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Research papers

Impacts of changing weather patterns on the dynamics of water pollutants in agricultural catchments: Insights from 11-year high temporal resolution data analysis

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ABSTRACT

Widespread and long-term shifts in weather patterns are contributing to further degradation of surface water quality. This challenge caused by the increasing frequency of extreme weather events requires appropriate adaptation of current mitigation strategies. But to confirm the need to redesign such strategies, an understanding of the impacts of increasing weather extremes on pollutant losses in different catchment types is required. With this in view, this study investigated the impact of changing weather patterns on the inter-seasonal and inter-annual dynamics of nutrient losses in six agricultural catchments in Ireland over 11 years. The high temporal resolution data (10-min) from these intensively managed catchments represented different characteristics and management practices. Mann-Kendall Trend Analysis and Generalised Additive Models were used to study nutrient concentration trends, and to investigate the significance of water discharge, precipitation, potential evapotranspiration, soil moisture deficit, air temperature, and soil temperature on the losses of nutrients, respectively. The analysis of historical data revealed changes in the trends of daily average nitrate (NO_3-N), phosphorus (P), and suspended sediment (SS) concentrations in association with significant increasing trends in air temperature, soil temperature, and precipitation across the same month over 11 years of monitoring. While discharge was significantly contributing to the concentrations of NO_3-N, P, and SS across different catchments, air and soil temperature were significantly correlated to NO_3-N losses, and precipitation was the major contributor to regulating P (total P and total reactive P) concentrations. In short, air temperature, soil temperature, soil moisture deficit, and precipitation were the main climatic drivers regulating the nutrient concentrations while the soil chemistry and drainage status were the non-climatically related drivers. The results revealed that the extent of the impact of climatic drivers depends on catchment characteristics. Therefore, expanding the application of this type of study would facilitate better understanding of current and future challenges to water management and provision of climate-resilient mitigation strategies for different catchment typologies.

1. Introduction

Excess nutrients (i.e. nitrogen (N) and phosphorus (P)) and suspended sediments coming from agriculture can be delivered into lakes, streams, estuaries, and coastal waters causing degradation of water quality (Maúre et al., 2021; Basu et al., 2022; Beusen et al., 2022). Current European Legislation requires the application of mitigation strategies to meet the goal of the Water Framework Directive (WFD) (2000/60/EC) to achieve 'good ecological status' in all waterbodies by 2027. However, the overall ecological status of waterbodies has declined in some countries, including Ireland, which has reported increasing nutrient concentrations, mainly from agricultural sources, over the period 2016–2021 (EPA, 2021a). Hence, a key challenge is the need to balance agricultural intensification for food security with achieving 'good status' in waterbodies (Moal et al., 2019). This is a global and growing issue which also impacts economic/social welfare as well as the sustainability of ecosystems and biodiversity (Weng et al., 2020).

To achieve an improvement in waterbody status, an understanding of both the nutrient sources (e.g., soils and farming practices), and climate drivers of water pollutant mobilisation/delivery are required.

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Recent research has particularly highlighted the need for a comprehensive analysis of the links between the weather patterns associated with changing climate and river pollutant concentrations (Mellander and Jordan, 2021). Climate change is exerting extra pressures on water quality as an increasing frequency of extreme weather events (drought and flood) is being observed (Gascuel-Odoux et al., 2023). For example, reduced discharge during drought conditions can lead to the reduced dilution of pollutant discharges from point-sources and therefore can increase fluvial nutrient concentrations (Hughes et al., 2021). Changes in soil and water temperature and soil water content can also modify water quality indirectly (Seyedhashemi et al., 2022). Drought can alter hydrological connectivity (Ehrhardt et al., 2021) and disconnect shallow flow pathways from the river network (Yang et al., 2018). Additionally, during the first heavy rain or so-called 'first flush' after drought conditions decreased denitrification and the subsequent flushing of accumulated nutrients have been observed (Outram et al., 2014; Strohmenger et al., 2020; Zhang et al., 2022a,b; Winter et al., 2023).

According to the Irish Environmental Protection Agency (EPA, 2021b), starting from 1980 s, every decade has been warmer than the previous one and during the last ten-year decade (2010–2019), the average temperature was the warmest on record. An increase in the magnitude, frequency and duration of droughts is further expected during summer times (Meresa and Murphy, 2023). While the average annual precipitation in Ireland has increased approximately 5 % (60 mm) during 1981–2010 compared to 1961–1900, substantial decreases in average annual spring and summer precipitation, and significant increase in frequency of extreme events in winter and autumn are expected (EPA, 2021b). Weather extremes have been shown to have diverse impacts on nutrient loads within different agricultural landscapes depending upon their specific characteristics (Mellander and Jordan, 2021; Ezzati et al., 2023) and boundary conditions (catchment boundaries) (Ehrhardt et al., 2021). These impacts generally correlate with changes in runoff volume (Coffey et al., 2018) and are therefore strongly controlled by precipitation and air temperature (Jordan et al., 2014; Paul et al., 2019; Ezzati et al., 2023; Hadush and Conor, 2023). On the other hand, catchments, in a global scale, also have contrasting characteristics such as soil type and texture (including average clay content), land use (the fraction of arable land), management, and hydrology (Sandström et al., 2020) which result in different responses to the same weather events. The differences between catchments are comprised of variations in the sensitivity of hydrological responses to climatic drivers (Sulis et al., 2011), and thus, variations in intrinsic controls relevant to nutrient mobilisation and delivery and differences in farming systems. Hence, nutrient dynamics in catchments, despite close geographic proximity but with different controls and mitigation strategies, have shown to respond differently to the same large-scale weather extremes (Mellander & Jordan, 2021).

Existing management efforts and mitigation strategies have not only failed to improve water quality in Ireland (EPA, 2023), but are also incapable of buffering the effects of weather extremes in the already-vulnerable agricultural sector at a global scale. This failure is of greater importance in countries where the agri-food sector is an integral part of the economy and society (Abbass et al., 2022). According to Samaniego et al. (2018), Europe may face a 40 (±24) % increase in drought affected areas in the absence of effective mitigation strategies during the 21st century (Caretta et al., 2022). Therefore, when considering the more frequently occurring extreme weather events, more targeted approaches and resilient management strategies are required to deliver catchment-specific and climate-resilient adaptation. However, uncertainty remains regarding the causes and severity of water quality degradation due to changing climate (Refsgaard et al., 2013).

