterns because of factors such as installed field drainage, or changes in land use and land disturbance and concomitant risk of pollutant losses (Kelly et al., 2017). Therefore, robust evidence on hydrochemical responses in catchment systems is critical to support the development of mitigation and adaptation strategies in support of sustainable intensification (Dicks et al., 2019).

Understanding the biogeochemical signatures of storm events has traditionally relied on grab sampling of runoff during forecast storm events. This cannot however, without considerable resources, capture the full temporal dynamic that occurs during storm hydrographs (Bieroza et al., 2014; Granger et al., 2010). Furthermore, it is virtually impossible to collect a sufficiently representative range of storm events given the true nature of each event cannot be known until afterwards. In recent years, the introduction of real-time, high-frequency monitoring with *in-situ* sensors has enabled fundamental questions about stream biogeochemistry to be addressed. Carey et. al. (2014) found that, while annual flux estimates of nitrate (NO_3-N) in a fifth-order suburbanising catchment were similar to those generated by weekly and monthly grab samples, comparisons on a sub-annual time scale were not. This was because seasonal variations in NO_3-N flux were shown to occur with sensor data which were missed using traditional routine, but less frequent, grab sampling. With rich datasets, it is possible to gain insights into catchment scale controls of water pollutant export. For example, Speir et. al. (2021) found that NO_3-N concentrations in two headwater agricultural catchments were largely chemostatic at an annual scale. At a seasonal scale however, while chemostasis was largely maintained, a shift to chemodynamic behaviour occurred in the winter at higher flows. Speir et. al. (2021) interpreted this as an indication of source limitation through the exhaustion of available soil NO_3-N. Using high temporal resolution data, the concentration-discharge (C-Q) response for individual storm events can be described through the calculation of the hysteresis index (HI) and flushing index (FI). When combined, these two empirical indices can be used to improve understanding of the mechanisms by which pollutants are mobilised and delivered within catchments (Butturini et al., 2008; Heathwaite and Bieroza, 2020; Speir et al., 2021). For example, Kincaid et. al. (2020) looked at the hysteresis patterns of NO_3-N and soluble reactive phosphorus (SRP) in three low-order watersheds with different dominant land uses (agricultural, forested, and urban). They found that NO_3-N and SRP exhibited different hysteresis patterns, and that SRP mobilization was more frequently transport-limited while NO_3-N was typically source-limited. Furthermore, land use/cover caused differences in NO_3-N, but not SRP, hysteresis patterns especially at the agricultural site. It was postulated that this was most likely caused by land use practices such as fertilization, artificial drainage, and irrigation, which alter the dominant sources and flow paths for NO_3-N.

Low-order agricultural catchments can export significant pollutant loads to downstream systems (Jarvie et al., 2008; Riley et al., 2018; Speir et al., 2021). Despite this, there remains a lack of understanding of how pollutants move through agricultural catchments at a range of temporal and spatial scales (Haygarth et al., 2005) and especially in low catchment orders (Dupas et al., 2016). This is critical if the mismatch between the scales of measurement used to inform land management, compared to the scales used for assessment of environmental quality, is to be addressed. Experimental measurements are usually made at core/plot spatial scales over short time periods, farmers and land managers operate at the field/farm scale over seasonal or annual timeframes, and environmental policy makers are interested in catchment, regional or national scales over years to decades.

In consideration of the above background, the principal aim of this study was therefore to understand how the mechanisms of water pollutant export may change when assessed at different spatial and temporal scales (Haygarth et al., 2005). Failure to understand this variability will deliver sub-optimal water pollution mitigation strategies in support of sustainable intensification. Herein, we examined two years of high temporal resolution water quality data from four nested agricultural catchments in southwest England to examine how the mechanisms of water pollutant export during storm events changed at different scales. Our first objective was to explore how spatial and temporal scale affected the mechanisms of pollutant export as interpreted using HI and FI. Our second objective was to use the hydrochemical data to explore the implications for on-farm management strategies for reducing the unintended consequences of farming on water quality.

2. Material and methods

2.1 Study site

The study was conducted within the upper River Taw observatory (URTO), an instrumented catchment within the headwaters of the River Taw in southwest England. The River Taw drains a total area of 914 km^2 with the headwaters located on the upland Dartmoor granite plateau ≈550 m above sea level before flowing northwards to the sea through lowlands, predominantly over Carboniferous interbedded sandstones and shales. The climate is classified as temperate and most precipitation falls in the winter months. Average annual rainfall for the period 1992 to 2014 ranged from 1601 mm on Dartmoor (50.7035, −3.9775) to 940 mm at the river mouth (51.0891, −4.1486) (Information provided by the National Meteorological Library and Archive – Met Office, UK.).

The URTO consists of a 19 km stretch of the river that drains an area of 41.3 km^2 from the river head to its outlet at 50.7806, -3.9059. Two nested sub-catchments are monitored in the URTO, 4.4 and 1.7 km^2 in size with outlets at 50.7496, -3.9148 and 50.7427, -3.9316 (Fig. 1.). Instruments at the catchment outlets measure Q and various other physio-chemical parameters on a 15-minute timestep. The soils of the lowland northern portion of the study catchment are typically poorly draining clay rich gley soils and brown earths, while to the south on the Dartmoor upland they consist of peat and podzols (National Rivers Authority, 1994). River hydrology is primarily surface water driven and Q is flashy in response to rainfall events. Base flow is maintained during extended dry periods by water stored within the peat soils on Dartmoor and rock fissures of the Carboniferous country rock. Land use in the URTO is presented in Table 1. The lowlands are predominantly improved agricultural land, mainly grassland supporting beef, dairy and sheep production, with a limited amount of cultivated land and deciduous woodland. The upland area is dominated by rough acidic grasslands, heaths and bog, which support low intensity extensive sheep and beef agriculture.

Also situated partially within the URTO is the North Wyke Farm Platform (NWFP), an instrumented field scale agricultural research facility. This is described extensively by Orr et. al. (2016); however, in short, this consists of 15 hydrologically-isolated field scale lysimeter plots ranging in size from 1.6 to 8.1 ha which are grouped into three management systems. Drainage from each plot is collected in interceptor drains and channelled to an outlet where Q and various water quality parameters are measured also on a 15-minute timestep. In this study, data from one large field unit (8.1 ha), which sits within the URTO, was used. This field catchment has been maintained under an intensive permanent grassland management regime for >30 years and with regular inorganic N and P fertiliser and manure amendments. The field catchment was grazed by a rotation of beef cattle and sheep. Cattle were housed over winter (typically October through to March) while sheep typically grazed longer into the winter season (late November to early January) before being housed.