The modelling of water quality, which is often used to guide policymakers in developing appropriate mitigation strategies, is facing new challenges in representing nutrient trends, legacies, delivery, and mobilization in view of current and projected climate change scenarios (Mellander et al., 2018; Mellander et al., 2022b). The impacts of the changing weather patterns have also been less considered in policy reviews (Mellander et al., 2018). According to Gascuel-Odoux et al. (2023), these challenges are due to three main reasons: 1. Lack of long time series data for water quality and chemical concentrations compared to hydrologic fluxes and storage measurements; 2. Lack of detailed understanding of climate-water quality relationships compared to well-developed, but highly generalised, climate-hydrology models at global and regional scales (Lintern et al., 2021); 3. Difficulty in distinguishing climate effects from those due to changes in farming activities (e.g. types of the crops) (Lungarska and Chakir, 2018). In addition, seasonality drives changes in nutrient concentrations as a consequence of changes in hydrologic flow pathways, climate change, and associated biological processes (Covino et al., 2021). However, understanding the seasonal dynamics of nutrients is highly complex and ensuring good water quality requires catchment-specific approaches (Warner et al., 2021).

Changes in **the** nutrient concentrations are influenced by mobilisation and hydrological processes, driven by weather and agricultural management, and controlled by physical catchments characteristics (e.g. soil/bedrock drainage and chemistry) and can as such be subtle (Mellander et al., 2018). While nutrient concentrations can vary within any span of time, the impacts of extreme runoff events are typically more drastic and can be exhibited immediately. Changes in the nutrient loads, on the other hand, represent the cumulative quantity without capturing fluctuations, while hydrology may also override any processes in mobilisation (Mellander et al., 2022a).

This study used 11-years (2010–2021) of sub-hourly (10-min basis) water quality (i.e., concentration data) and climatic data from six hydrologically contrasting agricultural catchments in Ireland. The objectives were to statistically assess the presence of seasonal and annual trends in nutrient and sediment concentrations using Mann-Kendall Trend Analysis, and to evaluate the impact of climatic data (i.e. precipitation, air/soil temperature, soil moisture deficit), on nutrient source loading and in view of management practices, using Generalised Additive Models. Such analysis may facilitate a better understanding to counter future challenges for water management and provision of climate-smart mitigation strategies.

2. Materials and Methods

In order to identify any existing trend in nutrient concentrations in view of recent extreme weather events in Ireland (prolonged draught periods and/or heavy precipitation), and in order to understand the importance of climatic variables in regulating nutrient losses throughout different months of the year, long-term high-resolution water quality data from agricultural catchments with contrasting physical and management factors were studied using different statistical modelling techniques.

2.1. Site study description

Six agriculturally-dominated catchments (one karst spring contribution zone and five river catchments) monitored by the Irish Agricultural Catchments Programme (Mellander et al., 2022a,[b]) were investigated (Fig. 1 and Table 1). The catchments are all intensive agriculture areas and comprise a varying mix of grassland (pasture) and arable land use. They all have different physical characteristics, i.e., slopes, soil types, drainage, and areas ranging from 3 to 31 km^2. The base-flow (Bf_i) indices and detailed fertiliser applications rates have been assessed in Mellander et al., 2022a.

Ballycanew (11.9 km^2-Co. Wexford) is in the southeast of Ireland. This catchment has mostly poorly drained soil with land use dominated by grasslands (77 %) grazed by dairy cows. There was a 30 % increase in stocking rate (livestock per area) between 2010–2018. Grazing intensity is highest in May and fertilisers are mostly N-based. December and January are a "closed period" as defined by Nitrate Action Programme in

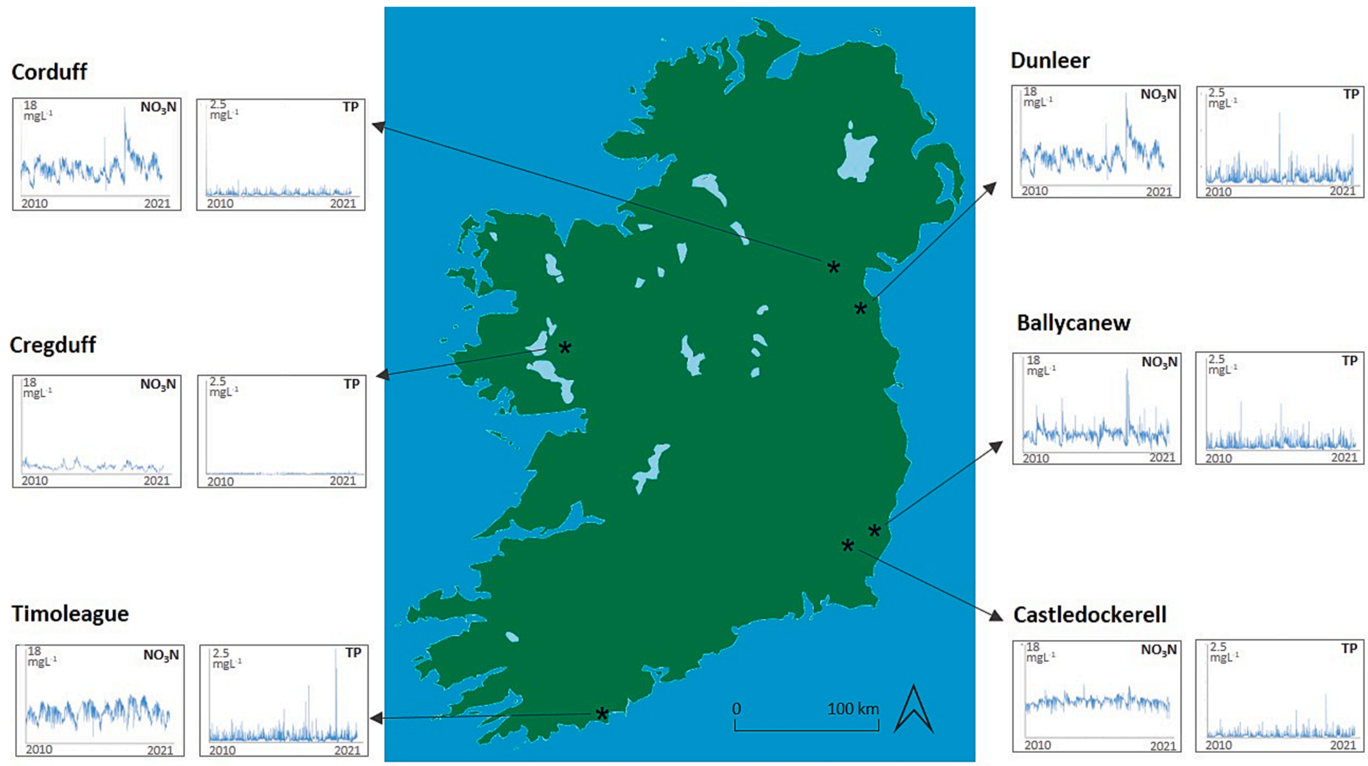

Fig. 1. Location of the six catchments monitored by the Agricultural Catchments Programme. The time series plots show daily average nitrate-N (NO_3-N) and total phosphorus (TP) concentrations (mg L^{-1}) for the time period of 2010–2021. The values on the y-axis represent maximum concentration detected in the catchments.