Data from both the URTO and NWFP were used for the period November 2018 to October 2020 inclusive, for this study, and the catchments are referred to as 1, 2, 3, and 4 with increasing size (Table 1).

Figure 1. Location of the upper River Taw Observatory in the UK, showing the nested catchments and their land use.

Table 1. Predominant land use within the four study catchments. Calculated using UKCEH Land Cover Map data (Morton et al., 2014) which was manually altered based on user knowledge and ariel imagery to reflect reality more accurately.

2.2. Site instrumentation and data collection

2.2.1. Discharge measurements

In the URTO, Q was gauged with streambed mounted sensors within a surveyed channel section. Water velocity was measured using an ultrasound sensor (Mainstream Measurements Ltd, U.K.), while water level was measured using a pressure sensor (OTT Hydrometry, U.K.). The combined outputs were converted to Q using a flow transmitter (Mainstream Measurements Ltd, U.K.). Intercepted drainage from the NWFP field catchment was channelled through an H flume (TRACOM Inc., GA, U.S.A.) with a known rating between water level and Q. Water level was measured using a pressure sensor (OTT hydromet, CO, U.S.A.).

2.2.2. Water quality data

At all URTO monitoring sites, stilling wells were installed to house a YSI 6600 multi-parameter sonde (YSI, Xylem Inc, NY, U.S.A.). The sondes held five sensors which measure amongst other things turbidity, and NO_3-N. Instruments were deployed for approximately one month before being returned to the laboratory for cleaning, assessment, and recalibration. The NO_3-N ion selective electrode which was typically replaced every three months.

Water quality was measured on the NWFP using a YSI EXO 2 sonde (YSI, Xylem, NY, U.S.A). Turbidity was measured using this sonde; however, NO_3-N was measured by a self-cleaning, optical UV absorption sensor (NITRATAX Plus SC, CO, U.S.A.). Unlike the sondes in the URTO, which were continuously submerged, the in-situ measurement of the water quality of Q from the NWFP is discontinuous since it is field scale and controlled by soil moisture conditions and rainfall events. Thus, to prevent sondes from drying out, water from a sump in the conduit that supplies the flume is automatically pumped every 15 mins when Q >0.2 l s^{-1} into a bespoke stainless-steel by-pass flow cell that holds the sondes.

2.2.3. Physical sampling

Targeted storm sampling was undertaken within the URTO to provide information for a calibration curve to convert turbidity units to suspended sediment concentrations (SSC) and to evaluate the reliability of the sonde to determine trends in NO_3-N during storm events. Autosamplers (Teledyne ISCO, NE, U.S.A.) were set to sample the expected duration of the forecasted event, with sampling occurring at the same time as sondes were running. Samples were retrieved as quickly as possible after sampling had ceased, and subsamples were filtered through 0.45 µm filter papers and analysed for NO_3-N on an Aquachem 250 analyser (Thermo Fisher Scientific, MA, U.S.A.). Unfiltered samples were analysed for SSC through the vacuum filtration and subsequent drying at 105°C, of a known sample volume through a pre-weighed glass fibre GF/C grade filter paper, with a particle size retention of 1.2 µm (UK Standing Committee of Analysts, 1980). Suspended sediment concentrations were calculated using a calibration curve developed from SSC data and corresponding turbidity values for each of the URTO catchments. Turbidity data collected from the NWFP was converted to SSC using the calibration curve already reported for this site (Peukert et al., 2014).

2.3. Data analysis

2.3.1. Storm event delineation

Storm events were delineated following base flow separation using the Lyne and Hollick filter implemented in the baseflow function of the Hydrostats package in R (Bond, 2021). Hydrographs were visually inspected and manually modified by: (i) including events that were missed by Hydrostats; (ii) revising the start point of an event if the selected point occurred too soon on the rising limb of the hydrograph; (iii) revising the end point of an event if the selected point was visually too far beyond the inflection point of the falling limb of the hydrograph, and; (iv) splitting an event into separate events if two hydrograph peaks could be clearly identified and separated by a sufficient amount of falling limb. Events were eliminated when: (i) they were not associated with a rainfall/runoff response (often due to sensor noise particularly in Catchment 2); (ii) events did not consist of at least 4 data points on the rising limb, and; (iii) events lacked corresponding water quality data. During this process, water quality data was screened in more detail, removing errant points where identified. Where small data gaps were present on falling limbs, data was infilled using a linear interpolation between the values either side of the gap. In the rare case of larger gaps on hydrograph falling limbs, data were infilled using the relationship that was constructed using the Q and existing falling limb water quality data. Occasionally, data exceeded the maximum measurable turbidity value of 1000 NTU, which lead to no value being recorded. Here, data was infilled as 1000 NTU to enable the storm event to be processed.

2.3.2. C-Q index calculations

We examined seasonal C-Q relationships in the four catchments on normalized data to allow for comparison of the different catchment areas (Lloyd et al., 2016). Normalization was undertaken using the following equations:

$$Q_{i,norm} = \frac{Q_i - Q_{min}}{Q_{max} - Q_{min}} \quad \text{(Eq. 1)}$$

$$C_{i,norm} = \frac{C_i - C_{min}}{C_{max} - C_{min}} \quad \text{(Eq. 2)}$$

where $Q_{i,\ norm}$ and $C_{i,norm}$ are the normalized discharge and water quality parameter concentrations corresponding to the i^{th} pair of measured data. Q_{min} and Q_{max} are the event minimum and maximum discharges, and C_{min} and C_{max} are the event minimum and maximum water quality parameter concentrations, respectively.

The data was categorised into four meteorological time periods: 'Autumn' (September-November), 'Winter' (December-February), 'Spring' (March-May), and 'Summer' (June-August).

The HI and FI indices were calculated to explore C-Q responses during storm events and were adapted from the methods reported in Lloyd et. al. (2016) and Vaughan et al. (2017). We briefly describe these methods here.

The HI at each Q interval HI_j was calculated using the equation:

$$HI_j = C_{j,rising} - C_{j,falling} \text{ (Eq. 3)}$$

where $C_{j,rising}$ and $C_{j,falling}$ are found by estimating $C_{i,norm}$ at 1% intervals of $Q_{i,norm}$ on the rising and falling limbs through linear regression of two adjacent values $C_{i,norm}$. The mean of all HI_j values for any given event were calculated to determine the overall HI. The HI ranges from -1 to +1 with negative values indicating an anticlockwise loop with concentrations on the falling limb higher than the rising limb, and positive values a clockwise loop with concentrations higher on the rising limb. The magnitude of the HI indicates the normalised difference between the rising and falling hydrograph limbs.

The FI is used to evaluate the flushing of sediment or associated nutrients during storm events and is given by the following equation:

$$FI = C_{Qpeak} - C_{Qstart} \text{ (Eq. 4)}$$

where C_{Qstart} and C_{Qpeak}, are the normalized parameter concentrations at the beginning of the event and at the peak Q of the rising limb, respectively. The FI also ranges from -1 to +1, with a negative FI value indicative of a dilution effect with concentrations falling on the rising limb, whereas a positive FI indicates a flushing effect with an increase in water quality parameter concentrations on the rising limb. The distance from zero indicates the magnitude of this difference.

2.3.3. Storm hysteresis analysis by catchment scale

Hysteresis indices are commonly used to describe hydrochemical behaviour. The HI describes the timing of the change, whereas the FI describes the nature and magnitude of the change in relation to Q (Heathwaite and Bieroza, 2020; Lloyd et al., 2016). This information can be used to infer the sources of solutes and particulates and their mechanisms of delivery from catchments. Positive HI values (clockwise loops) occur when concentrations were highest on the rising limb of the hydrograph, while negative HI values (anticlockwise loops) indicate the concentrations were highest on the falling limb (Bowes et al., 2005). Positive HI values can be interpreted as indicating the presence of a readily available source which could be proximal to, and/or have a strong connectivity to the watercourse. Negative HI values can indicate a source which is not readily mobilised and/or is distant or has poor connectivity to the watercourse (Rose et al., 2018). Positive values of FI indicate that event water has higher concentrations or becomes enriched in concentrations of a given solute or particulate indicating that it is transport-limited (i.e., a source is present in the catchment but without storm flows it is not mobilised and/or transported). Negative FI values indicate that storm water dilutes concentrations of a given solute or particulate indicating that it is source-limited (i.e., the source is somehow protected or rapidly exhausted from interaction with storm flows) (Speir et al., 2021).

It is important to note that during any given event, variations in the contributing source types and magnitude, and their proximity and connectivity to waterbodies can complicate the interpretation of HI/FI values (Chanat et al., 2002). Also, in common with other studies (e.g., Heathwaite and Bieroza, 2020; Speir et al., 2021; Vaughan et al., 2017), there was a large variation in C-Q responses observed across the different catchment scales especially for NO_3-N. This suggests that the availability and proximity of sources and the mechanisms of mobilization and delivery, change from storm event to storm event; however, mean HI and FI values demonstrated significant seasonal differences.

3. Results and discussion

3.1. Flow

The median Q in each of the four catchments increased with catchment scale (Table 2), with the minimum recorded Q of 0 l s^{-1} in Catchment 1 and a maximum of 3498 l s^{-1} in Catchment 4. While the Q in river Catchments 2-4 was continuous over the study period, the drainage from Catchment 1 was discontinuous as it was derived from more surface/through flow pathways, disconnected from ground water, and more directly linked to soil moisture patterns and rainfall events. This meant that ≈4% of recorded Q in Catchment 1 was 0. Furthermore, as the automated chemical analysis of drainage was only undertaken once Q was >0.2 l s^{-1}, about 43% of recorded Q was not associated with any water quality data. These periods of low Q occurred mainly during the drier Summer months; in contrast the maximum flows recorded occurred during the wetter Winter months.

Table 2. Summary of flow (Q), nitrate and suspended sediment concentration (SSC) of the storm events in the study catchments by season.

3.2. Storm hysteresis analysis by catchment scale

3.2.1. Catchment 1 – a 0.08 km^2 permanent grassland catchment

3.2.1.1. Nitrate

Mean seasonal HI values were slightly negative for all seasons (-0.25 to -0.07) indicating typically anticlockwise loop patterns, and season was only found to have a significant effect ($f_{3,95} = 2.7$; $p<0.05$) between Autumn and Winter. Mean FI values were also all negative for all seasons (-0.80 to -0.20) indicating dilution in response to Q; however, the effect of season on FI was more pronounced ($f_{3,95} = 8.8$; $p<0.001$) with Winter and Summer means at the extreme ends of the data range which indicated a reduction in the magnitude of the dilution response from Winter through to Summer. This dominant anticlockwise loop pattern with dilution effect (lowest concentrations occurring before peak Q) is interpreted as representing a source of NO_3-N which is not readily mobilised by storm events and/or is poorly connected to the catchment outlet (e.g. Kincaid et al., 2020). Given the small size of Catchment 1 and its homogenous management, it cannot be considered that the source was distal, or that multiple sources were contributing at different times (e.g. Vaughan et al., 2017). The mechanisms that cause this response have been well reported and typical of these well-structured soils which contain relatively immobile soil water (and NO_3-N). In the absence of any soil surface amendments, storm event water passes rapidly over the soil surface either through saturation-excess overland flow (in winter) or by infiltration-excess overland flow combined with rapid movement through the soil via drying cracks and macro-pores (in summer). This NO_3-N poor water has limited interaction with soil, or groundwater and leads to a dilution response at the catchment outlet (Barraclough, 1989).

It is clear that season in important in the spread of individual storm HI/FI responses. The individual Winter events consistently had a FI <0; however, Summer FI data shows that the response to summer storm events was more varied, with individual FI values ranging between -1.0 and 0.91. It is this spread of values that cause the mean Summer FI to be significantly greater than Winter FI. It was not so much that Summer FI had a lower magnitude dilution response, but more that events ranged between large concentrating responses and large dilution responses. Therefore, while the mechanisms of the Winter response are widely understood and consistent, the mechanisms of the Summer response are far more variable. In the summer, there tends to be a far greater potential mixture of factors that can affect individual storm event NO_3-N FI. These include amongst other things, a wider range of soil moistures, rainfall intensities, and agricultural activities. These different factors can combine to both cause flushing (Withers et al., 2003) and diluting responses (Scholefield et al., 1993) in the same season.