Ireland (NAP) (DAFM, 2017), during which grazing and the spreading of fertilisers are prohibited. Excess slurry stored in tanks is typically spread on silage fields at the end of March. The hydrology is flashy (base-flow index (Bf_i) of 0.63) with dominating surface/near surface pathways (Mellander et al., 2015).

Castledockrell (11.2 km^2-Co. Wexford) is also located in southeast Ireland. This catchment has mostly well-drained soils with 72 % of the catchment under arable land use (66 % of the total area is under tillage which is the highest of the catchments studied). Hydrological pathways are primarily subsurface (Mellander et al., 2016) with Bf_i of 0.78.

Corduff (3.3 km^2-Co. Monaghan) is in northeast Ireland. This poorly drained catchment has no tillage, has low chemical fertiliser application rates (as detailed in Mellander et al., 2022a), and is dominated by grassland for sheep and suckler cows. The catchment has a flashy hydrology (Bf_i of 0.57) dominated by surface/near surface pathways.

Cregduff (31.2 km^2-Co. Mayo) is a mainly permanent grassland karst spring contribution zone, located in west Ireland. Sheep are primarily grazed and have a longer grazing period than cattle. The soil is well drained and relatively thin. Hydrological pathways are dominantly subsurface (Mellander et al., 2013) and Bf_i is 0.82. The rate of N-application in this catchment is low relative to other catchments.

Dunleer (9.5 km^2-Co. Louth) is in northeast Ireland. Farm types in this catchment are mixed at approximately 40 % grassland, half of which is grazed by dairy and half by beef cattle. This catchment has moderately drained soils with flashy hydrology (Bf_i of 0.66) and mostly surface/near surface pathways (Mellander et al., 2012). Chemical N fertilisers are spread in April/March but available soil P has been notably increasing during the recent years. The ploughing/sowing take place during October and November.

Timoleague (7.6 km^2-Co. Cork) is in southwest Ireland, is well-drained and dominated by grassland and subsurface hydrological pathways (Mellander et al., 2016) with Bf_i of 0.73. There has been an increase in livestock grazing intensity and the percentage of land under derogation (allowance to farm at livestock above the limit of 170 kg N ha^{-1} under the EU Nitrates Directive). The P-index (soil fertility) is also increasing more than expected. Maize is one of the dominant crops which requires substantial slurry spreading typically between mid-January and October.

The management practices for a typical farming calendar in each catchment were collated from discussion with the local farm advisor and knowledge transfer expert (Fig. 2).

2.1.1. Hydrochemistry data collection

Bankside P analysers (Hach-Lange Sigmatax-Phosphax) (Melland et al., 2012) were located at the catchments outlets which measure total digested P (TP) and total reactive phosphorus (TRP) concentrations on unfiltered samples. The measuring range is 0.010 mg L^{-1} to 5.000 mg L^{-1}, and the detection limit is 0.010 mg L^{-1}. Total oxidized N (TON) was monitored using Hach-Lange Nitratax SC-Plus UV instruments (co-located at the outlets). The measuring range is 0.1–50 mg L^{-1} and assuming a low NO_2-N concentration (Melland et al., 2012), TON is considered equivalent to NO_3-N. The measuring of all nutrients was carried out based on a 10-min basis.

Stage-discharge rating curves on Corbett flat-v non-standard weirs have been established at the individual catchment outlets. The ratings are based on the velocity-area method with an OTT Acoustic Doppler Current meter (in WISKI-SKED software). An OTT Orpheus Mini vented pressure instrument installed in a stilling well adjacent to the weirs records the water level every 10 min. The river discharge is calculated by converting the water level to flow. In Cregduff, the discharge is calculated using an ultrasonic sensor (Thermo-Fisher time-of-flight area velocity) which is placed in an engineered uniform cross-section.

Suspended sediment (SS) concentrations were estimated using turbidity reading and corresponding concentration-turbidity conversion relationships (excluding the Cregduff catchment given its karst geology) (Sherriff et al., 2016).

Table 1
Catchments characteristics. Precipitation, soil and air temperatures, potential evapotranspiration (PET), and soil moisture deficit (SMD) values are averaged for the 11 hydrological years (1st October 2010 – 30th September 2021).

Catchments	Area (km^2)	Dominant land use	Drainage status	Avg. organic stocking rate ($kg\ ha^{-1}$)		Geology	Elevation (MAMSL)	Precipitation (mm)		Air Temp. (°C)			Soil Temp. (°C)	PET (mm)	SMD (mm)
				N-based	P-based			Avg. daily	Avg. annual sum	Avg. daily	Max	Min			
Ballycanew	11.9	Grass	Poor	101.9	12.5	Rhyolite, slate stone	19–230	2.9	1059.8	9.9	25.0	−7	10.9	1.5	9.2
Castledockrell	11.2	Arable	Well	41.8	7.5	Slate, siltstone	18–215	2.8	1020.3	9.9	26.6	−6	11.1	1.5	14.7
Corduff	3.3	Grass	Poor	87.5	20.8	Greywacke	110–221	2.9	1032.8	8.7	25.4	−8	10.3	1.6	4.9
Cregduff	31.2	Grass	Well	90.3	16.6	Limestone	27–62	3.3	1187.4	9.7	27.5	−7	10.3	1.4	8.4
Dunleer	9.5	Arable	Moderate	69.2	10.6	Greywacke, mud stone	26–223	2.3	870.3	9.7	25.7	−4	10.6	1.7	12.3
Timoleague	7.6	Grass	Well	164	18.1	Sand stone, silt stone, mud stone	2–122	4.3	1108	10.2	23.7	−4.5	11.2	1.6	6.1

2.1.2. Weather data collection

Precipitation, air temperature (Tair), soil temperature (Tsoil), relative air humidity, solar radiation, wind speed and wind direction are measured at ten-minute intervals by a weather station (BWS200, Campbell Scientific, https://www.acpmet.ie) located in the central valley floor within each study catchment. The effective rainfall was calculated by subtracting potential evapotranspiration (derived from the Penman-Monteith equation (Monteith, 1965)) from measured rainfall.