3.2.1.2. Sediment

All SSC HI values were all positive indicating a consistent clockwise loop pattern and the seasonal means (0.40 to 0.49) were not found to be significantly different. All FI values were also found to be positive indicating a flushing response with an increase in SSC with increased Q, and again seasonal means (0.55 to 0.63) were not found to be significantly different. These data suggest the mechanisms for sediment delivery from grassland, at this spatial scale, were not affected by season and consistently showed rising and peak SSC on hydrograph rising limbs before peak Q occurred. This response can be interpreted as sediment being transport-limited (e.g. Kincaid et al., 2020; Vaughan et al., 2017) with a source that was either proximal and/or well connected to the catchment outlet. Our data match the findings of Pulley and Collins (2019) examining field scale sediment losses on these lowland grazing grassland systems and concluding that soil detachment and transport by raindrop-impacted-saturation-excess overland flow was the dominant mechanism. They also noted that SSC changes in Q responded to the onset and cessation of rainfall and that SSC generally dropped sharply after rainfall had stopped even when Q remained elevated. Although Pulley and Collins (2019) did not examine these mechanisms during the summer, when the catchment is not typically saturated, the same overarching transport-limitation would still appear to be occurring.

Figure 2. Biplots of the hysteresis (HI) and flushing (FI) index of the captured storm events for nitrate (NO_3-N) and suspended sediment concentrations (SSC) in the study catchments by season. The larger points represent the mean for each season with 1 standard deviation error bars. The different levels of significance are indicated by letters within the plots.

3.2.2. Catchment 2 – a 1.7 km^2 predominantly permanent grassland catchment.

3.2.2.1. Nitrate

In Catchment 2 all seasonal mean HI values were negative which indicated anticlockwise loop patterns were dominant and the mean HI values were slightly more negative than Catchment 1 (-0.36 to -0.19). As in Catchment 1, mean FI values ranged between Winter and Summer extremes (-0.61 to 0.36) and were significantly different ($f_{3,63}$ = 12.9; p<0.001). The mean Winter response is similar to that seen in Catchment 1; an anticlockwise loop with dilution effect interpreted as representing source limitation of NO_3-N which was not readily mobilised by storm events. Mechanistically, NO_3-N poor storm runoff had little interaction with soil water and its associated NO_3-N, and with no seasonal surface agricultural NO_3-N sources which lead to dilutions of base flow NO_3-N at the catchment outlet.

The seasonal shift in response from Winter to Summer was more exaggerated in Catchment 2 than in Catchment 1. While all Winter FI values were still <0, Summer FI values were mostly >0 with the seasonal mean describing an anticlockwise loop pattern with a flushing effect and peak NO_3-N concentrations typically occurring after peak Q. This form of seasonal variation in response has been reported elsewhere (Webb and Walling, 1985), whereby both diluting and concentrating effects can occur at any time of the year, but predominantly dilution occurs in the wet winter months and concentration in the summer. At this catchment scale, the NO_3-N response is interpreted as shifting to predominantly transport-limitation in the Summer with NO_3-N now being mobilised by storm events although the source is distil and/or not directly connected to the catchment outlet. The flushing responses seen predominantly in the Summer could be representing, in part, ‘incidental losses’ (Haygarth and Jarvis, 1999) of agricultural amendments being washed off the land surface. Such amendments would not be present in the Winter and start to occur in the Spring and Summer months. However, it might be expected that this would lead to more clockwise loop patterns with peak concentrations occurring on the rising limbs of hydrographs, before peak Q. The lack of such responses suggests that these processes are not dominant. The mechanisms leading to NO_3-N flushing were probably due to a combination of increased soil NO_3-N (soil nitrification and amendments), and an increased interaction time between precipitation and soil, leading to elevated soil throughflow when conditions were conducive (e.g. Davis et al., 2014; Torbert et al., 1999).

3.2.2.2. Sediment

The distribution of HI and FI values in Catchment 2 was greater than in Catchment 1. Mean seasonal HI were all >0 (0.00 to 0.29) indicating that clockwise loops patterns were still dominant, typical of low-disturbance rural catchments (Zarnaghsh and Husic, 2021). However, at this scale, significant seasonal variations were found to occur, with Summer having a significantly lower HI than Winter ($f_{3,62} = 6.825$; $p<0.001$). All seasonal FI values were also positive (0.50 to 0.73), although not significantly different, which combined with the HI values, indicated that peak SSC occurred on or before peak Q. Positive FI values, as with Catchment 1, indicate that sediment sources were transport-limited while the lower seasonal mean HI values, compared to Catchment 1, indicated a general shift in timing of peak SSC to slightly later on the hydrograph. This suggests the mechanisms for sediment delivery were like those in Catchment 1 with sediment sources that were either proximal and/or well connected to the catchment outlet (e.g. Perks et al., 2015).

An important difference between Catchments 1 and 2 is the seasonal change in HI between Winter and Summer. While all seasons showed a decrease in HI values, Summer showed the clearest effect with several individual storm events having negative HI values (-0.40 to 0.41). This indicated that peak SSC occurred on both rising and falling hydrograph limbs during different storm events. While positive HI values are in keeping with Catchment 1, indicating SSC concentrations peeked before peek Q, the presence of negative HI values represents a noticeable shift between Catchment scales 1 and 2. Peaks of SSC peaks on the hydrograph falling limb have been observed elsewhere and have been interpreted as a delayed bank collapse ‘drawdown’ failure mechanism (Lawler et al., 1997). However, this is not believed this is the case in this study as the channels are steeply incised with a bedrock component and well vegetated in the summer. Furthermore, the negative HI values indicated that remobilization of within channel sediment (e.g. Keesstra et al., 2019) was not significant as this too would lead to an increase in SSC on the rising limb. The pattern could be interpreted as a shift between proximal and distal sources (e.g. Perks et al., 2015) being more pronounced in the Summer. However, given the catchment was of a small size and the land use largely consistent, under permanent grassland, it seems unlikely that different areas are becoming sediment sources at different times of the year. A more likely explanation would be that the main mechanisms for soil detachment and transport seen in Catchment 1 (Pulley and Collins, 2019) still hold for Catchment 2, but that a separation of hydrological and SSC responses was occurring (e.g. Keesstra et al., 2019) and this becomes more evident in the Summer. This could be caused by a combination of a greater variety of Summer antecedent conditions which can affect hysteresis (Perks et al., 2015) and an increase in catchment 'urban' hard surfaces (e.g. Zarnaghsh and Husic, 2021) (when compared to Catchment 1) which can cause higher variability in timings. In the Winter, when the catchment was predominantly 'saturated', hydrological connectivity to the drainage network was high. Raindrop detached sediment was rapidly transported in overland flows to the catchment outlet leading to clockwise loop patterns. In the Summer however, the hydrological conditions of the catchment can be more varied with both wet and dry soils occurring depending on the prevailing meteorological conditions. These antecedent conditions have implications for, amongst other things, sediment erosion (e.g. Pulley et al., 2022), overland flow generation (e.g. Meyles et al., 2003) and hydrological connectivity (e.g. Williams et al., 2003). Furthermore, the 'urban' land use component had near zero infiltration capacity and often a direct connection to the drainage network. Therefore, in the Summer under wet conditions, sediment can be detached and transported rapidly to the drainage network leading to clockwise loop patterns. Under dry conditions, however, an increased capacity for infiltration within the catchment can hinder the arrival time of hydrological flows and associated sediment whereas the 'urban' surfaces can lead to rapid increases in Q while potentially transporting little of sediment. Therefore, these hard surfaces can cause Q to rise and fall rapidly before hydrological connectivity with the rest of the 'agricultural' component of the catchment is established, thus leading peak SSC to occur after peak Q.

3.2.3. Catchment 3 - A 4.4 km^2 catchment consisting of predominantly agricultural land, mainly improved grassland but now also with a significant arable land component.

3.2.3.1. Nitrate

In Catchment 3, all seasonal mean HI values were again negative indicating that anticlockwise loop patterns were typical. The range of the mean HI values (-0.58 to -0.03) was, however, greater than Catchments 1 and 2 with a significant ($f_{3,71} = 16.7$; $p<0.001$) difference between Winter (-0.03) and the other seasons which were more negative with Summer again being the other extreme of the range (-0.58). The same spread of seasonal FI means observed in Catchments 1 and 2 continued to be observed in Catchment 3 with a significant difference ($f_{3,71} = 17.3$; $p<0.001$) between Winter (-0.72) and Summer (0.07) at each end of the mean FI range. Mechanistically, the interpretation of these data is like that of Catchment 2 with seasonal shifts in mechanisms of NO_3-N delivery to the catchment outlet (Webb and Walling, 1985). The mean Winter dilution response indicated source-limitation of soil NO_3-N which was not readily mobilised by storm events and/or is poorly connected to the catchment outlet. This response shifts in the Summer to more transport-limitation although the mean Summer response is more 'neutral' than in Catchment 2 (Heathwaite and Bieroza, 2020). However, as noted previously in Catchment 2, both diluting and concentrating events can occur at any time of the year but primarily dilution events are typical in the Winter and flushing events more common in the Summer (Webb and Walling, 1985) depending on prevailing environmental conditions.

3.2.3.2. Sediment

The SSC mean seasonal HI values in Catchment 3 were slightly lower than Catchment 2 (-0.08 to 0.28). This indicated that clockwise loop patterns were typical for most seasons apart from Summer, with peak SSC occurring before peek Q, but with the SSC peek occurring slightly later on the hydrograph. As with Catchment 2, significant seasonal variations were found to occur with Summer having a significantly lower HI (-0.08) than Winter (and Spring) ($f_{3,68}$ = 4.854; p<0.01) meaning that peak SSC occurred on or just after peak Q. Seasonal FI values remained positive and comparable to Catchment 2 (0.56 to 0.83); however, at this scale, significant differences were observed with the Summer FI (0.56) being significantly lower than Winter (and Autumn) ($f_{3,68}$ = 5.077; p<0.01). Positive seasonal FI values continue to indicate that sediment sources were transport-limited while the trend to lower seasonal mean HI values was associated with the timing of peak SSC being later in the hydrograph. In this more diverse land use catchment, the mechanisms for sediment delivery are interpreted as to have remained like those at the previous smaller scales with sediment sources that were either proximal and/or well connected to the catchment outlet dominating.

These data describe a very similar pattern to those a short distance upstream at Catchment 2. The mean seasonal FI values however, tended to be higher than those measured in Catchments 1 and 2 for all seasons except Summer which remained similar throughout. While no significant differences in FI between season were present in Catchments 1 and 2, in Catchment 3, Autumn and Winter mean FI were significantly higher (p<0.01) than Summer. The increase in seasonal FI values in Catchment 3 were most likely related to the presence of arable land, proportions of which lie bare or are subject to disturbance throughout most of the year. In the wetter seasons, rainfall and good hydrological connectivity means that these land areas yield more sediment than grassland to drainage. The effect of this land use on the Summer FI values would appear to be negligible, probably due to dry, hydrologically disconnected land units, minimal erosive rainfall, and increased vegetation cover in the form of mature crops. In contrast, while mean Summer FI remained like Catchment 2, the Summer HI became negative. Individual Summer storm HI values were much more variable with >50% of the storms having a FI<0 indicating that, for most storm events, peak Q occurred before peek SSC. Again, this is perhaps not unsurprising given that was what was being observed a short distance upstream in Catchment 2, and that the response of any hard surfaces upstream, and those in Catchment 3, would continue to be reflected. However, it does indicate that in the short distance downstream between the outlets of Catchments 2 and 3, the temporal delay in the delivery of sediment was becoming more pronounced.

3.2.4. Catchment 4 - A 41.3 km^2 catchment consisting mostly of extensive and intensive agricultural land, mostly grasslands but also some arable land.

3.2.4.1. Nitrate

Catchment 4 exhibited a completely different HI/FI response to the previous three smaller catchments. All HI values are slightly negative and close to 0 (-0.01 to -0.09), while FI values were slightly positive but also close to 0 (0.01 and 0.07). The similarity in the means meant that there were no significant seasonal differences for either index and that the mean seasonal response was consistently ‘linear’ and ‘neutral’ (Heathwaite and Bieroza, 2020). This would indicate that at this scale river NO_3-N was chemostatic. However, despite the consistently linear/neutral seasonal indices, the spread of individual storm values across all seasons ranged from -0.57 to 0.54 for HI and -0.66 to 0.70 for FI indicating that, regardless of season, the response to individual storm events was highly variable. This chemostatic response we interpret to be a homogenisation effect created by the increase in scale (e.g. Creed et al., 2015). An increase in the variability of different source types and strengths, environmental conditions, pathways and travel times within this larger catchment combine to obscure the seasonal patterns which are occurring within the catchment and observable at smaller scales. However, it is worth noting that seasonality in NO_3-N responses have been reported in catchments far larger than Catchment 4 (e.g. Zimmer et al., 2019) although those seasonal trends remain inconsistent.