The soil moisture deficit (SMD), which responds to changes in air temperature and rainfall, was calculated as the amount of rain needed to bring the soil back to field capacity using a SMD model (Schulte et al., 2005).

2.2. Data analysis

2.2.1. Monthly trend analysis

To investigate the seasonality that may be hidden in inter-annual trends, and compare the nutrient concentrations dynamics in each month across different years, the temporal trends in average daily values of climatic-related explanatory drivers and nutrient concentrations were calculated using the non-parametric rank-based Mann-Kendall test (Kendall, 1948). The analysis was carried out over 11 years of the monitoring period. This test accounts for non-normality of hydrological (Yue et al., 2002) and climatological data (Partal and Kahya, 2006). Hence, the method provided accurate estimation and enabled comparison of any increasing or decreasing trends of variables in each particular month over more than a decade. The null hypothesis assumed that the data (x_1, …,x_n) consist of n independent and identically distributed random variables and $P < 0.05$ was considered as a significant trend for calculating slopes of time series (Sen, 1968). The intercept (α) was calculated as followed:

$$\alpha = x_{0.5} - s^{*}y_{0.5} \quad (1)$$

where $x_{0.5}$ and $y_{0.5}$ are median values of variables.

2.2.2. GAM analysis of significance of drivers

Generalised Additive Models (GAMs) (Hastie and Tibshirani, 1990) were fitted to the daily average time series data, in order to evaluate the significance of the impact of different climate variables on regulating water pollutant losses over different months of the year (on condition that an increasing/decreasing trend existed, see section 2.3.1). GAMs, as an extension to generalized linear models with smoothing functions, are becoming a widely applied statistical test for evaluation of changes in water quality at large scales (Murphy et al., 2019) with multiple variables (Wood, 2006) and consider uncertainty and random effects of both parametric and non-parametric variables. Hence, GAMs add flexibility to the modelling of complex non-linear relationships between response and explanatory variables. This is especially useful since water chemistry variables are influenced by each other or by the climatic drivers (von Brömssen et al., 2021, Ezzati et al., 2023).

$$F(E(y)) = f(x_1, \cdots, x_n) = \beta + s_1(x_1) + s_2(x_2) + \cdots + s_n(x_n) \quad (2)$$

where y_i is the response variable for $i = 1,\ldots,n$ and x_1, …, x_n are independent variables. E(y) is the expected value of y [as an alternative for the response distribution apart from the normal distribution], β is the model intercept, and $s_{i=1\text{-}n}$ (x) is a smooth function wrapping the independent variable.

The resulting accuracy in capturing the relationships between response variables (water quality dynamics, i.e. nutrient losses) and explanatory data (climatic drivers of Tair, Tsoil, Precipitation, and discharge) was checked based on the flexibility of the curve fitting to multiple variables (Ezzati et al., 2023). A low p-value indicated that residuals were not randomly distributed (hence there is enough data to capture subtle non-linear linkage between variables and showing significance of explanatory variables), and a significant downward or

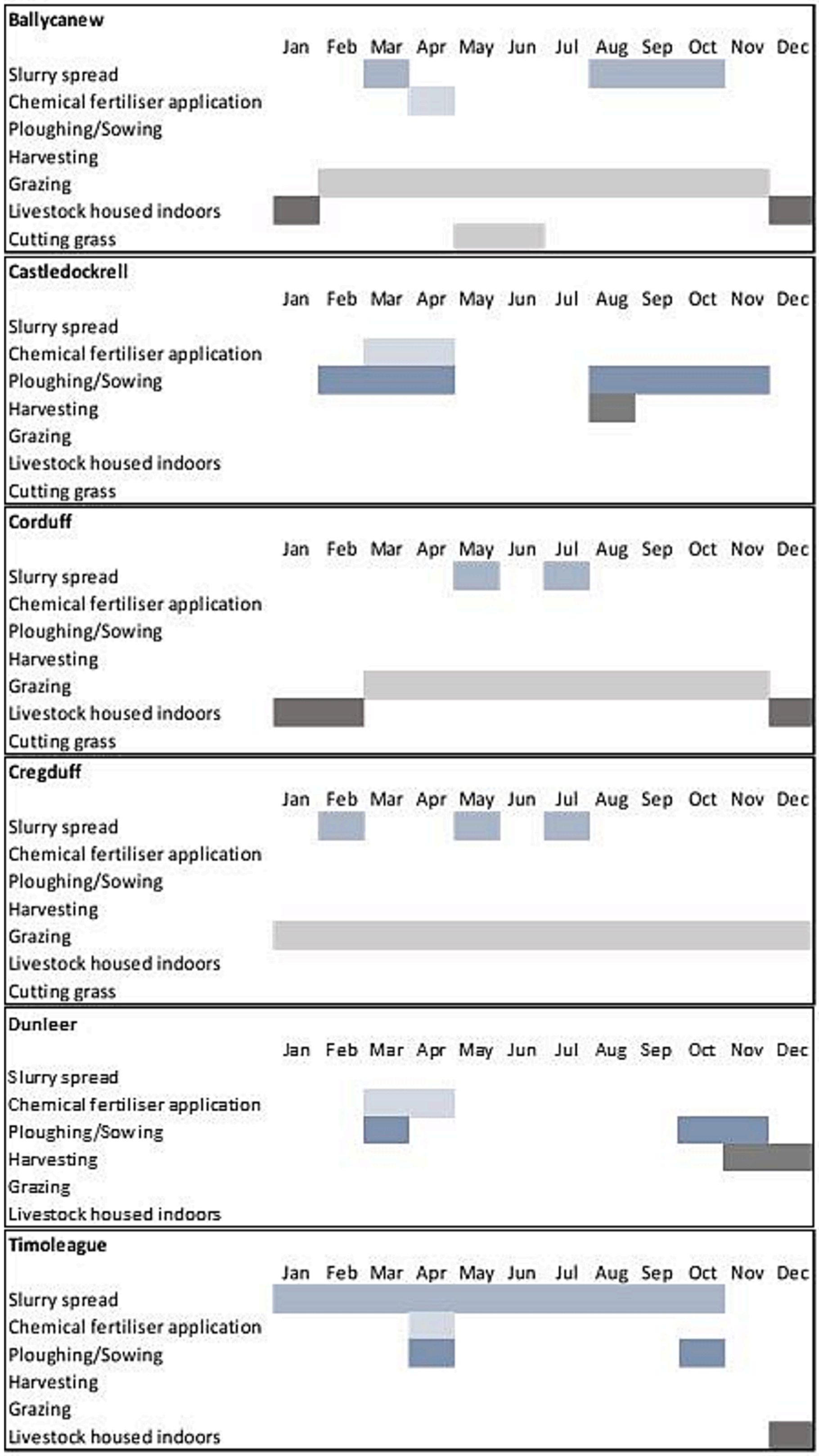

Fig. 2. Summary of the typical farming calendar for each of the six catchments monitored by the Irish Agricultural Catchments Programme. In order to assist visualisation, similar bar colour are used for similar activity across different catchments.

upward trend was identified if the entire confidence band of the derivate of the trend smoothness was below or above zero, respectively (von Brömssen et al., 2021). Here, the "mgcv" package in the R statistical software (Wood, 2017) was applied while "gam.check" (as a tool provided by "mgcv") was used to check model assumptions and assess effective degrees of freedom for the model terms.

3. Results

3.1. Hydrochemistry

Timoleague and Corduff had the highest annual average water discharge with 643 and 616 mm yr^{-1} respectively. Cregduff outlet is in an estimated spring contribution zone which explains its very low discharge compared to the rest. However, among the other remaining five catchments, Dunleer had the lowest mean annual discharge (402 mm yr^{-1}) (Fig. 3). The values of the other response variables varied significantly among the six study catchments due to their diverse

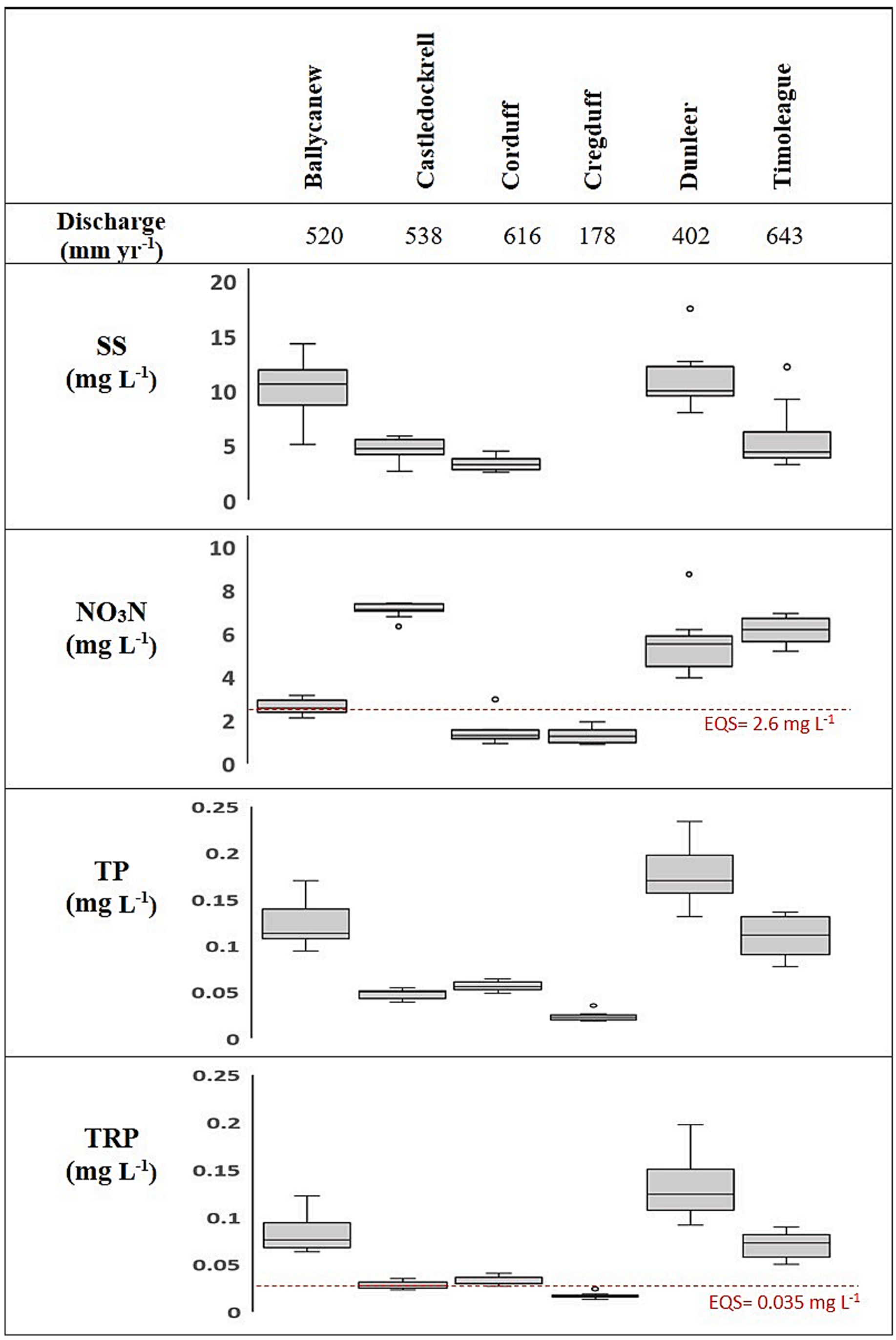

Fig. 3. Box and whisker plots of daily concentrations of SS, NO_3-N, TP and TRP, and the average annual total discharge leaving the catchment outlets for the period 2010– 2021. Cregduff is a karst spring contribution zone and therefore does not have SS data. The line in the boxplots marks the median point of the data. Whiskers show the upper and lower quartiles (75th and 25th percentiles, respectively). Outliers are shown as circles. The dotted horizontal line shows environmental quality standards (EQS) for NO_3-N and TRP.

characteristics and management. Ballycanew had the largest mean SS concentration with a negatively skewed observed concentrations. Cregduff and Corduff had the lowest middle quartile in all water pollutant variables, while the ranges of TP and TRP in Castledockrell were as low as in those two catchments, but the NO_3-N range was the highest among all catchments. Dunleer and Timoleague had normally distributed observed concentrations in NO_3-N and TP and TRP concentrations, and a positively skewed SS with outliers.

According to the farming calendar and local catchment advisors, slurry spread during spring/summer time is more common in grassland areas where as ploughing and fertiliser application take place during spring on arable land (Fig. 2). For example, in Castledockrell, in which the NO_3-N concentration was highest among all the study catchments (Fig. 3), the significant increase of this nutrient in April coincided with chemical fertiliser application and ploughing/sowing (Fig. 2).

3.2. Monthly trend analysis

The poorly drained catchments of Ballycanew and Corduff and the moderately-drained Dunleer had more frequently occurring monthly trend changes in the concentrations of **NO_3-N** and P compared to the other study catchments (Fig. 4). The increase in monthly trends of nutrient losses in Ballycanew occurred during January, May, and September, while in Dunleer, the increase occurred during October-April. Corduff experienced an increase in monthly trend in nutrient losses throughout the year except in April and December (Fig. 4).

The monthly trend analysis of climatic drivers in Ballycanew and Corduff also showed more fluctuations compared to the other study catchments (Fig. 4). The air and soil temperature increased during summer in Ballycanew and Castledockrell. These two catchments are geographically close, yet, the changes in weather pattern were not identical.

There was a highly significant increase in TP and TRP concentrations leaving the Timoleague catchment during September; however, it does

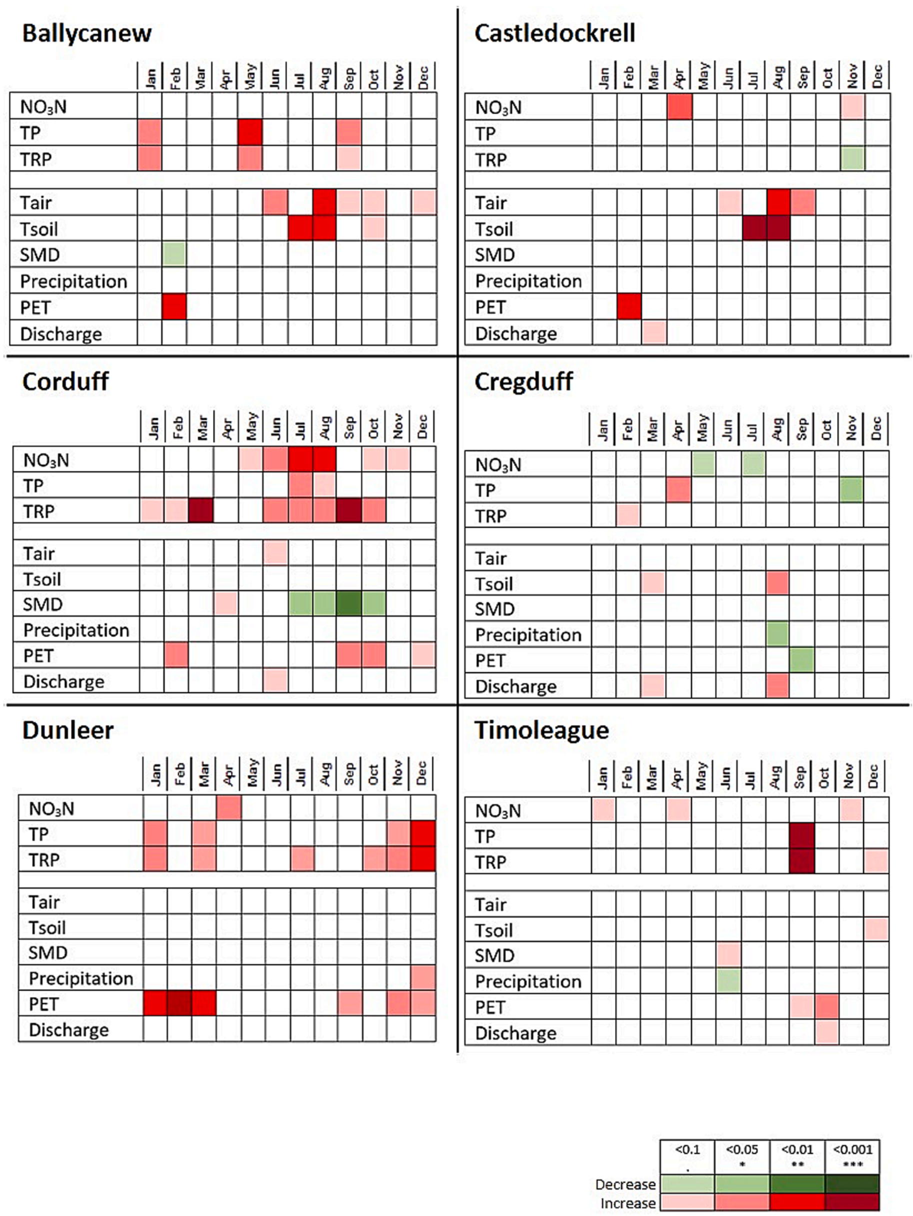

Fig. 4. The average monthly trend analysis of NO_3-N, TP, TRP concentrations, and explanatory variables during 2010–2021 using Mann-Kendall tests. The red colour indicates increasing trends and the green colour indicates decreasing trends. The level of significance is presented by the different shades of any individual colour.

not coincide with a significant increase in the corresponding monthly trends of any of the climatic variables (Fig. 4).

Changes in monthly trends in climatic drivers were observed more frequently in Corduff compared to the other study catchments (Fig. 4). Dunleer experienced significant changes in potential evapotranspiration during September-March. There was also overlaps of the changes in monthly trends in nutrient concentrations with monthly trends in climatic drivers in Dunleer (during January, March, November, December).

3.3. Significance of drivers from GAMs

None of the climatic drivers were significant in regulating NO_3-N losses during January-March, September, and December. Similarly, none of the drivers were significant in regulating TP/TRP concentration trends during April-May, and October, in any of the study catchments (Table 2 and 3). However, May-August and October-January were generally the time windows when significant changes in monthly trends occurred.

Discharge appeared to be one of the main regulators of NO_3-N losses during months in which, a significant increase of NO_3-N concentrations was observed. The significance of discharge occurred alongside its climatic drivers of Tair, Tsoil, and Precipitation. Tair was more associated with increases in NO_3-N and Precipitation with P. Summer time appeared to be the period in which most of the trend changes in the concentrations of both nutrients (Fig. 4) and the drivers of concentrations including climatic drivers (Tables 2 and 3) took place.

In terms of NO_3-N losses, Corduff was mostly influenced by climatic drivers followed by Dunleer, Castledockrell, and Timoleague (Table 2). In terms of P (TP and/or TRP) losses, Dunleer and Corduff, followed by Timoleague and Ballycanew exhibited more susceptibility to changes in weather patterns manifested in the 11 year long time series (Table 3).

4. Discussion

Discharge, in relation to its fluctuations with weather changes, was one of the most significant drivers of regulating concentrations of both N and P. Investigation of the dynamics between discharge and nutrient concentrations under changing climate (and different hydrometeorological conditions) is gaining more interest (D'Amario et al., 2021; Pettersen et al., 2021). It is now understood that NO_3-N and TP concentration patterns in relation to discharge tend to vary for different geographical settings and be influenced by other drivers e.g., anthropogenic activities (D'Amario et al., 2021; Vystavna et al., 2023), or changes in weather (Ramos et al., 2022; Ezzati et al., 2023). Studies on the efficiency of management practices under climate change scenarios have shown that depending on the influential catchment characteristics, some watersheds would be more resilient in face of increased intensity of rainfall (Yuan and Koropeckyj-Cox, 2022). Extreme rainfall events and rainfall outside the growing season are known to not only influence agricultural production by prolonging the growing season, but they are also strongly correlated to discharge, N concentration (Øygarden et al., 2014), and P concentration (Ramos et al., 2022). For example a year with normal precipitation has shown strong chemodynamic behaviour in terms of N concentration-discharge while a year with above normal precipitation suggested chemoststiatic behaviour (Miller and Lyon, 2021). Chemostatic behaviour is hydrologically controlled in the catchment (Pohle et al., 2021), hence, the concentrations remain stable over a wide range of flows in a concentration-discharge (c-q) pattern due to transport limitation (Bieroza et al., 2018). On the contrary, the rate of change in pollutant concentration in a chemodynamic c-q pattern, is larger than the flow change suggesting a source-limitation mechanism (Basu et al., 2010). Precipitation can change the quantity of discharge as well, which would consequently impact the nutrient fluxes (Grusson et al., 2021). This impact would show itself as either a sudden increase in concentrations due to washing out of diffuse sources of nutrients and sediments (Delkash et al., 2018), e.g. increasing the average P loads by 9 % (Ockenden et al., 2016), or gradual decreases due to dilution by the water flow (Zhao et al., 2018).

Significant increases in Tair and Tsoil were observed in both Ballycanew and Castledockrell study catchments during summer months (June, July, August). These drivers suggested to have significant impacts on nutrient concentrations in all catchments. The impact of higher temperature on NO_3-N concentrations in diverse geographical locations has also been observed in other studies (Bučienė et al., 2019; Ezzati et al., 2023). Higher temperatures (warmer summer or winter) will create large N pools in soils and increase mineralisation and nitrification rates (Wang et al., 2016) which leads to an increased risk of concentrations at the start of any ensuing wet period (Melander & Jordan, 2021). Rising temperatures would not only increase the risk of droughts and fluctuating quantities of discharge (Vystavna et al., 2023), but will also change soil shear strength (Zhang et al., 2022a,b), which would consequently cause decreases in multi-year flow and mean active water storage capacity in catchments (Vystavna et al., 2023). On the other hand, water limitation in summer droughts affects grass growth by reducing uptake from spring N fertilizers. In order to compensate for that, higher mineral N fertilizers may in some cases be applied (Kundel et al., 2021) which would increase the risk of concentrations during

Table 2
The significance of climatic drivers in regulating NO_3N concentrations with a significant monthly trend during water years spanning 2010–2021.

Catchments		Apr	May	Jun	Jul	Aug	Oct	Nov
Castledockrell	**NO_3N**	Discharge * Tair * SMD * Prcp·						Discharge * SMD * Tair * Prcp·
Corduff	**NO_3N**		Discharge * Precp·	Discharge*** Prcp*** Tair*** Tsoil*** PET***	Discharge* Prcp** Tair** Tsoil** PET*	Tsoil ** Precp·	Tsoil ** Tair * Discharge·	Discharge ** Precp * Tair * PET *
Cregduff	**NO_3N**				Discharge· Prcp· Tair·			
Dunleer	**NO_3N**	Discharge * Prcp * PET * Tair. Tsoil·			Prcp * Tsoil * SS *			
Timoleague	**NO_3N**	Tair * Prcp·						Discharge *

Prcp stands for Precipitation. The asterisks show the significance of each variable: $p \leq 0.001$ "***";$p \leq 0.01$ "**";$p \leq 0.05$ "*";$p \leq 0,1$ "*".

Table 3
The significance of climatic drivers in regulating TP and/or TRP concentrations with a significant monthly trend during water years spanning 2010–2021.

Catchments		Jan	Feb	Mar	Jun	Jul	Aug	Sep	Nov	Dec
Ballycanew	**TRP**							Tsoil ** SMD * Tair * Discharge·		
	TP	Precp *						Tsoil * SMD· Discharge·		
Corduff	**TRP**		Precp * Discharge· SS·	SS *	Discharge* Precp * Tair * Tsoil·	Tsoil * Tair·	SS * Discharge· Precp·			
	TP					Discharge* Tsoil * Tair *				
Cregduff	**TRP**		Tsoil· Tair·							
	TP			Discharge*** Tair *** Tsoil** Precp *						
Dunleer	**TRP**			Precp ** Discharge* Tair· Tsoil·					Precp ** Tair * Tsoil * Discharge * SS·	Precp·
	TP			Precp ** Discharge* Tair· Tsoil·					Precp * Discharge·	Precp * Discharge·
Timoleague	**TP**	Discharge*** Precp *** SS ***						Precp * Discharge·		

Prcp stands for Precipitation. The asterisks show significance of each variables: $p \leq 0.001$ “***”;$p \leq 0.01$ “**”;$p \leq 0.05$ “*”;$p \leq 0.1$ “*”.

winter time. Also, as a large pool of excessive N has been built up, a higher water discharge will increase losses with the first rain after a prolonged summer period (Ulén and Johansson, 2009; Outram et al., 2014; Mellander and Jordan, 2021). However, if the groundwater has a high storage potential or long residence time (Fenton et al., 2011), or the ditches have low equilibrium phosphorus concentration (Ezzati et al., 2021), the excess N and P, respectively, will be naturally attenuated before leaving the catchment.

The three groundwater-fed catchments (Castledockrell, Cregduff, and Timoleague with dominant soil types of Al-rich, Al and Ca rich, and Fe-rich, respectively) showed a chemostatic behaviour for P which was not affected by changes in the weather patterns (Mellander et al., 2022b). Catchment characteristics can significantly change the relationships between discharge and stream water nutrient concentrations by changing the strength and nature of stream flows (Gao et al., 2021) or provide a natural attenuation function due to soil chemistry (Ezzati et al., 2021). The biogeochemical properties of soils in these catchments are also indicative of soil high affinity to bind P as long as the soil has not become P-saturated to act as a P-source rather than a P-sink (Ezzati et al., 2020). In Castledockrell, the significant increase in NO_3-N concentrations in April over the 11 years coincided with chemical fertiliser application and ploughing/sowing (Fig. 2). This catchment is not hydrologically risky (i.e., extreme hydrological events do not create a shift in nutrient dynamics), and was categorised as chemostatic in terms of P (i.e., higher flow will not lead to higher nutrient losses (Bieroza et al., 2018)). According to Mellander & Jordan (2021), the groundwater-fed well drained “N loss risky” Castledockrell catchment, becomes “P loss risky” during winter storms. This transition happens when SMD has been 0 mm for two or more consecutive days, and the effective rain exceeded 15 mm/day (Mellander and Jordan, 2021). Timoleague catchment experienced a significant ($P < 0.001$) increase in P-concentrations during September and a first-level significant increase ($P < 0.1$) in NO_3-N concentrations in January, April, and November, over the 11 year study period. Spring barley, wheat, and maize were the dominant crops, with the latter requiring a large amount of slurry spreading which starts from mid-January and continues until October (inclusive). Chemical fertilisers were applied in April. The maize fields are also closer to the catchment outlet, which may contribute to the high concentrations in the outlet.

In the Ballycanew catchment, the increases in TP and TRP concentrations occurred during January, May, and September; yet, no particular farming practice could be associated with increases in P flux during January. Grazing (which occurs February-November) coincided with cutting grasses in May. However, slurry spreading in September coincided with a significant increase in the trend of monthly Tair values. Assessment of the high-resolution data revealed that precipitation exceeding 10 mm per day consistently caused a sharp increase in P concentrations. The elevated level of concentration returned to background values after few days when the nutrient sources were exhausted or not hydrologically connected. In addition, continuous rainfall over several days caused an increase in TP concentrations, regardless of the amount of rainfall as more source areas were connected. Remarkably, an extreme hydrological event can turn the P-risky catchment of Ballycanew to N-risky as well. Ireland experienced a series of extreme weather events including a severe summer drought in 2018 (Falzoi et al., 2019). Following the rainfalls in September in the same year, the daily average concentration of NO_3-N reached about 6 times larger than the Environmental quality Standard (EQS) in Ballycanew and it remained high throughout the year (Mellander and Jordan, 2021).

Corduff exhibited the highest chemodynamic behaviour among the studied catchments. According to Mellander et al. (2018), the average annual runoff coefficients (fraction of rainfall that appears as runoff) between 2009–2015, in descending order, were Corduff (0.57), Timoleague (0.55), Castledockrell (0.54), Dunleer (0.48), and Ballycanew (0.48), (Cregduff is a spring contribution zone). This explains the high chemodynamic behaviour (Bieroza et al., 2018) of Corduff (highly affected by changes in the climate due to hydrological characteristics). The slurry spread during July seemed to have a significant impact on the concentrations of all nutrients. Corduff is mainly permanent grassland with sheep being the main grazing animal from March-November. Increasing trends in P (TP and TRP) and NO_3-N concentrations in Dunleer **were** observed in six months and one month, respectively. This increase in monthly losses occurred almost as frequently as in Corduff, during October-January, and March-April. However, potential evapotranspiration seemed to be the only driver with an increasing trend (i.e. less precipitation), which may lead to slurry spreading as the weather condition is good. According to local knowledge transfer expert, the ploughing/sowing in Dunleer take place during October and November, potatoes are harvested during November, and beets are harvested during November/December. Hence, further farm-scale investigation is required to understand the changes in nutrient concentrations leaving the Dunleer catchment outlet as it is the most complex catchment among all those included herein.

The results of analysing high temporal resolution historical weather and water quality data of the past 11 years suggested a relationship between increasing trends in climatic drivers and trends in within-stream nutrient concentrations. However, the significance of the correlation between nutrient concentrations and changes in weather patterns was defined by the catchment characteristics including the drainage status and soil chemistry. The present study showed that the non-climatic indices, such as discharge and SS, which are also affected by the changing weather patterns, were significant drivers of nutrient concentrations mostly during the warmer time period of the study years. Hence, current mitigation strategies require explicit consideration of the more frequent occurrence of extreme weather events and their impacts on water pollutant concentrations. It is important to note that there may be inter-seasonal trends that are not identified when assessing inter-annual trends. For example, in the arable Castledockrell catchment, it is recommended to focus on improving N mitigation measures and/or changes in management decisions during April and November. However, in the other grassland catchments of Corduff and Timoleague, the summer period (May-August) plus October-November; and January, April, and November are important, respectively. Meanwhile, an improved focus on P mitigation and management is required in Ballycanew during January, May, and September; in Dunleer during March, July, October-January, and in Timoleague during September and December.

5. Conclusions

This study used long-term and high temporal resolution data (10-min) to investigate the N, P, and SS concentration trends in relation to the changing hydro-meteorological patterns in six agricultural catchments during 2010–2021. The results of historical data analysis showed that some of the catchments exhibited changes in the daily average trends of NO_3-N, TP, TRP, and/or SS concentrations with an associated significant increasing trend of climatic drivers, i.e. air temperature, soil temperature, and precipitation across the same months over the 11 years of monitoring period. The soil chemistry and drainage status of the study catchments are the non-climatically related drivers of nutrients concentrations while changes in air and soil temperature, SMD, and precipitation are the main climatic drivers regulating the nutrient concentrations. The extent of the impact of these climatic drivers highly depend on unique catchment characteristics. Discharge had a significant impact on the concentrations of NO_3-N, TP, TRP, and SS; air and soil temperature were significantly correlated to NO_3-N losses; and precipitation was the major contributor to regulating TP and TRP concentrations across the different catchments.

The inter-seasonal and inter-annual trends of losses revealed that the climatically driven changes during the same month over the 11 years are manifested differently in different catchments due to their individual hydroclimatological characteristics and management practices. Hence, catchment specific mitigation strategies are required to overcome future challenges to water quality management and the selection of climate-resilient mitigation measures in view of more frequently occurring extreme weather events and projected climate change scenarios.

Hence, building upon the results of the current study herein, we recommend that further studies are needed to investigate possible increases of nutrient concentrations into water bodies from agricultural catchments, using the current projected climate change scenarios in Ireland. This would eventually lead to developing future climate-resilient mitigation strategies.

CRediT authorship contribution statement

G. Ezzati: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **A.L. Collins:** Writing – review & editing, Funding acquisition, Conceptualization. **S. Pulley:** Writing – review & editing, Investigation. **J. Galloway:** Writing – review & editing, Investigation, Data curation. **D. Hawtree:** Writing – review & editing, Methodology, Data curation. **P. Mellander:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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.

Data availability

The data that has been used is confidential.

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