3.2.4.2. Sediment

The HI seasonal means in Catchment 4 ranged between 0.23 and 0.37, were not significantly different, and continued the dominance of clockwise loop patterns. The gradual shift to lower HI values observed through the previous increasing catchment scales was no longer present, and all seasonal mean HI values were now higher than those observed in Catchment 3. In particular, the Summer mean HI value, which had previously shown the most significant shifts to lower values when compared to other seasonal means, was again now positive (0.23). This was due to very few individual storm events having negative HI values, a trend which had been developing through Catchments 1 to 3. As observed at the previous catchment scales, all individual storm event FI values were >0 with mean seasonal FI values ranging from 0.51 to 0.64 with no significant difference between them. The seasonal FI mean values, which in Catchment 3 had increased in value in some cases compared to the small-scale catchments leading to significant differences in seasonal FI, had now returned to values similar to Catchments 1 and 2. This indicated that all seasons were demonstrating a predominantly clockwise hysteresis loop pattern with SSC increasing on the rising limb of the hydrograph, but where peak SSC was now occurring earlier than in Catchment 3. The positive FI values continue to indicate that sediment sources were transport-limited and suggests the mechanisms for sediment delivery from a diverse land use catchment at this scale continue to be the same as those at previous, less diverse scales in that the sediment sources were either proximal and/or well connected to the catchment outlet. As with NO_3-N, this more subtle shift in HI and FI values from Catchment 3 to 4 is interpreted as an effect of increased catchment scale causing a loss of resolution of different sources and processes. The contribution of the arable land, which had been interpreted as causing the increase in some seasonal FI values in Catchment 3, was now not as clear as its proportion of the catchment area was reduced (Table 1). Furthermore, the shifts in peek Q and SSC responses potentially caused by areas of low or nil infiltration, which had caused Summer HI values to reduce through catchment scales 1 to 3, were also now not discernible. This too was probably due to the buffering of hard surface responses by other contributing areas within the larger catchment.

3.3. Scaling implications for on-farm best management interventions

Indices such as HI and FI, based on relationships between chemical constituents and Q, reflect the combined integration of pollutant source contributions, flow pathways, biogeochemical cycling and controls exerted by climate, lithology and soils (Knapp et al., 2020). Calculating such indices can improve our understanding of hydrochemical responses in support of mitigation plans to protect water resources. Here, the biplots of HI and FI scores (Figure 2) can be used to improve our understanding of the source and transport of nutrients and sediment across the scales monitored in our study area (de Barros et al., 2020). In turn, the mechanistic understanding can be used to select interventions for which uncertainty ranges for efficacy in reducing NO_3-N or sediment losses have been reported (Gooday et al., 2014). For Catchment 1, the HI and FI indices suggest there is no readily mobilised source of NO_3-N. Here, recommended mitigation options should include those to ensure soil N does not increase to elevate mobilisation risk, to help manage disconnected less rainfall driven nutrient sources such as manure heaps and the interception of what nutrient-poor water is leaving the field. For managing soil nutrient levels, specific options might include using plants with improved nitrogen use efficiency (efficacy uncertainty range of 2-25%), making use of improved livestock genetic resources (0-10%), monitoring and amending soil pH (0-10%), using a fertiliser recommendation system (0-10%) and integrating fertiliser and manure inputs (2-18%). For the interception of the nutrient-poor water leaving the field, mitigation options could include re-siting gateways away from high-risk areas (2-25%), establishing new hedges (0-10%), constructing in-field ponds (2-25%) and establishing riparian buffer strips (2-25%). For sediment losses from Catchment 1, relevant measures already implemented on the NWFP include reducing field stocking rates when soils are wet (2-25%) and constructing troughs with a concrete base (2-25%). Here, however, it has already been demonstrated that sediment losses are primarily controlled by field size on the NWFP rather than the extent of poached areas (Pulley and Collins, 2019), meaning that field-wide interventions are most relevant

(Collins et al., 2021), including reducing the length of the grazing season (10-50%), locating grazing out-wintered livestock away from watercourses (0-10%), loosening compacted soil layers in grassland fields (0-10%) and using correctly inflated low ground pressure tyres (2-25%). For Catchment 2, the same interventions for reducing NO_3-N and sediment loss would be relevant, but the switch between from source-limited diluting responses in winter to transport-limited flushing responses in summer in the case of NO_3-N, particularly underscore the relevance of those measures listed above for Catchment 1 to control soil nutrient levels for minimising mobilisation risk and to intercept waterborne nutrients on route to the river channel. Turning to Catchment 3, those interventions listed above for reducing NO_3-N and sediment losses from grassland, would also be relevant. Since Catchment 3 also includes arable land and concomitant elevated risks for sediment loss exhibited by flushing transport-limited responses, relevant interventions for reducing the sediment loss would need to target both source/mobilisation risk and pathway delivery for arable fields. Interventions for targeting the former could include establishing cover crops in the autumn (50-95%), early harvesting and establishment of crops in the autumn (25-80%), adopting reduced cultivation systems (25-80%), cultivating compacted tillage soils (10-50%) and manage compaction associated with over-winter tramlines (10-50%). Delivery pathway interventions could include establishing in-field grass buffers (10-50%), establishing riparian buffer strips (25-80%) and management of arable field corners (2-25%). The same sediment interventions relevant for Catchments 2 and 3 would also be suitable for Catchment 4 as the HI and FI responses remain largely the same; however, the mean responses for NO_3-N are very different. Based on this evidence alone, no definable suite of NO_3-N interventions could be recommended.

4. Conclusions

The results presented here underscore the benefits of nested monitoring for extracting mechanistic understanding for designing tailored mitigation of the unintended consequences of agriculture on water quality. Previous work has reported that increasing catchment scale can result in homogenisation of hydrochemical responses (Basu et al., 2011; Bieroza et al., 2018; Creed et al., 2015). This was clearly manifest in our NO_3-N data for Catchment 4, but not exhibited at any scale for SSC. Internal nutrient stores in agricultural catchments, including the unsaturated zone, frequently contribute to such homogenisation and chemostatic responses (Ascott et al., 2016; Dupas et al., 2016). The tendency for such responses is indicative of land use overriding structural controls (Basu et al., 2011), pointing to the need to consider the intensity of farm nutrient inputs and structural land cover.

Given financial pressures in many countries, water resource managers face critical decisions regarding the locations and frequency of water quality monitoring (Bieroza et al., 2018). The application of HI and FI indicates that priority should be given to monitoring locations at smaller scales. At large scales, the complexity of the hydrochemical response can mean that mechanisms can become obscured by a homogenisation of different responses and timings. Smaller catchments are more likely to represent critical areas within larger catchments where mechanistic dynamics can be extracted from conventional water quality monitoring and used to underpin the selection of on-farm mitigation measures. Following extraction of mechanistic understanding from chemo-dynamic hydrochemical responses using HI and FI under baseline conditions, extended monitoring and repeat calculation of such indices can be used to assess the impacts of targeted best management.

Acknowledgements

Rothamsted Research receives strategic funding from UKRI-BBSRC (UK Research and Innovation-Biotechnology and Biological Sciences Research Council) and this work was funded by the Soil to Nutrition strategic programme under Project 3 (grant award BBS/E/C/000I0330). The North Wyke Farm Platform is a UK National Capability supported by the UKRI-BBSRC (BBS/E/C/000J0100). We acknowledge the interests of the Ecological Continuity Trust (ECT), whose national network of LTEs includes the NWFP experiment on which part of this research was conducted. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising. We thank Hadewij Sint for her help with data quality control, Yusheng Zhang for his help with data preparation and the landowners for access to the monitoring sites.

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Table 1.

	Catchment 1	Catchment 2	Catchment 3	Catchment 4
Catchment area (km^2)	0.08	1.7	4.4	41.3
Extensive grassland area (%)	0	0	0	38.3
Improved grassland area (%)	100	88.2	70.5	43.5
Woodland area (%)	0	7.5	10.1	9.5
Arable area (%)	0	0	17.6	6.5
Urban area (%)	0	4.3	1.8	2.2

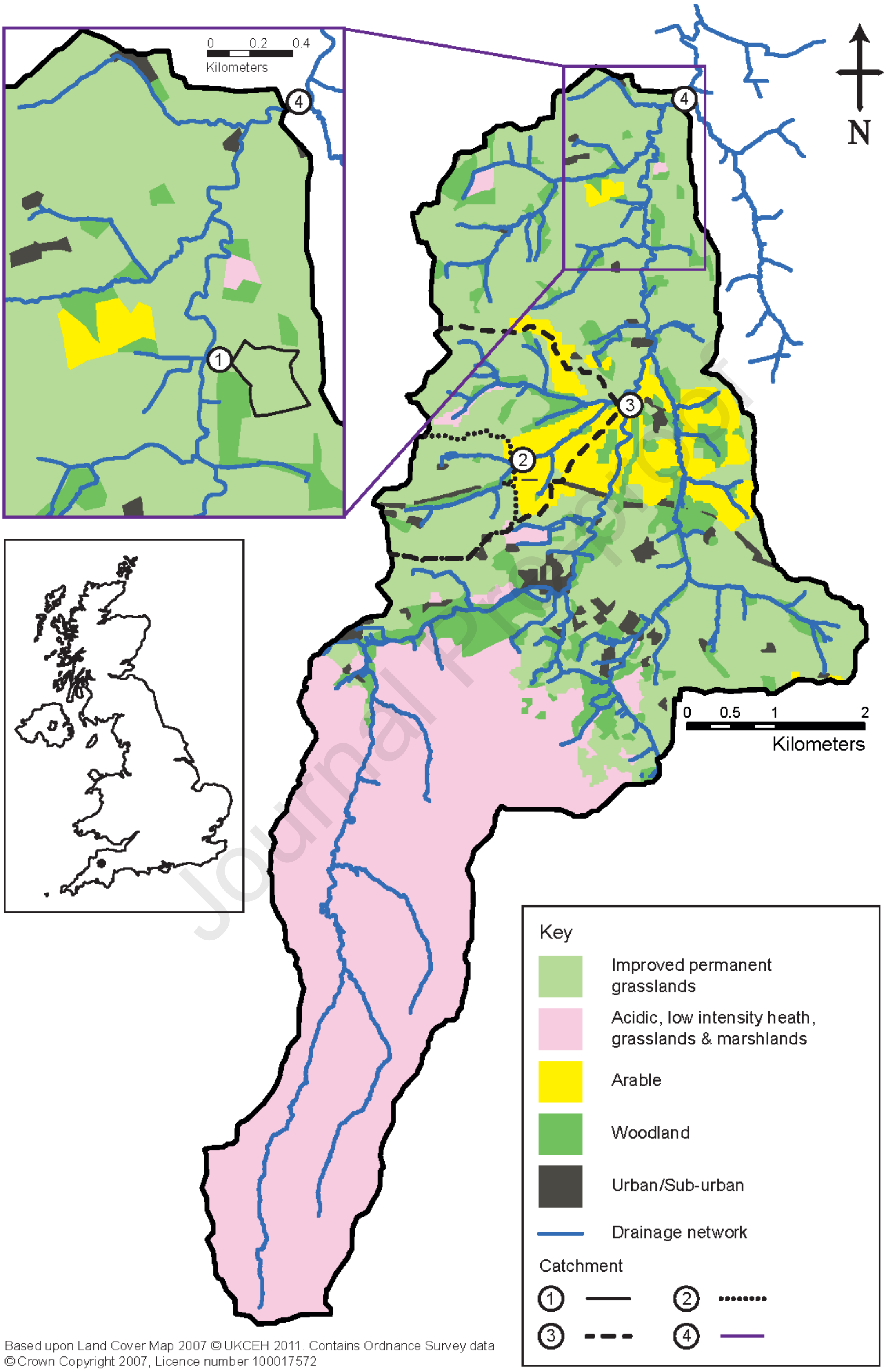
Table 2.

		Median Q (min-max) l s^{-1}	Median NO_3 (min-max) mg N l^{-1}	Median SSC (min-max) mg l^{-1}	Storm events analysed†
Catchment 1	Autumn	0.3 (0.0-199)	2.3 (0.5-8.2)	7 (0-1145)	36
	Winter	1.3 (0.2-138)	1.8 (0.4-4.6)	4 (1-599)	58
	Spring	0.68 (0.1-92)	2.4 (1.0-4.4)	3 (1-178)	14
	Summer	0.0 (0.0-30)	2.3 (1.6-11.8)	9 (0-414)	16
Catchment 2	Autumn	0.0 (0.0-0.3)	1.8 (0.8-5.3)	5 (0-795)	16
	Winter	0.1 (0.0-0.5)	2.4 (1.1-4.1)	6 (1-374)	30
	Spring	0.0 (0.0-0.2)	1.3 (0.6-2.3)	4 (2-835)	10
	Summer	0.0 (0.0-0.1)	1.0 (0.5-2.2)	4 (1-1496*)	16
Catchment 3	Autumn	0.1 (0.0-2.3)	2.4 (0.7-7.9)	6 (0-1285*)	19
	Winter	0.2 (0.1-3.5)	3.1 (1.3-5.3)	6 (1-1285*)	36
	Spring	0.1 (0.0-1.6)	2.0 (0.7-10.6)	4 (1-1285*)	9
	Summer	0.0 (0.0-1.4)	0.9 (0.2-5.2)	2 (1-1285*)	15
Catchment 4	Autumn	1.4 (0.3-20)	1.7 (0.2-7.3)	3 (0-564)	18
	Winter	2.1 (0.6-35)	1.4 (0.6-8.1)	5 (0-902)	28
	Spring	0.6 (0.2-13)	1.2 (0.6-5.0)	2 (1-568)	9
	Summer	0.3 (0.2-7.7)	1.2 (0.4-3.5)	1 (0-519)	14

†For at least one determinant

*Maximum sensor turbidity limit exceeded

Figure 1.



Based upon Land Cover Map 2007 © UKCEH 2011. Contains Ordnance Survey data
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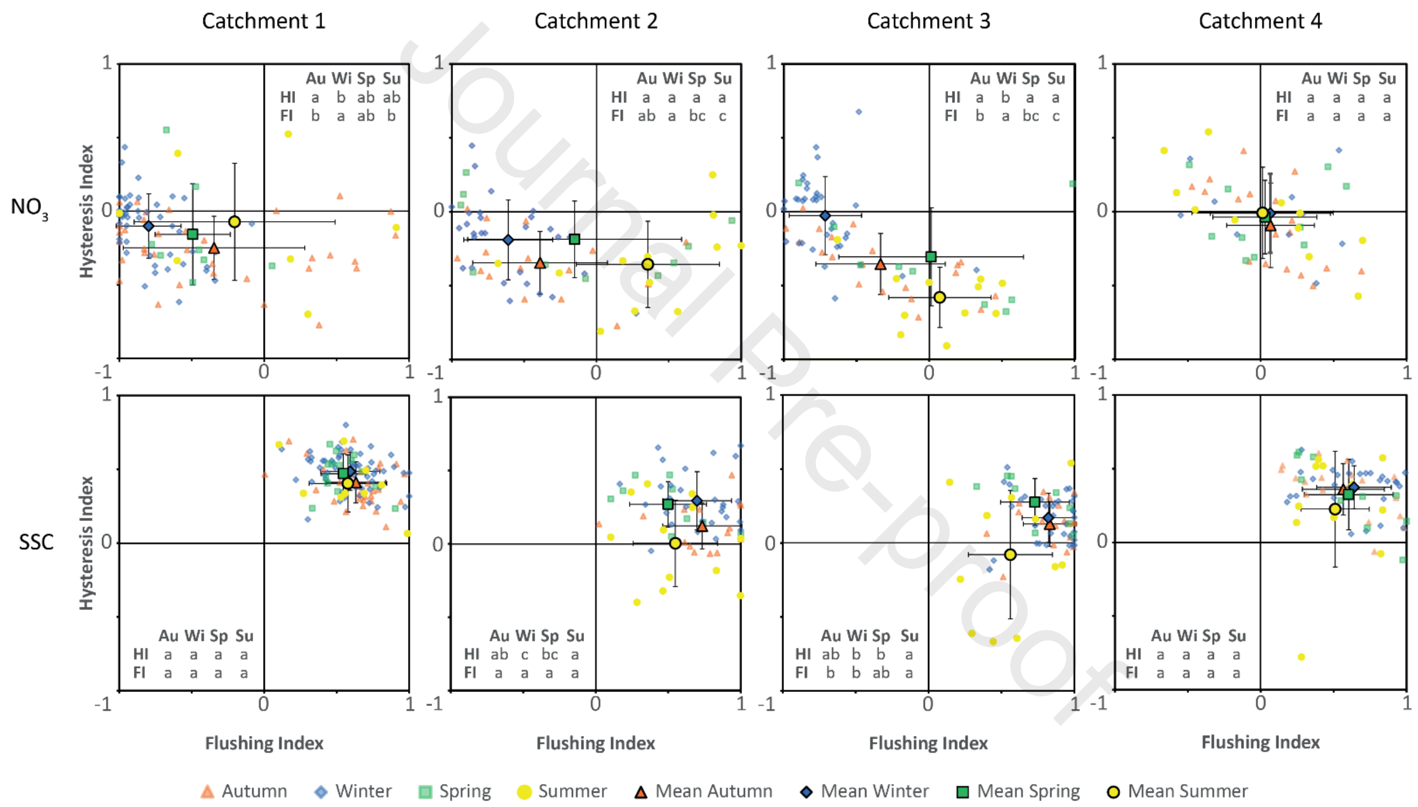
Figure 2.


Catchment 1
Catchment 2
Catchment 3
Catchment 4
NO3
SSC
Hysteresis Index
Flushing Index
1
0
-1
Au Wi Sp Su
HI a b ab ab
FI b a ab b
Au Wi Sp Su
HI a a a a
FI ab a bc c
Au Wi Sp Su
HI a b a a
FI b a bc c
Au Wi Sp Su
HI a a a a
FI a a a a
Au Wi Sp Su
HI a a a a
FI a a a a
Au Wi Sp Su
HI ab c bc a
FI a a a a
Au Wi Sp Su
HI ab b b a
FI b b ab a
Au Wi Sp Su
HI a a a a
FI a a a a
Autumn
Winter
Spring
Summer
Mean Autumn
Mean Winter
Mean Spring
Mean Summer

- Nested hydrochemical monitoring undertaken in a headwater catchment
- HI and FI indices calculated for NO_3-N and suspended sediment (SSC) for all sites
- NO_3-N was chemodynamic at most scales and displayed seasonal variability
- SSC was chemodynamic but consistent across spatial and temporal scales
- Mechanistic understanding informs mitigation but is affected by scale of assessment

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Collins, A.L. reports financial support was provided by Biotechnology and Biological Sciences Research Council.

Steve Granger: Conceptualization, Methodology, Investigation, Data Curation, Writing - Original Draft, Visualization

Hari Ram Upadhayay: Software, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Visualization

Adrian Collins: Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition