Chemosphere

Can large-scale climate patterns predict nitrate export mechanisms from agricultural land?

--Manuscript Draft--

Manuscript Number:	CHEM147253R2
Article Type:	Research paper
Section/Category:	Environmental Chemistry
Keywords:	NAO Western European Pressure Anomaly flushing index nitrogen soil moisture
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Abstract:	Nitrate losses to waterbodies are particularly associated with intensive agricultural and rainfall events are important periods of mobilisation, it is therefore important to understand the drivers for these transfers. In western Europe, weather is strongly influenced by large scale atmospheric systems in the North Atlantic. Here, we explore the link between such atmospheric systems and temporal changes in water quality using 12 years of high frequency nitrate and discharge data. The data was collected from 5 hydrologically isolated field scale grassland catchments. Rainfall driven discharge and associated flushing index (FI) for nitrate was calculated. Most events had a negative FI, but the proportion of events that were positive increased over the summer. Values of two large scale climate indices (NAOi and WEPAi) were obtained for each month of the study period and the corresponding monthly mean values for FI and soil moisture were compared considering differences between season, and field catchments. The best model for explaining mean monthly FI was as a function of the WEPAi, allowing for differences between catchments and seasons with the differences between winter and summer being significant. For both seasons, a positive WEPAi had a negative response on FI; however, the divergence in slope between the two seasons was most likely due to a potentially greater range of soil moisture conditions in the summer compared to winter. Furthermore, nitrate export from grassland field-scale catchments could be predicted using the WEPAi, but prediction was slightly better with a more local measure of soil moisture.
Opposed Reviewers:	

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29 July 2025

To whom it may concern

We wish to submit an original research article entitled "Large-scale climate patterns control soil moisture and nitrate export from agricultural land" for consideration by Chemosphere.

We confirm that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere.

In this paper, we report on how large-scale climate systems affect nitrate mobilisation from agricultural grasslands. Specifically, we compare how the North Atlantic Oscillation Index and the recently developed Western European Pressure Anomaly Index relate to the flushing index of nitrate concentrations in runoff from agricultural land. To the best of our knowledge, this is the first time that the flushing index as a means of examining solute mechanistic behaviours has been linked to large scale climate systems. The scientific gap targeted by our new paper is important because, with the amplified weather patterns predicted through climate change models, understanding how large-scale atmospheric systems can affect solute movement from soil systems has significant implications for agriculture and water management.

We believe that this manuscript is appropriate for publication by Chemosphere because it falls within the journals scope, specifically of monitoring studies which present new findings and interpretations of environmental chemistry which would be of interest for an international readership.

We have no conflicts of interest to disclose.

Thank you for your consideration of this draft manuscript.

Sincerely,

Dr. Steve Granger

Dr Hari Ram Upadhayay

Dr Andrew Mead

Prof. Adrian Collins

Title Page (with author names and complete affiliations)

Can large-scale climate patterns predict nitrate export mechanisms from agricultural land?

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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 Resilient Farming Futures (grant award BB/X010961/1) institute strategic programme - specifically work package 2 - BBS/E/RH/230004B; Detecting agroecosystem 'resilience' using novel data science methods. The North Wyke Farm Platform National Bioscience Research Infrastructure was supported by BBSRC grant: BBS/E/RH/23NB0008. 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. Adrian Collins was also funded by the UKRI-EPSRC (UK Research and Innovation-Engineering and Physical Sciences Research Council via the Global Nitrogen Innovation Centre for Clean Energy and the Environment (NICCEE) (EP/Y025776/1). 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 acknowledge the sea level pressure data providers in the ECA&D project (http://www.ecad.eu, {Klein Tank, 2002 #2602}) and the Irish Meteorological Service (http://www.met.ie/climate) for the Valentia Observatory data, which were used to compute the WEPA index.

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:

Highlights (3-5. 85 characters long)

- 5 established grassland hydrologically isolated field scale catchments monitored
- 12 years of high temporal resolution NO_3 and discharge data analysed
- Flushing indexes mostly negative but a higher proportion positive in the summer
- West European Pressure Anomaly and North Atlantic Oscillation investigated
- NO_3 export may potentially be predicted by measures of large-scale climate systems

Second response to reviewers.

1) I agree with the authors opinion that distinguishing the differences between catchments remains challenging. It appears unlikely, from a local scale perspective, that the relationship with climate indices would vary significantly across catchments. Therefore, are the primary differences in the FI mostly due to nitrogen inputs from agricultural practices? The authors state that land management is fairly consistent throughout the studied catchments. We thank the reviewer for acknowledging that at this geographical scale it seems unlikely that any relationship of NO_3 FI to climate indices is likely to differ markedly between catchments. This is why the slope for the models was constrained to that which best fitted the data consistently across the 5 field catchments. The magnitude of the response was allowed to be different between the five field catchments however, hence the model allowing for variable intercepts across this factor. Regarding the query about the 'primary differences in the FI (being) mostly due to (differences in) nitrogen inputs from agricultural practices', we would draw the reviewer's attention to our previous response. In short, manures and excreta are unlikely to be a major issue. Firstly, managed manures from overwintering are generally low in NO_3 and are typically applied at one time of year, normally mid spring, ground conditions permitting. Secondly direct livestock excreta was/is introduced to the system pretty much consistently throughout the summer. Only urine would be a primary source of inorganic N and this would be in low volumes and consistently throughout the summer, entering the soil inorganic N pool and that which is not lost through NH_3 volatilisation would be rapidly nitrified to NO_3 within the soil. The primary potential source of inorganic N that maybe lost directly to catchment drainage would be inorganic N fertilizer applications. While it cannot be guaranteed that this never happened throughout the 14 years of data represented within this manuscript, the timing of amendments were applied specifically to reduce the chances of these 'incidental' losses direct to drainage. Therefore, we discount these losses as a cause of the increase in frequency of flushing FI events in the summer. The increase in the number of flushing FI events was ascribed to the increases in soil NO_3 (through organic matter mineralisation, excretal returns, and inorganic agricultural amendments), and the wider range of soil moistures allowing for a greater variety of NO_3 mobilisation mechanisms. Therefore, we would ascribe the differences in the y-axis intercept between the field scale catchments as being typical of environmental variability, which is inevitable at this scale in real world, complex systems. Factors such as differences in catchment size and slope, in soil rewetting rates, in livestock numbers and type, and in analytical downtime all contribute to variability between the 5 systems. Given this, it seems remarkable that any relationship can be discerned at all.

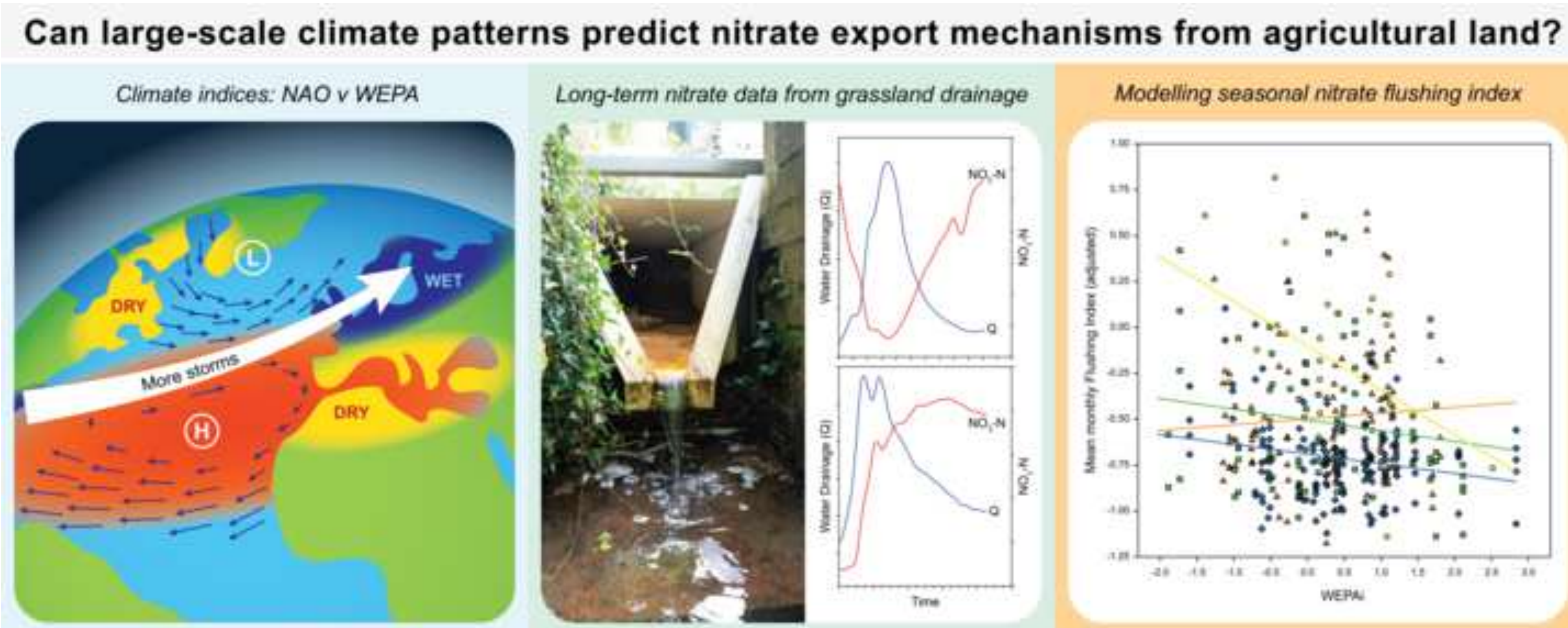
   We have added some text to the manuscript to help clarify this to the reader. (e.g. lines 241-252 & 283-286)

2) It is quite evident that soil moisture is one of the most important factors influencing the FI. The authors explicitly mention that the relationship with WEPAi and NAOi is not particularly strong. Given the research objectives, I do not find it especially informative/innovative that adding WEPAi to a model already containing soil moisture did not enhance the model fit, whereas including soil moisture in a model with WEPAi did improve it. From a scientific perspective, it's essential to clearly demonstrate the "added value" and "potential limitations" of considering large-scale climate indices as compared to location-specific hydrological parameters (e.g soil moisture) or e.g. local rainfall data which I believe are widely available.

Why shouldn't we use soil moisture/rainfall data alone to assess the FI states of the catchments without involving WEPAi and NAOi? It is clearly presented that these indices account for only a small proportion of the total variance in monthly FI. The limitations of utilizing large-scale climate indices should be openly addressed, including discussion of other factors that were not directly considered in this study.

The objectives of the study were to examine whether large scale climate systems had any effect on NO_3 mobilisation mechanisms from agricultural land using a long-term data set. As stated in our response to point 1 above and given the huge amount of variability present in datasets collected at this scale and under very limited environmental control, it was remarkable that any relationship was discernible at all. Given our interpretation of how these systems affected the NO_3 FI and the potential local mechanisms driving those observations we thought it prudent to examine the effect of soil moisture as a mediating factor. Again, the reviewer is correct that it is unsurprising that a more local measure provided a better predictor of NO_3 FI than the measure of large scale climate systems, but it was only slightly better, and the climate indices do provide a potentially useful prediction, though clearly with additional sources of variability that we have not able to incorporate in this study. Where we would disagree with the reviewer is on the availability of more local soil moisture/rainfall data. We strongly suggest that this data is not widely available and given the huge infrastructure costs of installing and maintaining soil moisture monitoring networks, that only slightly improve the assessment of FI states of field scale catchments, that using the WEPAi is a reasonable and cheap option to consider. We state this in our conclusions. We also acknowledge that "considerable variability remains around both relationships, indicating that other factors are involved which were not captured in our study". For clarity, we have expanded these areas of uncertainty, and on the reasons why the WEPAi might be considered over more local measures in our conclusions.

Graphical Abstract



Abstract

Nitrate losses to waterbodies are particularly associated with intensive agricultural and rainfall events are important periods of mobilisation, it is therefore important to understand the drivers for these transfers. In western Europe, weather is strongly influenced by large scale atmospheric systems in the North Atlantic. Here, we explore the link between such atmospheric systems and temporal changes in water quality using 12 years of high frequency nitrate and discharge data.

The data was collected from 5 hydrologically isolated field scale grassland catchments. Rainfall driven discharge and associated flushing index (FI) for nitrate was calculated. Most events had a negative FI, but the proportion of events that were positive increased over the summer. Values of two large scale climate indices (NAOi and WEPAi) were obtained for each month of the study period and the corresponding monthly mean values for FI and soil moisture were compared considering differences between season, and field catchments.

The best model for explaining mean monthly FI was as a function of the WEPAi, allowing for differences between catchments and seasons with the differences between winter and summer being significant. For both seasons, a positive WEPAi had a negative response on FI; however, the divergence in slope between the two seasons was most likely due to a potentially greater range of soil moisture conditions in the summer compared to winter. Furthermore, nitrate export from grassland field-scale catchments could be predicted using the WEPAi, but prediction was slightly better with a more local measure of soil moisture.

Keywords: NAO, Western European Pressure Anomaly, flushing index, nitrogen

1. Introduction

While nutrients are critical to the functioning of waterbodies, excessive quantities often have unintended consequences, including eutrophication and subsequent harmful algal blooms in downstream systems (Turner and Rabalais, 2003; Conley et al., 2009). Nitrogen (N), primarily in the form of nitrate, is one such nutrient and is the predominant form of inorganic N lost from soils to aquatic systems. Here, losses are particularly associated with intensive agricultural systems e.g. (Scholefield et al., 1993; Heaton et al., 2012), with diffuse nutrient transfers from agricultural land often constituting the bulk of annual loads in river catchments (Smith et al., 2005). The mechanisms of how nitrate moves from soil into aquatic systems are well understood and depend upon factors such as soil type, structure, moisture and rainfall intensity (Barraclough, 1989). Rainfall events can be important periods for nitrate mobilisation (e.g. Smith and Kellman, 2011; Vaughan et al., 2017). Indeed, Royer et. al. (2006) found that in three agricultural catchments in east-central Illinois, U.S.A., nearly all nitrate export occurred when drainage discharge was ≥ median discharge, and extreme discharges (≥90th percentile) were responsible for >50% of the nitrate export. Therefore, it is important to understand the drivers for nitrate transfers associated with discharge from land driven by rainfall events.

In the past, understanding the biogeochemical signature of storm events has been a challenge because grab samples of drainage cannot fully capture the temporal dynamics across an entire hydrograph (Granger et al., 2010; Bieroza et al., 2014). Furthermore, it is virtually impossible to collect a sufficiently representative range of differing drainage events given the true nature of each event cannot be known *a priori*. However, with improvements in real-time sensor technologies, it has been possible to collect data at ever finer temporal resolutions which allows for the capture of more detailed changes in water chemistries that occur during such events (e.g. Burns et al., 2019; Speir et al., 2021). For example, Zimmer et. al. (2019) found that interannual riverine nitrate concentration-discharge relationships were different when using near continuous data compared to those using traditional discrete grab samples. Carey et al. (2014) found that, while annual flux estimates of nitrate in a catchment generated by continuous sensor deployment were like those generated by weekly and monthly grab samples, important differences in flux occurred at seasonal time scales which was missed by manual sampling. Such rich datasets can enable fundamental questions about the drivers for nutrient mobilisation and transport in the environment to be addressed.

Using high temporal resolution data, the concentration-discharge (C-Q) response for individual discharge events can be described through the calculation of the hysteresis index (HI) and flushing index (FI). The HI can provide information on source proximity, while the FI can provide information on the mechanistic behaviour (Speir et al., 2021). Discharge event nitrate responses can be both flushing (FI>1) and diluting (FI<1) and these differences can allow for different interpretations of the mechanisms of nitrate mobilisation (e.g. Webb and Walling, 1985; Liu et al., 2022; Granger et al., 2023). At larger catchment scales, temporal variations in the HI/FI may be lost due to the amalgamation of different sources, as well as variations in their proximities and connectivity to stream networks (Creed et al., 2015; Marinos et al., 2020). At smaller scales however, these temporal variations can often be more clearly discerned (Speir et al., 2021; Granger et al., 2023).

In western Europe, weather is strongly influenced by large scale atmospheric circulation over the North Atlantic, particularly during winter (Rodwell et al., 1999). Variations in pressure between the Azores High and Icelandic Low are known as the North Atlantic Oscillation (NAO) which has a strong influence on changes in the intensity of the jet stream (Woollings and Blackburn, 2012) which in turn affects the location and intensity of weather systems. The variability in the intensity between these large-scale pressure systems from the long-term mean can be expressed as an index (NAOi). In general, when the pressure difference is large the NAOi is positive, which leads to a strong jet stream and warmer, wetter, winters. When the pressure difference is small, the NAOi is negative, the jet stream is weak, and winters can be cooler and drier with more easterly air streams. However, the effects of the NAO do differ temporally and spatially (West et al., 2019). Recently, a new climate index has been developed by Castelle et. al. (2017) which is based on the sea level pressure gradient between stations in Ireland and the Canary Islands. The Western European Pressure Anomaly (WEPA) when in positive phase reflects a southward-shifted, intensified, Icelandic Low and Azores High surface pressure dipole. Work by Jalón-Rojas and Castelle (2021) has shown that, while the NAOi was still relevant in explaining precipitation variability in western

Europe, the WEPA index (WEPAi) increased correlations with winter precipitation by up to 0.8, particularly in the UK and France.

In attempts to link large scale climatic processes and temporal changes in water quality, Monteith et. al. (2000) found that the variation in winter nitrate concentration in upland lakes and streams had a strong negative correlation with the NAOi. Mellander et. al. (2018) and Ulén et al. (2019) both found that the NAO can influence nitrogen and phosphorus losses from agricultural catchments. More recently Granger et. al. (2025) found that flow-weighted mean suspended sediment concentrations in agricultural drainage were more strongly linked to the WEPAi than the NAOi and that link was present at multiple scales. Given the importance that storm events can have in the elevated nitrate fluxes from catchments, an understanding of how large-scale climatic systems influence these exports, and the intermediary controls remains an extant evidence gap. The need to address this gap is also underscored by the increased stress on water regulating services delivered by agricultural land in the context of changing climate and extreme weather. To this end, we explore he link between nitrate mobilisation from agricultural land and large-scale climate systems as key drivers of water quality regulation. In this paper, we analyse a long-term (2012 – 2024), high frequency dataset of field scale nitrate concentration dynamics in rainfall driven drainage from a permanent grass pasture management system.

2. Methods

2.1. Field site

The North Wyke Farm Platform (NWFP) is described in detail by Orr et. al. (2016). In short, this experimental platform was established in 2010 in the southwest of England (Figure 1a). The climate in the region is described as temperate with a mean annual precipitation at North Wyke of 1040 mm (1984-2013) with the majority falling in the winter (Dec – Feb). The NWFP comprises three 21 ha farmlets, each consisting of 5 hydrologically isolated field-scale catchments ranging in size from 1.6 to 8.1 ha. The soil belongs predominantly to two similar series; Hallsworth and Halstow (Harrod and Hogan, 2008) with the topsoil a slightly stony clay loam that overlies a mottled stony clay subsoil which is impermeable to water and is therefore seasonally waterlogged. Drainage water moves by surface and sub-surface lateral flow across the clay layer and is intercepted by a bounding drainage system at the plot edge. This water is then channelled to an outlet where Q and various physio-chemical properties are measures on a 15-minute timestep. One of the farmlet treatments is 'permanent pasture' and has remained an untilled grassland for over 30 years. This is currently managed through cattle and sheep grazing and silage production. The pasture typically receives up to 200 kg ha^{-1} of inorganic N and farmyard manure which is returned after winter housing. Phosphorus, potassium, and pH are all managed to grassland recommended indices (Agriculture and Horticulture Development Board, 2025). This study utilised the data collected from 2012-24 from the 5 field scale catchments of the permanent pasture treatment referred to hereafter as catchments FP4, FP5, FP6, FP12, and FP13 (Figure 1b; Table S1).

2.2. Hydrology and water chemistry measurements

Discharge (Q) from each of the catchments is currently measured using H type flumes which are engineered structures such that discharge can be determined through them by a known relationship between the height of the liquid within it at a known point. Until 2015 the depth of the water was determined using bubble meters (4230, Teledyne ISCO, U.S.A.). In 2015 these were replaced with pressure level sensors (OTT Hydrometry, U.K.). As the Q exported from agricultural land at this scale can be discontinuous, drainage water is collected and analysed by sensors in a flow cell to prevent sensors drying out. When $Q>0.2$ l s^{-1} water is pumped from a drainage sump to the flow cell where sensors collect various water physiochemical properties. However, when Q is low ($Q<0.2$ l s^{-1}) water is not pumped into the flow cell, and returned sensor measurements are discarded. Combined nitrate-N and nitrite-N (referred to as NO_3-N hereafter) concentrations are measured by a dedicated, self-cleaning, optical UV absorption sensor (NITRATAX Plus SC, Loveland, Colorado, USA). Dissolved NO_3-N absorbs UV light at wavelengths below 250 nm. The NO_3-N concentration is then calculated by passing UV light through the water in the by-pass flow cell and measuring the absorption using a 2-beam turbidity compensated photometer. The Nitratax

UV absorption sensors remain *in situ* and are calibrated monthly in the field using a 2-point calibration. Sensor drift that may be due to lens contamination is checked prior to cleaning the instrument lenses and wiper blades. The instruments are serviced annually including a 3-point factory calibration.

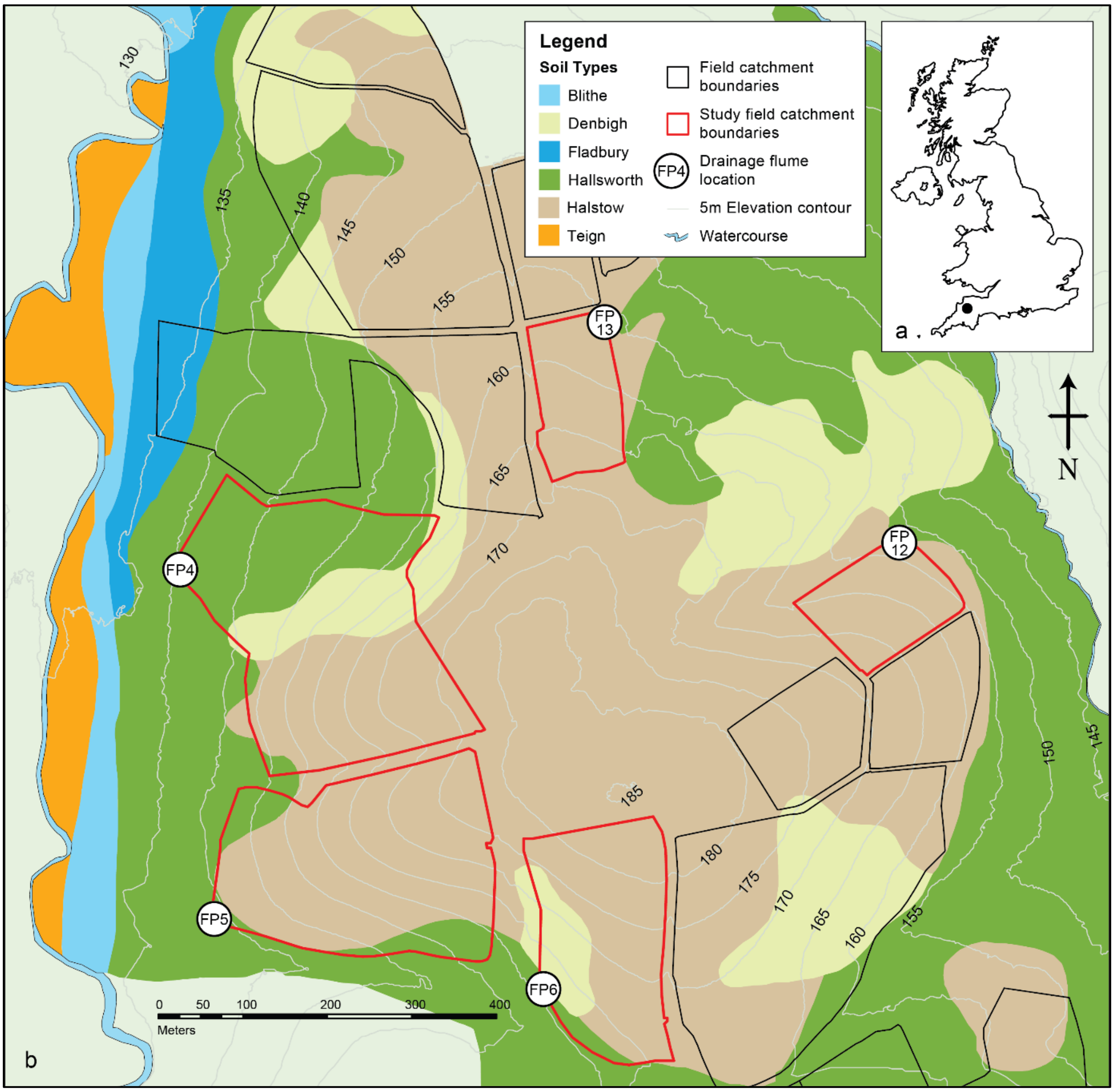


Figure 1. The North Wyke Farm Platform (a) location within the United Kingdom, and (b) the field-scale catchments (FP4, FP5, FP6, FP12, and FP13) used within this study.

2.3. Soil moisture measurements

A soil moisture sensor was sited in each of the field-scale catchments, consisting of an A723 addIT Series 4 telemetry unit and a SM1 combination soil moisture and temperature probe (Adcon, OTT HydroMet GmbH, Vienna, Austria) which measures soil moisture every 15 minutes using capacitance at a depth of 10 cm.

2.4. Calculation of FI

Rainfall event driven Q (hereafter described as 'storm event/s') were extracted from the 15-minute resolution Q data using the method described by Musolff et. al. (2021), in R (Ver 4.4.3), which facilitates automated separation of storm events. Briefly, a storm event was defined as starting when the Q increased by 20% within one hour and ending when the Q decreased and stabilized with a variation of <10%. Storm events defined by this process were then analysed and visually assessed, with previously defined separate events being reclassified if it was deemed that they were in fact one event with more than one peak Q.

Only storm events lasting ≥3 hours were used for the calculation of storm event FI. As this calculation only requires NO_3-N concentration data for the start of the defined storm event and at peak Q, storm events missing either value were identified and, where possible, missing values were manually infilled. This was done either through a simple interpolation using surrounding data, or by assuming the nearest existing value was the same as the missing value if that value was temporally close to the missing value and where NO_3-N did not appear to be in flux.

For each storm event which had ≥70% NO_3-N data available for its defined duration, the NO_3-N data was first normalised:

$$C_{iN} = \frac{C_i - C_{min}}{C_{max} - C_{min}}$$

where C_{iN} is the normalized NO_3-N concentrations corresponding to the i^{th} measured data and C_{min} and C_{max} are the event minimum and maximum NO_3-N concentrations, respectively. The FI was calculated using the following equation (Butturini et al., 2008):

$$FI = C_{Qpeak} - C_{Qstart}$$

Here, C_{Qstart} and C_{Qpeak} refer to normalised concentrations of NO_3-N at the beginning of the defined storm event and at the peak Q of the rising limb. The FI ranges from -1 to +1, with a negative FI value indicative of a dilution of NO_3-N concentrations on the rising limb, whereas a positive FI indicates a flushing effect with an increase in NO_3-N concentrations on the rising limb.

2.5. Climate data

Climate index data, as calculated as a monthly value were used. Time series of the station based North Atlantic Oscillation index (NAOi) extracted from the NSF National Centre for Atmospheric Research, Climate Analysis Section (https://ncar.ucar.edu/). The WEPAi data was calculated and provided by Castelle (personal communication).

2.6. Statistical analysis

Values of the two climate indices were obtained for each month from October 2012 to February 2024 inclusive. For each of the five field-scale catchments, corresponding arithmetic mean values for FI and % soil moisture were calculated. Months where there were no FI values obtained or no data available for soil moisture, were omitted from the modelled dataset. Months were additionally classified into four meteorological seasons (Winter: December-February, Spring: March-May, Summer: June-August, Autumn: September-November). A general linear regression modelling framework was used to explore possible models to explain the observed variability in the mean monthly FI and soil moisture (%) responses, as functions of the climate indices, soil moisture (when not the response), season, and catchment, the framework allowing the effect of explanatory variables to vary between seasons and between catchments. Our aim was to find parsimonious models that added insights. Initially simple regression models were fitted, but the most complex fitted models included a single quantitative explanatory variable (either climate index or soil moisture) and allowed both for separate intercept parameters for each catchment, and for separate intercept and slope parameters for each season. Models for mean monthly FI were also fitted that considered the impact of including both a climate index and soil moisture. The general linear regression modelling framework allows the comparison of related models through the additional sums of squares principle, identifying whether additional model complexity improves the model fit. All linear regression analyses were fitted using Genstat (VSN International, 2022). F-tests were used to assess for the importance of adding model complexity, with t-tests used to assess for differences in parameter values. The overall goodness-of-fit for each model was assessed using the adjusted coefficient of determination (percentage variance accounted for).

3. Results and Discussion

In western Europe, the weather effects of the NAO differ seasonally and spatially (e.g. West et al., 2019). However, in general, it presents itself in the winter as milder, wetter conditions when the NAOi is positive, and cooler, drier conditions when the NAOi is negative. Conversely, a positive NAOi in the summer tends to be associated with warmer, drier conditions, whereas a negative NAOi tends to bring wetter conditions (Hall and Hanna, 2018). The WEPA, however, does not have this seasonal variation, with a positive WEPAi being associated with warmer, wetter weather in both winter and summer (Castelle et al., 2017). The effect of large-scale climate patterns on the weather at the study site have already been examined by Granger et al. (2025) who have already shown that long-term monthly precipitation totals are strongly linked to the NAOi and WEPAi. Given the potential differences in the seasonal precipitation response of the NAOi, monthly rainfall totals were examined for winter months and summer months separately. The NAOi was found to be positively related to monthly winter precipitation totals ($r_{(160)} = 0.23$, $p<0.01$), but there was no relationship to summer rainfall totals. The WEPAi however, was found to be more strongly positively related to winter rainfall ($r_{(160)} = 0.77$, $p<0.001$) and also related to summer totals ($r_{(163)}$ – 0.64, $p<0.001$).

The hydrological dataset used from the NWFP spanned 125 months, from Oct 2012 to Feb 2024 inclusive, from which 3137 storm events were delineated across the 5 'permanent pasture' field-scale catchments. From the delineated storm events, 2809 were ≥3h in duration and had ≥70% NO_3-N data coverage and were selected for calculation of their FI (Table S1). Due to the seasonal, ephemeral, nature of the drainage in the study catchments, 59% of the storm events occur in winter (n=1668) with the highest median peak Q occurred in either winter or spring. Only 2% of the selected events occurred in the summer (n=54) which also had the lowest median peak Q.

All catchments produced a wide range of FI values which spanned diluting to flushing storm events. The mean FI from all catchments were all negative and ranged between -0.78 and -0.49 although these values are heavily skewed to winter storm event FI values (Figure 2). The FI range from all catchments had a minimum FI of -1.0 to a maximum of between +0.55 and +1.0 (Table S2). The months with the most negative mean FI values from the 5 catchments over the study period were typically December, January and February (i.e. winter), while the months which had the least negative FI were May, June and August. The month of June also had the least available storm event data such that no recorded storm events were available from either catchments FP12 or FP13, the two smallest field catchments and only one storm event was recorded in FP6. Dilution responses accounted for >92% of the storm event NO_3-N behaviours during the study period; however, as indicated above, there was a clear seasonal distribution in the diluting and flushing responses similar to that reported elsewhere (e.g. Webb and Walling, 1985; Granger et al., 2023). While dilution responses were always the dominant response, the prevalence of flushing responses increases noticeably from April, was highest over the summer months, and declined through the autumn (Figure 2). So, while the number of measured events dropped markedly over the summer, the proportion of those events which demonstrated a flushing response noticeably increased. It is possible that changes in agricultural management between the summer and winter are, in part, responsible for this increase in flushing responses. For example, animals are present on the land and nitrogen amendments are applied during the summer while both are absent during the winter however while interactions of nitrogen amendments and rainfall cannot be discounted, they are considered minimal. As stated previously within section 2.1, the timing of inorganic N amendments is done strategically such that 'incidental' losses (Preedy et al., 2001) are minimised. The main difference between summer and winter is simply that the soil inorganic N pool is larger, but also uptake of inorganic N is increased. For each of the 125 months of the study period for each of the

5 catchments, a mean FI was calculated based on the events that started within that month. The monthly mean FI could then be related to the monthly climate index, providing a realistic temporal scale to detect variation. Furthermore, it reduces the influence of any potential singular storm event that might contain an incidental NO_3-N loss, hence accounting for the finer temporal variability that the systems are likely to exhibit. Flushing index values were not available for all months due to various reasons, such as a lack of rainfall, or equipment downtime, such that the combined dataset across all catchments contained 388 values.

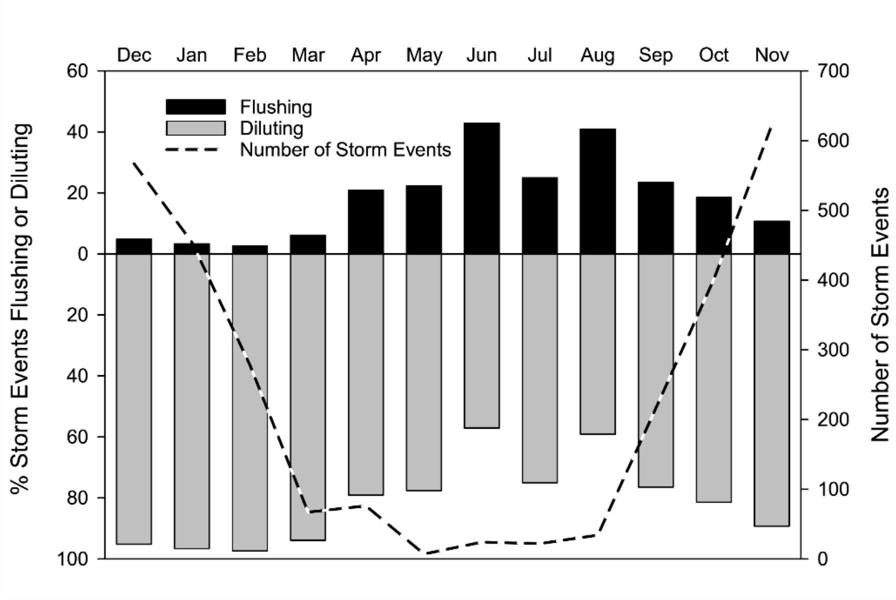


Figure 2. The number of storm events during each calendar month measured over the period of the study and the percentage of which that were classified as either diluting or flushing.

Simple linear regressions of monthly mean FI against either climate index (Figure 3) indicated a significant relationship for both the NAOi (t_{386}=3.84, p<0.001, 3.4% variance accounted for) and the WEPAi (t_{386}=2.04, p=0.009, 1.5% variance accounted for) with the NAOi being most significantly related but still only accounting for a small percentage of the total variance indicating other factors may be involved. However, given that FI can also differ seasonally (e.g. Liu et al., 2022; Granger et al., 2023), and that the expression of the NAOi in weather is known to vary seasonally (West et al., 2019), it is reasonable to examine the relationships in terms of seasonal variation and it is also important to allow for differences in the relationships between the 5 catchments.

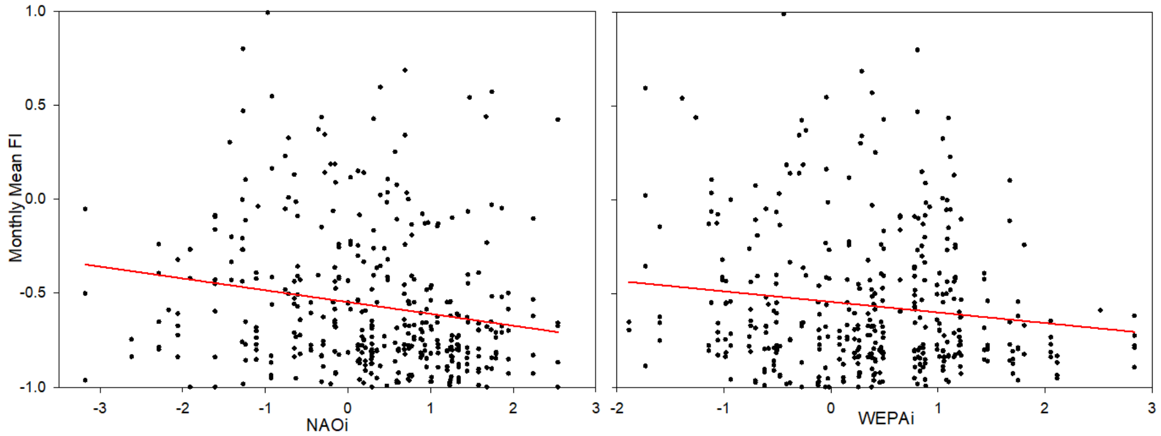


Figure 3. The relationship of the monthly mean NO_3-N FI data of storm events from 5 permanent grassland field-scale catchments and the NAOi or the WEPAi

Firstly, allowing only for separate intercept parameters for each season, but constraining the slopes to be common across seasons, significantly improved the model fit and increased the variance accounted for. This was more so for the WEPAi (F_{3383}=23.82, p<0.001, 16.4% variance accounted for) than for the NAOi (F_{3383}=18.71, p<0.001, 15.1% variance accounted for). However, it is unreasonable to constrain the slope of the models for season given the variability of the expression of the NAOi in weather during summer and winter. Also, allowing for separate slopes for each season gave a further significant improvement for the WEPAi (F_{3380}=3.45, p=0.017, 17.9% variance accounted for) but not for the NAOi (F_{3380}=0.35, p=0.786, 14.7% variance accounted for). Secondly, because the data was obtained from 5 separate catchments, albeit under the same management regime, we anticipated that there will be some variation in the response between them and allowing for that variation may improve the model. This model allowed for variation between catchments but was constrained to have a common slope, because there was no logical reason why the underlying relationships for monthly mean FI with either climate indices should vary between catchments. Allowing different intercepts for each catchment means that the magnitude of the response could vary between the 5 field scale catchments as they were not all identical, and real-world environmental differences between the catchments, such as size, slope, presence or absence of livestock etc could lead to different outcomes. Comparing this model with the initial single line model (Figure 3) gave a highly significant improvement in model fit for both the NAOi (F_{4382}=11.58, p<0.001, 13.0% variance accounted for) and the WEPAi (F_{4382}=11.00, p<0.001, 10.8% variance accounted for). Thirdly, combining these two factors, and allowing both separate intercept and separate slope parameters for each season gave similar patterns of improvements in model fit as described previously where models did not allow for differences between catchments. Therefore, the best model for explaining mean monthly FI was as a function of the WEPAi, allowing for additive differences between catchments (separate intercepts) and both separate intercepts and separate slopes for each season (Figure 4a). The differences in both the intercepts and slopes between winter and summer were significant (intercept: t_{376}=7.86, p<0.001; slope: t_{376}=2.38, p=0.018), with the relationships for spring and autumn being intermediate between the two seasonal extremes.

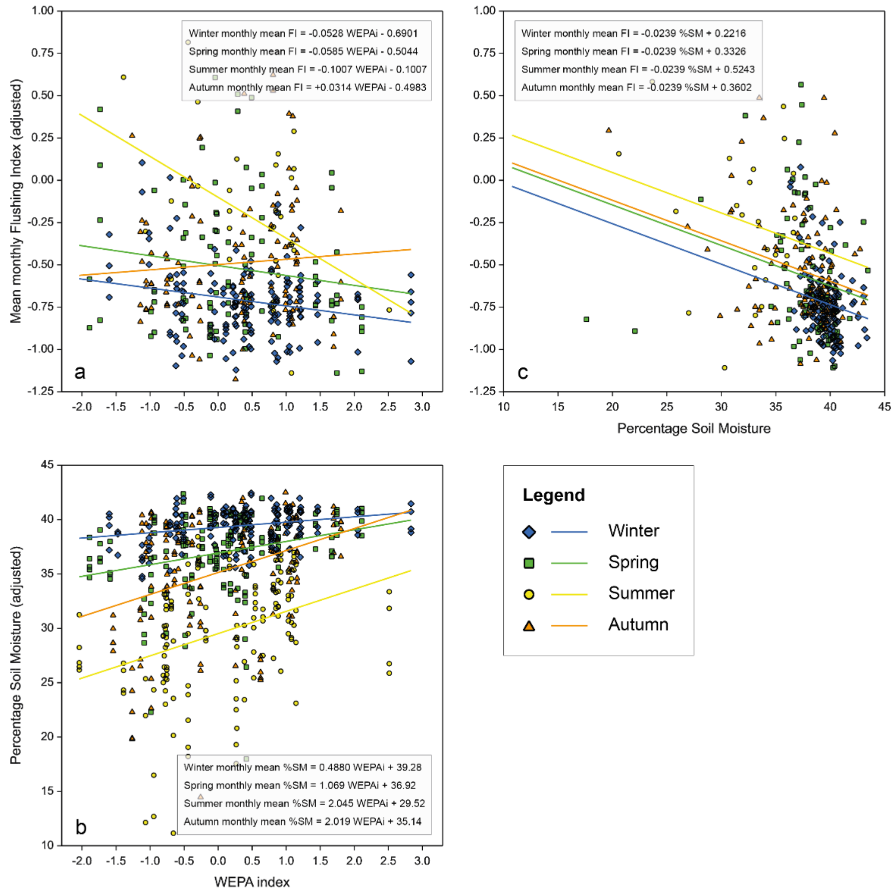


Figure 4. Best statistical model for (a) mean monthly FI, as a function of the WEPAi; (b) monthly mean soil moisture (%) as a function of the WEPAi; (c) monthly mean FI, as a function of the monthly mean soil moisture (%). All seasonal differences in parameter values have been adjusted for differences between the 5 field-scale catchments.

The seasonal differentiation of summer and winter FI, with summer FI elevated compared to that of winter, and with spring and autumn intermediate to these endmembers was the same as previously reported at this site for NO_3-N (Granger et al., 2023). This pattern has also been reported at other sites (Heathwaite and Bieroza, 2020) although not at others (Vaughan et al., 2017; Kincaid et al., 2020) and the catchment scale can be a relevant factor (Granger et al., 2023). In this study, while the actual slopes and intercepts of the models, fitted for the different seasons, are not particularly revealing as they simply reflect the conditions of this specific site over the study period, the significant difference in slope between winter and summer season is interesting. While for both seasons, a strongly positive WEPAi had a similarly strongly negative FI (≈-0.75), the divergence between the seasons increases with an increasingly more negative WEPAi such that with a WEPAi of -2 the difference between summer and winter is ≈1, with a winter FI of ≈-0.5 and a summer FI of ≈+0.5. This seems likely due to the range of soil moisture conditions that each season may experience. In the winter, it is likely that the soil is at, or near, saturation all the time due to higher rainfall volumes and little or no evapotranspiration. This would mean that nearly all storm events would lead to a diluting FI response with low NO_3-N concentration rainwater having minimal interactions with what NO_3-N there was present in soil water. This low NO_3-N rainwater would then move rapidly over the saturated land surface and directly into drainage pathways causing a drop in NO_3-N concentrations. Even in months where the WEPAi was more positive, and rainfall was reduced, the overarching mechanism would not change dramatically as the soils would remain wet. In the summer, the ground conditions have more scope to vary, from very wet to very dry and so storm events could have very different FI responses as soils either wet up or dry within the same month, as different mechanisms for NO_3-N mobilisation predominate. Therefore, changes in the WEPAi potentially present themselves more dramatically in summer mean monthly FI. When very wet, the same dilution responses as occur in the winter should dominate, while drier soils would see storm event water move through the soil more, interacting with soil water and soil NO_3-N leading to flushing responses.

Given the importance of soil moisture in the mechanisms of NO_3-N delivery in our interpretation of the differences in seasonal response, it is prudent to examine this variable as a potential mediating factor in the relationships between the WEPAi and monthly mean FI. Monthly mean % soil moisture values were produced from soil moisture stations situated within each field-scale catchment. Over the study period, monthly means ranged from 40.1% in February (FP4) to 26.5% in June (FP13). A clear seasonal pattern of the highest soil moisture values occurring in the winter months, and the lowest in the summer months within all catchments can be clearly observed (Table S3). Simple linear regressions examining the mean monthly % soil moisture as a function of climate indices indicated a significant relationship; stronger for the WEPAi than for the NAOi, but again only explaining a relatively small percentage of the total variance (NAOi: t_{608}=3.11, p=0.002, 1.4% variance accounted for; WEPAi: t_{608}=7.21, p<0.001, 7.7% variance accounted for). There was no evidence for differences in intercepts between catchments (NAOi: F_{4604}=1.63, p=0.165; WEPAi: F_{4604}=1.74, p=0.140), but highly significant effects of allowing separate intercepts for each season (NAOi: F_{3605}=145.37, p<0.001, 42.4% variance accounted for: WEPAi: F_{3605}=148.92, p<0.001, 46.7% variance accounted for) and additionally for allowing separate slopes for each season (NAOi: F_{3602}=10.89, p<0.001, 45.1% variance accounted for; WEPAi: F_{3602}=4.65, p=0.003, 47.6% variance accounted for). Therefore, once again, the best fitting model for mean monthly % soil moisture was as a function of the WEPAi allowing for (non-significant) additive differences between catchments, and both separate intercepts and separate slopes for each season (Figure 4b).

The differences in both the intercepts and slopes between winter and summer were significant (intercept: t_{598}=20.76, p<0.001; slope: t_{598}=3.14, p=0.002), with the relationships for spring and autumn again being intermediate. This finding, that the WEPAi strongly and positively affects monthly mean soil moisture is not surprising given that a more positive WEPAi has been strongly linked to increased monthly rainfall totals (Granger et al., 2025). Also, the seasonal separation between winter and summer soil moisture is unsurprising given the differing rainfall totals in winter and summer. That the slopes between winter and summer differ significantly further indicates that the capacity for monthly mean soil moisture variability is greater in the summer than the winter when the ground conditions will nearly always be at or near saturation regardless of changes in the WEPAi. When the relationship between monthly mean soil moisture and monthly mean FI was examined, a highly significant relationship was found (t_{343}=7.71, p<0.001, 14.5% variance accounted for), far stronger than that seen for either the WEPAi or the NAOi as explanatory variables. There was significant evidence for differences in the intercepts between catchments (F_{4336}=6.09, p<0.001), and significant evidence for additional differences in intercept between seasons (F_{3336}=6.75, p<0.001), but no evidence for differences in slopes between seasons (F_{3333}=1.27, p=0.283). The best model accounted for 23.2% of the variance of the monthly mean FI (Figure 4c) and again, the difference between summer and winter was significant (intercept: t_{336}=3.94, p<0.001) with summer having the highest intercept and winter the lowest.

Adding a potential effect of the WEPAi to this model gave no additional effect (F_{1335}=0.69, p=0.408), with the percentage variance accounted for reducing slightly to 23.1%. In contrast, adding a potential effect of monthly mean soil moisture to the best model identified above for the effect of WEPAi, did produce a significant improvement in the fit (F_{1335}=16.80, p<0.001), increasing the percentage variance accounted for to 23.1%, as indicated for the above combined model. Therefore, the WEPAi has more effect on the monthly mean % soil moisture, which in turn exerts a greater effect on monthly mean FI than the WEPAi itself.

4. Conclusions

Nitrate losses from agricultural land remain a concern globally in the context of both private (loss of expensive nutrient additions) and public (water quality degradation and clean-up costs) goods. Most storm events measured from the grassland field-scale catchments occurred in the months between September to February, with the majority of these events exhibiting a negative, diluting, FI response. Over the March to August period, due to the decrease in rainfall totals over this period, far fewer storm events were recorded. The FI response of these events also changed with an increase in the proportion of storm events that exhibited a positive, flushing, FI although diluting events remained the common response.

Simple linear regression analysis found that the WEPAi appears to affect monthly mean NO_3-N FI more strongly than the NAOi. When differences between the 5 catchments and seasons were considered, it was found that there was a significantly different relationship between the summer FI response to the WEPAi and the winter response. Both seasons exhibited a negative response, with an increased WEPAi leading to a decreased, more diluting, FI. The main difference presented as a much steeper slope in the summer when compared to the winter indicating that the same positive change in WEPAi in the summer leads to a greater change in FI, towards a diluting response, than in the winter. When soil moisture was examined as a potential mediating factor in the relationship between climate indices and FI it was found that the WEPAi provided a better prediction of monthly mean soil moisture than the NAOi, allowing for differences between both catchments and season. There were significant differences in intercept and slope between winter and summer responses with the slope of the summer response being steeper. This again indicates that the same positive change in the WEPAi leads to a greater increase in soil moisture content in the summer than in the winter. When examining the relationship between monthly mean soil moisture and monthly mean FI, this was found to be the best model for explaining variation in FI. The inclusion of the WEPAi did not improve the model and therefore could not be considered as mediating the effect of the WEPAi. The effects on FI present themselves most strongly in the summer rather than the winter, as soil moisture variability is much smaller in the winter than the summer, but most storm events in any given month are still likely to be negative FI, diluting events. Therefore, whilst NO_3-N export from the grassland field-scale catchments were best predicted using a more local measure of soil moisture, this was only slightly better than models using the WEPAi, a measure calculated at a near global-scale. Where using the WEPAi over the slightly better measure of soil moisture is advantageous however is that soil moisture data is not widely available at the field scale and that the cost and maintenance of installing soil moisture monitoring networks would be prohibitive. Considerable variability remains around both relationships, indicating that other factors are involved which were not captured in our study. Furthermore, this study only examines one geographically localised dataset. To establish the predictive capabilities of the WEPAi on NO_3-N FI more widely, other datasets in different regions with differing environmental variables would need to be examined such that other environmental factors influencing NO_3-N export could be identified. The challenge here is then to build a dataset from a sufficiently diverse set of locations to be able to identify the key environmental variables influencing the responses. That said, given changing weather patterns and the need to build improved resilience for the water regulating services delivered by agricultural land, the work herein indicates that the WEPAi can provide a level of predictive capability for NO_3-N export at the field-scale. This work point to the challenge encapsulated in managing prolonged or changing periods of seasonal elevated soil moisture given its key role in linking climate patterns and NO_3-N export.

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 Resilient Farming Futures (grant award BB/X010961/1) institute strategic programme - specifically work package 2 - BBS/E/RH/230004B; Detecting agroecosystem 'resilience' using novel data science methods. The North Wyke Farm Platform National Bioscience Research Infrastructure was supported by BBSRC grant: BBS/E/RH/23NB0008. 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. Adrian Collins was also funded by the UKRI-EPSRC (UK Research and Innovation-Engineering and Physical Sciences Research Council via the Global Nitrogen Innovation Centre for Clean Energy and the Environment (NICCEE) (EP/Y025776/1). 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 acknowledge the sea level pressure data providers in the ECA&D project (http://www.ecad.eu, Klein Tank, et al. 2002) and the Irish Meteorological Service (http://www.met.ie/climate) for the Valentia Observatory data, which were used to compute the WEPA index.

References

Agriculture and Horticulture Development Board, 2025. Nutrient Management Guide (RB209). https://ahdb.org.uk/nutrient-management-guide-rb209

Barraclough, D., 1989. A usable mechanistic model of nitrate leaching 1. The model. J. Soil Sci. 40, 543–554.

Bieroza, M.Z., Heathwaite, A.L., Mullinger, N.J., Keenan, P.O., 2014. Understanding nutrient biogeochemistry in agricultural catchments: the challenge of appropriate monitoring frequencies. Environ. Sci. Process. Impacts 16, 1676–1691.

Burns, D.A., Pellerin, B.A., Miller, M.P., Capel, P.D., Tesoriero, A.J., Duncan, J.M., 2019. Monitoring the riverine pulse: Applying high-frequency nitrate data to advance integrative understanding of biogeochemical and hydrological processes. Wiley Interdisciplinary Reviews-Water 6.

Butturini, A., Alvarez, M., Bernal, S., Vazquez, E., Sabater, F., 2008. Diversity and temporal sequences of forms of DOC and NO3-discharge responses in an intermittent stream: Predictable or random succession? J. Geophys. Res. (Biogeosci.) 113.

Carey, R.O., Wollheim, W.M., Mulukutla, G.K., Mineau, M.M., 2014. Characterizing Storm-Event Nitrate Fluxes in a Fifth Order Suburbanizing Watershed Using In Situ Sensors. Environ. Sci. Technol. 48, 7756–7765.

Castelle, B., Dodet, G., Masselink, G., Scott, T., 2017. A new climate index controlling winter wave activity along the Atlantic coast of Europe: The West Europe Pressure Anomaly. Geophys. Res. Lett. 44, 1384–1392.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling Eutrophication: Nitrogen and Phosphorus. Science 323, 1014–1015.

Creed, I.F., McKnight, D.M., Pellerin, B.A., Green, M.B., Bergamaschi, B.A., Aiken, G.R., Burns, D.A., Findlay, S.E.G., Shanley, J.B., Striegl, R.G., Aulenbach, B.T., Clow, D.W., Laudon, H., McGlynn, B.L., McGuire, K.J., Smith, R.A., Stackpoole, S.M., 2015. The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. Can. J. Fish. Aquat. Sci. 72, 1272–1285.

Granger, S.J., Hawkins, J.M.B., Bol, R., White, S.M., Naden, P., Old, G., Bilotta, G.S., Brazier, R.E., Macleod, C.J.A., Haygarth, P.M., 2010. High temporal resolution monitoring of multiple pollutant responses in drainage from an intensively managed grassland catchment caused by a summer storm. W. Air Soil Pollut. 205, 377–393.

Granger, S.J., Upadhayay, H.R., Castelle, B., Collins, A.L., 2025. The influence of large-scale climate patterns on sediment loss from agricultural land-exploration using an instrumented field and catchment scale platform. Environmental Research Letters 20.

Granger, S.J., Upadhayay, H.R., Collins, A.L., 2023. Hydro-chemical responses at different scales in a rural catchment, UK, and implications for managing the unintended consequences of agriculture. Environ. Res. 228, 115826.

Hall, R.J., Hanna, E., 2018. North Atlantic circulation indices: links with summer and winter UK temperature and precipitation and implications for seasonal forecasting. Int. J. Clim. 38, E660–E677.

Harrod, T.R., Hogan, D.V., 2008. The soils of North Wyke and Rowden. Unpublished report to North Wyke Research, revised edition of original report by T.R. Harrod,

Soil Survey of England and Wales (1981). North Wyke Research, Okehampton, Devon.

Heathwaite, A.L., Bieroza, M., 2020. Fingerprinting hydrological and biogeochemical drivers of freshwater quality. Hydrol. Process. 35.

Heaton, T.H.E., Stuart, M.E., Sapiano, M., Sultana, M.M., 2012. An isotope study of the sources of nitrate in Malta's groundwater. J. Hydrol. 414, 244–254.

Jalón-Rojas, I., Castelle, B., 2021. Climate Control of Multidecadal Variability in River Discharge and Precipitation in Western Europe. Water 13, 257.

Kincaid, D.W., Seybold, E.C., Adair, E.C., Bowden, W.B., Perdrial, J.N., Vaughan, M.C.H., Schroth, A.W., 2020. Land Use and Season Influence Event-Scale Nitrate and Soluble Reactive Phosphorus Exports and Export Stoichiometry from Headwater Catchments. Water Resour. Res. 56, e2020WR02736.

Klein Tank, A.M.G., Wijngaard, J.B., Können, G.P., Böhm, R., Demarée, G., Gocheva, A., Mileta, M., Pashiardis, S., Hejkrlik, L., Kern-Hansen, C., Heino, R., Bessemoulin, P., Müller-Westermeier, G., Tzanakou, M., Szalai, S., Pálsdóttir, T., Fitzgerald, D., Rubin, S., Capaldo, M., Maugeri, M., Leitass, A., Bukantis, A., Aberfeld, R., van Engelen, A.F.V., Forland, E., Mietus, M., Coelho, F., Mares, C., Razuvaev, V., Nieplova, E., Cegnar, T., Antonio López, J., Dahlström, B., Moberg, A., Kirchhofer, W., Ceylan, A., Pachaliuk, O., Alexander, L.V., Petrovic, P., 2002. Daily dataset of 20th-century surface air temperature and precipitation series for the European Climate Assessment. Int. J. Clim. 22, 1441–1453.

Liu, W.L., Tian, S.Y., Youssef, M.A., Birgand, F.P., Chescheir, G.M., 2022. Patterns of long-term variations of nitrate concentration - Stream discharge relationships for a drained agricultural watershed in Mid-western USA. J. Hydrol. 614.

Marinos, R.E., Van Meter, K.J., Basu, N.B., 2020. Is the River a Chemostat?: Scale Versus Land Use Controls on Nitrate Concentration-Discharge Dynamics in the Upper Mississippi River Basin. Geophys. Res. Lett. 47.

Mellander, P.E., Jordan, P., Bechmann, M., Fovet, O., Shore, M.M., McDonald, N.T., Gascuel-Odoux, C., 2018. Integrated climate-chemical indicators of diffuse pollution from land to water. Scientific Reports 8, 944.

Monteith, D.T., Evans, C.D., Reynolds, B., 2000. Are temporal variations in the nitrate content of UK upland freshwaters linked to the North Atlantic Oscillation? Hydrol. Process. 14, 1745–1749.

Musolff, A., Zhan, Q., Dupas, R., Minaudo, C., Fleckenstein, J.H., Rode, M., Dehaspe, J., Rinke, K., 2021. Spatial and Temporal Variability in Concentration-Discharge Relationships at the Event Scale. Water Resour. Res. 57.

Orr, R.J., Murray, P.J., Eyles, C.J., Blackwell, M.S.A., Cardenas, L.M., Collins, A.L., Dungait, J.A.J., Goulding, K.W.T., Griffith, B.A., Gurr, S.J., Harris, P., Hawkins, J.M.B., Misselbrook, T.H., Rawlings, C., Shepherd, A., Sint, H., Takahashi, T., Tozer, K.N., Whitmore, A.P., Wu, L., Lee, M.R.F., 2016. The North Wyke Farm Platform: effect of temperate grassland farming systems on soil moisture contents, runoff and associated water quality dynamics. Eur. J. Soil Sci. 67, 374–385.

Preedy, N., McTiernan, K., Matthews, R., Heathwaite, L., Haygarth, P., 2001. Rapid incidental phosphorus transfers from grassland. J. Environ. Qual. 30, 2105–2112.

Rodwell, M.J., Rowell, D.P., Folland, C.K., 1999. Oceanic forcing of the wintertime North Atlantic Oscillation and European climate. Nature 398, 320–323.

Royer, T.V., David, M.B., Gentry, L.E., 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. Environ. Sci. Technol. 40, 4126–4131.

Scholefield, D., Tyson, K.C., Garwood, E.A., Armstrong, A.C., Hawkins, J., Stone, A.C., 1993. Nitrate leaching from grazed lysimeters: effects of fertilizer input, field drainage, age of sward and patterns of weather. J. Soil Sci. 44, 601–613.

Smith, E.L., Kellman, L.M., 2011. Nitrate Loading and Isotopic Signatures in Subsurface Agricultural Drainage Systems. J. Environ. Qual. 40, 1257–1265.

Smith, R.V., Jordan, C., Annett, J.A., 2005. A phosphorus budget for Northern Ireland: inputs to inland and coastal waters. J. Hydrol. 304, 193–202.

Speir, S.L., Tank, J.L., Bieroza, M., Mahl, U.H., Royer, T.V., 2021. Storm size and hydrologic modification influence nitrate mobilization and transport in agricultural watersheds. Biogeochemistry 156, 319–334.

Turner, R.E., Rabalais, N.N., 2003. Linking landscape and water quality in the Mississippi river basin for 200 years. Bioscience 53, 563–572.

Ulén, B., Lewan, E., Kyllmar, K., Blomberg, M., Andersson, S., 2019. Impact of the North Atlantic Oscillation on Swedish Winter Climate and Nutrient Leaching. J. Environ. Qual. 48, 941–949.

Vaughan, M.C.H., Bowden, W.B., Shanley, J.B., Vermilyea, A., Sleeper, R., Gold, A.J., Pradhanang, S.M., Inamdar, S.P., Levia, D.F., Andres, A.S., Birgand, F., Schroth, A.W., 2017. High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. Water Resour. Res. 53, 5345–5363.

VSN International, 2022. Genstat for Windows 22nd Edition. VSN International, Hemel Hempstead, UK.

Webb, B.W., Walling, D.E., 1985. Nitrate behaviour in streamflow from a grassland catchment in Devon, U.K. Water Res. 19, 1005–1016.

West, H., Quinn, N., Horswell, M., 2019. Regional rainfall response to the North Atlantic Oscillation (NAO) across Great Britain. Hydrology Research 50, 1549–1563.

Woollings, T., Blackburn, M., 2012. The North Atlantic Jet Stream under Climate Change and Its Relation to the NAO and EA Patterns. J. Clim. 25, 886–902.

Zimmer, M.A., Pellerin, B., Burns, D.A., Petrochenkov, G., 2019. Temporal Variability in Nitrate-Discharge Relationships in Large Rivers as Revealed by High-Frequency Data. Water Resour. Res. 55, 973–989.

Abstract

Nitrate losses to waterbodies are particularly associated with intensive agricultural and rainfall events are important periods of mobilisation, it is therefore important to understand the drivers for these transfers. In western Europe, weather is strongly influenced by large scale atmospheric systems in the North Atlantic. Here, we explore the link between such atmospheric systems and temporal changes in water quality using 12 years of high frequency nitrate and discharge data.

The data was collected from 5 hydrologically isolated field scale grassland catchments. Rainfall driven discharge and associated flushing index (FI) for nitrate was calculated. Most events had a negative FI, but the proportion of events that were positive increased over the summer. Values of two large scale climate indices (NAOi and WEPAi) were obtained for each month of the study period and the corresponding monthly mean values for FI and soil moisture were compared considering differences between season, and field catchments.

The best model for explaining mean monthly FI was as a function of the WEPAi, allowing for differences between catchments and seasons with the differences between winter and summer being significant. For both seasons, a positive WEPAi had a negative response on FI; however, the divergence in slope between the two seasons was most likely due to a potentially greater range of soil moisture conditions in the summer compared to winter. Furthermore, nitrate export from grassland field-scale catchments could be predicted using the WEPAi, but prediction was slightly better with a more local measure of soil moisture.

Keywords: NAO, Western European Pressure Anomaly, flushing index, nitrogen

1. Introduction

While nutrients are critical to the functioning of waterbodies, excessive quantities often have unintended consequences, including eutrophication and subsequent harmful algal blooms in downstream systems (Turner and Rabalais, 2003; Conley et al., 2009). Nitrogen (N), primarily in the form of nitrate, is one such nutrient and is the predominant form of inorganic N lost from soils to aquatic systems. Here, losses are particularly associated with intensive agricultural systems e.g. (Scholefield et al., 1993; Heaton et al., 2012), with diffuse nutrient transfers from agricultural land often constituting the bulk of annual loads in river catchments (Smith et al., 2005). The mechanisms of how nitrate moves from soil into aquatic systems are well understood and depend upon factors such as soil type, structure, moisture and rainfall intensity (Barraclough, 1989). Rainfall events can be important periods for nitrate mobilisation (e.g. Smith and Kellman, 2011; Vaughan et al., 2017). Indeed, Royer et. al. (2006) found that in three agricultural catchments in east-central Illinois, U.S.A., nearly all nitrate export occurred when drainage discharge was ≥ median discharge, and extreme discharges (≥90th percentile) were responsible for >50% of the nitrate export. Therefore, it is important to understand the drivers for nitrate transfers associated with discharge from land driven by rainfall events.

In the past, understanding the biogeochemical signature of storm events has been a challenge because grab samples of drainage cannot fully capture the temporal dynamics across an entire hydrograph (Granger et al., 2010; Bieroza et al., 2014). Furthermore, it is virtually impossible to collect a sufficiently representative range of differing drainage events given the true nature of each event cannot be known *a priori*. However, with improvements in real-time sensor technologies, it has been possible to collect data at ever finer temporal resolutions which allows for the capture of more detailed changes in water chemistries that occur during such events (e.g. Burns et al., 2019; Speir et al., 2021). For example, Zimmer et. al. (2019) found that interannual riverine nitrate concentration-discharge relationships were different when using near continuous data compared to those using traditional discrete grab samples. Carey et al. (2014) found that, while annual flux estimates of nitrate in a catchment generated by continuous sensor deployment were like those generated by weekly and monthly grab samples, important differences in flux occurred at seasonal time scales which was missed by manual sampling. Such rich datasets can enable fundamental questions about the drivers for nutrient mobilisation and transport in the environment to be addressed.

Using high temporal resolution data, the concentration-discharge (C-Q) response for individual discharge events can be described through the calculation of the hysteresis index (HI) and flushing index (FI). The HI can provide information on source proximity, while the FI can provide information on the mechanistic behaviour (Speir et al., 2021). Discharge event nitrate responses can be both flushing (FI>1) and diluting (FI<1) and these differences can allow for different interpretations of the mechanisms of nitrate mobilisation (e.g. Webb and Walling, 1985; Liu et al., 2022; Granger et al., 2023). At larger catchment scales, temporal variations in the HI/FI may be lost due to the amalgamation of different sources, as well as variations in their proximities and connectivity to stream networks (Creed et al., 2015; Marinos et al., 2020). At smaller scales however, these temporal variations can often be more clearly discerned (Speir et al., 2021; Granger et al., 2023).

In western Europe, weather is strongly influenced by large scale atmospheric circulation over the North Atlantic, particularly during winter (Rodwell et al., 1999). Variations in pressure between the Azores High and Icelandic Low are known as the North Atlantic Oscillation (NAO) which has a strong influence on changes in the intensity of the jet stream (Woollings and Blackburn, 2012) which in turn affects the location and intensity of weather systems. The variability in the intensity between these large-scale pressure systems from the long-term mean can be expressed as an index (NAOi). In general, when the pressure difference is large the NAOi is positive, which leads to a strong jet stream and warmer, wetter, winters. When the pressure difference is small, the NAOi is negative, the jet stream is weak, and winters can be cooler and drier with more easterly air streams. However, the effects of the NAO do differ temporally and spatially (West et al., 2019). Recently, a new climate index has been developed by Castelle et. al. (2017) which is based on the sea level pressure gradient between stations in Ireland and the Canary Islands. The Western European Pressure Anomaly (WEPA) when in positive phase reflects a southward-shifted, intensified, Icelandic Low and Azores High surface pressure dipole. Work by Jalón-Rojas and Castelle (2021) has shown that, while the NAOi was still relevant in explaining precipitation variability in western Europe, the WEPA index (WEPAi) increased correlations with winter precipitation by up to 0.8, particularly in the UK and France.

In attempts to link large scale climatic processes and temporal changes in water quality, Monteith et. al. (2000) found that the variation in winter nitrate concentration in upland lakes and streams had a strong negative correlation with the NAOi. Mellander et. al. (2018) and Ulén et al. (2019) both found that the NAO can influence nitrogen and phosphorus losses from agricultural catchments. More recently Granger et. al. (2025) found that flow-weighted mean suspended sediment concentrations in agricultural drainage were more strongly linked to the WEPAi than the NAOi and that link was present at multiple scales. Given the importance that storm events can have in the elevated nitrate fluxes from catchments, an understanding of how large-scale climatic systems influence these exports, and the intermediary controls remains an extant evidence gap. The need to address this gap is also underscored by the increased stress on water regulating services delivered by agricultural land in the context of changing climate and extreme weather. To this end, we explore he link between nitrate mobilisation from agricultural land and large-scale climate systems as key drivers of water quality regulation. In this paper, we analyse a long-term (2012 – 2024), high frequency dataset of field scale nitrate concentration dynamics in rainfall driven drainage from a permanent grass pasture management system.

2. Methods

2.1. Field site

The North Wyke Farm Platform (NWFP) is described in detail by Orr et. al. (2016). In short, this experimental platform was established in 2010 in the southwest of England (Figure 1a). The climate in the region is described as temperate with a mean annual precipitation at North Wyke of 1040 mm

(1984-2013) with the majority falling in the winter (Dec – Feb). The NWFP comprises three 21 ha farmlets, each consisting of 5 hydrologically isolated field-scale catchments ranging in size from 1.6 to 8.1 ha. The soil belongs predominantly to two similar series; Hallsworth and Halstow (Harrod and Hogan, 2008) with the topsoil a slightly stony clay loam that overlies a mottled stony clay subsoil which is impermeable to water and is therefore seasonally waterlogged. Drainage water moves by surface and sub-surface lateral flow across the clay layer and is intercepted by a bounding drainage system at the plot edge. This water is then channelled to an outlet where Q and various physio-chemical properties are measures on a 15-minute timestep. One of the farmlet treatments is 'permanent pasture' and has remained an untilled grassland for over 30 years. This is currently managed through cattle and sheep grazing and silage production. The pasture typically receives up to 200 kg ha^{-1} of inorganic N and farmyard manure which is returned after winter housing. Phosphorus, potassium, and pH are all managed to grassland recommended indices (Agriculture and Horticulture Development Board, 2025). This study utilised the data collected from 2012-24 from the 5 field scale catchments of the permanent pasture treatment referred to hereafter as catchments FP4, FP5, FP6, FP12, and FP13 (Figure 1b; Table S1).

2.2. Hydrology and water chemistry measurements

Discharge (Q) from each of the catchments is currently measured using H type flumes which are engineered structures such that discharge can be determined through them by a known relationship between the height of the liquid within it at a known point. Until 2015 the depth of the water was determined using bubble meters (4230, Teledyne ISCO, U.S.A.). In 2015 these were replaced with pressure level sensors (OTT Hydrometry, U.K.). As the Q exported from agricultural land at this scale can be discontinuous, drainage water is collected and analysed by sensors in a flow cell to prevent sensors drying out. When Q>0.2 l s^{-1} water is pumped from a drainage sump to the flow cell where sensors collect various water physiochemical properties. However, when Q is low (Q<0.2 l s^{-1}) water is not pumped into the flow cell, and returned sensor measurements are discarded. Combined nitrate-N and nitrite-N (referred to as NO_3-N hereafter) concentrations are measured by a dedicated, self-cleaning, optical UV absorption sensor (NITRATAX Plus SC, Loveland, Colorado, USA). Dissolved NO_3-N absorbs UV light at wavelengths below 250 nm. The NO_3-N concentration is then calculated by passing UV light through the water in the by-pass flow cell and measuring the absorption using a 2-beam turbidity compensated photometer. The Nitratax UV absorption sensors remain *in situ* and are calibrated monthly in the field using a 2-point calibration. Sensor drift that may be due to lens contamination is checked prior to cleaning the instrument lenses and wiper blades. The instruments are serviced annually including a 3-point factory calibration.

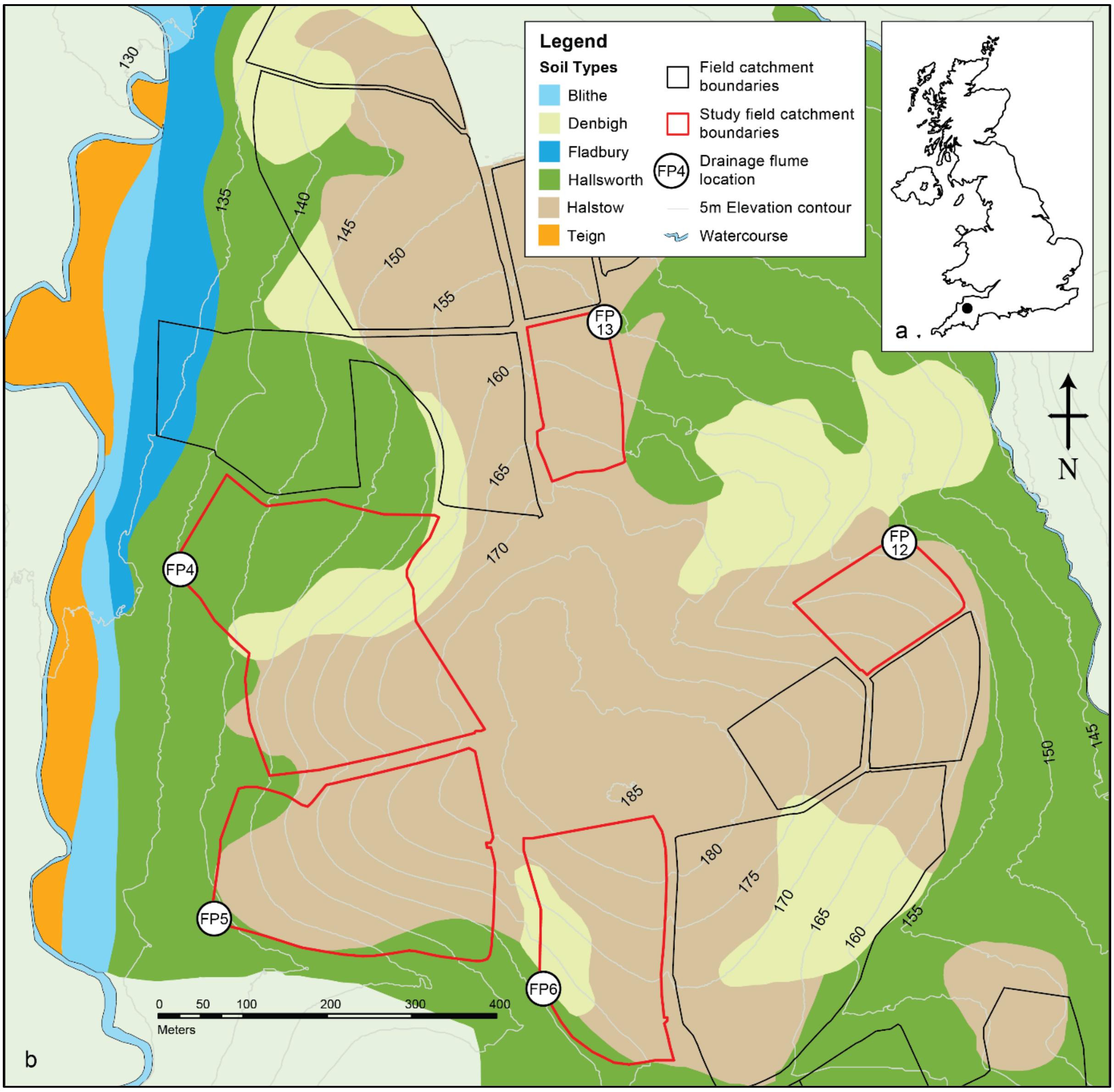


Figure 1. The North Wyke Farm Platform (a) location within the United Kingdom, and (b) the field-scale catchments (FP4, FP5, FP6, FP12, and FP13) used within this study.

2.3. Soil moisture measurements

A soil moisture sensor was sited in each of the field-scale catchments, consisting of an A723 addIT Series 4 telemetry unit and a SM1 combination soil moisture and temperature probe (Adcon, OTT HydroMet GmbH, Vienna, Austria) which measures soil moisture every 15 minutes using capacitance at a depth of 10 cm.

2.4. Calculation of FI

Rainfall event driven Q (hereafter described as ‘storm event/s’) were extracted from the 15-minute resolution Q data using the method described by Musolff et. al. (2021), in R (Ver 4.4.3), which facilitates automated separation of storm events. Briefly, a storm event was defined as starting when the Q increased by 20% within one hour and ending when the Q decreased and stabilized with a variation of <10%. Storm events defined by this process were then analysed and visually assessed, with previously defined separate events being reclassified if it was deemed that they were in fact one event with more than one peak Q.

Only storm events lasting ≥3 hours were used for the calculation of storm event FI. As this calculation only requires NO_3-N concentration data for the start of the defined storm event and at peak Q, storm events missing either value were identified and, where possible, missing values were manually infilled. This was done either through a simple interpolation using surrounding data, or by assuming the nearest existing value was the same as the missing value if that value was temporally close to the missing value and where NO_3-N did not appear to be in flux.

For each storm event which had ≥70% NO_3-N data available for its defined duration, the NO_3-N data was first normalised:

$$C_{iN} = \frac{C_i - C_{min}}{C_{max} - C_{min}}$$

where C_{iN} is the normalized NO_3-N concentrations corresponding to the i^{th} measured data and C_{min} and C_{max} are the event minimum and maximum NO_3-N concentrations, respectively. The FI was calculated using the following equation (Butturini et al., 2008):

$$FI = C_{Qpeak} - C_{Qstart}$$

Here, C_{Qstart} and C_{Qpeak} refer to normalised concentrations of NO_3-N at the beginning of the defined storm event and at the peak Q of the rising limb. The FI ranges from -1 to +1, with a negative FI value indicative of a dilution of NO_3-N concentrations on the rising limb, whereas a positive FI indicates a flushing effect with an increase in NO_3-N concentrations on the rising limb.

2.5. Climate data

Climate index data, as calculated as a monthly value were used. Time series of the station based North Atlantic Oscillation index (NAOi) extracted from the NSF National Centre for Atmospheric Research, Climate Analysis Section (https://ncar.ucar.edu/). The WEPAi data was calculated and provided by Castelle (personal communication).

2.6. Statistical analysis

Values of the two climate indices were obtained for each month from October 2012 to February 2024 inclusive. For each of the five field-scale catchments, corresponding arithmetic mean values for FI and % soil moisture were calculated. Months where there were no FI values obtained or no data available for soil moisture, were omitted from the modelled dataset. Months were additionally classified into four meteorological seasons (Winter: December-February, Spring: March-May, Summer: June-August, Autumn: September-November). A general linear regression modelling framework was used to explore possible models to explain the observed variability in the mean monthly FI and soil moisture (%) responses, as functions of the climate indices, soil moisture (when not the response), season, and catchment, the framework allowing the effect of explanatory variables to vary between seasons and between catchments. Our aim was to find parsimonious models that added insights. Initially simple regression models were fitted, but the most complex fitted models included a single quantitative explanatory variable (either climate index or soil moisture) and allowed both for separate intercept parameters for each catchment, and for separate intercept and slope parameters for each season. Models for mean monthly FI were also fitted that considered the impact of including both a climate index and soil moisture. The general linear regression modelling framework allows the comparison of related models through the additional sums of squares principle, identifying whether additional model complexity improves the model fit. All linear regression analyses were fitted using Genstat (VSN International, 2022). F-tests were used to assess for the importance of adding model complexity, with t-tests used to assess for differences in parameter values. The overall goodness-of-fit for each model was assessed using the adjusted coefficient of determination (percentage variance accounted for).

3. Results and Discussion

In western Europe, the weather effects of the NAO differ seasonally and spatially (e.g. West et al., 2019). However, in general, it presents itself in the winter as milder, wetter conditions when the NAOi is positive, and cooler, drier conditions when the NAOi is negative. Conversely, a positive NAOi in the summer tends to be associated with warmer, drier conditions, whereas a negative NAOi tends to bring wetter conditions (Hall and Hanna, 2018). The WEPA, however, does not have this seasonal variation, with a positive WEPAi being associated with warmer, wetter weather in both winter and summer (Castelle et al., 2017). The effect of large-scale climate patterns on the weather at the study site have already been examined by Granger et al. (2025) who have already shown that long-term monthly precipitation totals are strongly linked to the NAOi and WEPAi. Given the potential differences in the seasonal precipitation response of the NAOi, monthly rainfall totals were examined for winter months and summer months separately. The NAOi was found to be positively related to monthly winter precipitation totals ($r_{(160)} = 0.23$, $p<0.01$), but there was no relationship to summer rainfall totals. The WEPAi however, was found to be more strongly positively related to winter rainfall ($r_{(160)} = 0.77$, $p<0.001$) and also related to summer totals ($r_{(163)}$ – 0.64, $p<0.001$).

The hydrological dataset used from the NWFP spanned 125 months, from Oct 2012 to Feb 2024 inclusive, from which 3137 storm events were delineated across the 5 'permanent pasture' field-scale catchments. From the delineated storm events, 2809 were ≥3h in duration and had ≥70% NO_3-N data coverage and were selected for calculation of their FI (Table S1). Due to the seasonal, ephemeral, nature of the drainage in the study catchments, 59% of the storm events occur in winter (n=1668) with the highest median peak Q occurred in either winter or spring. Only 2% of the selected events occurred in the summer (n=54) which also had the lowest median peak Q.

All catchments produced a wide range of FI values which spanned diluting to flushing storm events. The mean FI from all catchments were all negative and ranged between -0.78 and -0.49 although these values are heavily skewed to winter storm event FI values (Figure 2). The FI range from all catchments had a minimum FI of -1.0 to a maximum of between +0.55 and +1.0 (Table S2). The months with the most negative mean FI values from the 5 catchments over the study period were typically December, January and February (i.e. winter), while the months which had the least negative FI were May, June and August. The month of June also had the least available storm event data such that no recorded storm events were available from either catchments FP12 or FP13, the two smallest field catchments and only one storm event was recorded in FP6. Dilution responses accounted for >92% of the storm event NO_3-N behaviours during the study period; however, as indicated above, there was a clear seasonal distribution in the diluting and flushing responses similar to that reported elsewhere (e.g. Webb and Walling, 1985; Granger et al., 2023). While dilution responses were always the dominant response, the prevalence of flushing responses increases noticeably from April, was highest over the summer months, and declined through the autumn (Figure 2). So, while the number of measured events dropped markedly over the summer, the proportion of those events which demonstrated a flushing response noticeably increased. It is possible that changes in agricultural management between the summer and winter are, in part, responsible for this increase in flushing responses. For example, animals are present on the land and nitrogen amendments are applied during the summer while both are absent during the winter however while interactions of nitrogen amendments and rainfall cannot be discounted, they are considered minimal. As stated previously within section 2.1, the timing of inorganic N amendments is done strategically such that 'incidental' losses (Preedy et al., 2001) are minimised. The main difference between summer and winter is simply that the soil inorganic N pool is larger, but also uptake of inorganic N is increased. For each of the 125 months of the study period for each of the 5 catchments, a mean FI was calculated based on the events that started within that month. The monthly mean FI could then be related to the monthly climate index, providing a realistic temporal scale to detect variation. Furthermore, it reduces the influence of any potential singular storm event that might contain an incidental NO_3-N loss, hence accounting for the finer temporal variability that the systems are likely to exhibit. Flushing index values were not available for all months due to various reasons, such as a lack of rainfall, or equipment downtime, such that the combined dataset across all catchments contained 388 values.

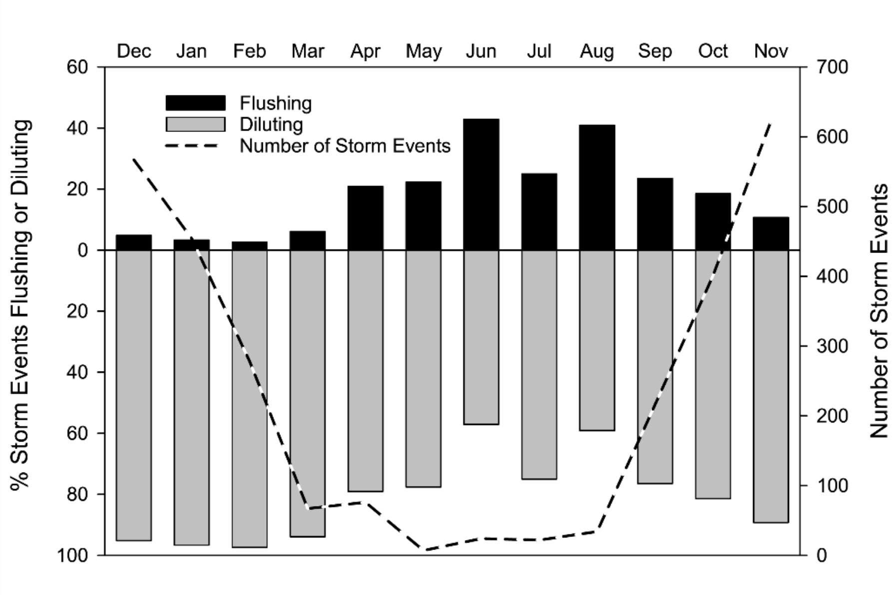


Figure 2. The number of storm events during each calendar month measured over the period of the study and the percentage of which that were classified as either diluting or flushing.

Simple linear regressions of monthly mean FI against either climate index (Figure 3) indicated a significant relationship for both the NAOi (t_{386}=3.84, p<0.001, 3.4% variance accounted for) and the WEPAi (t_{386}=2.04, p=0.009, 1.5% variance accounted for) with the NAOi being most significantly related but still only accounting for a small percentage of the total variance indicating other factors may be involved. However, given that FI can also differ seasonally (e.g. Liu et al., 2022; Granger et al., 2023), and that the expression of the NAOi in weather is known to vary seasonally (West et al., 2019), it is reasonable to examine the relationships in terms of seasonal variation and it is also important to allow for differences in the relationships between the 5 catchments.

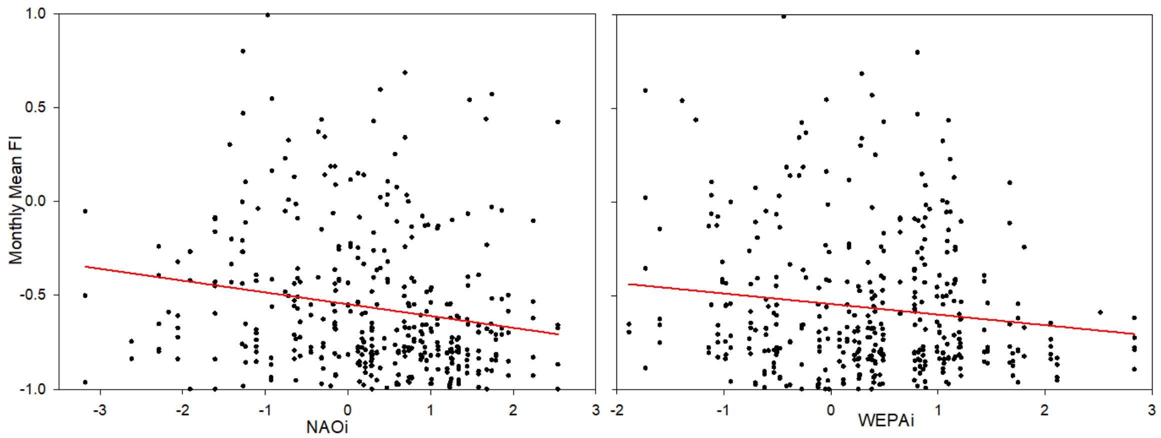


Figure 3. The relationship of the monthly mean NO_3-N FI data of storm events from 5 permanent grassland field-scale catchments and the NAOi or the WEPAi

Firstly, allowing only for separate intercept parameters for each season, but constraining the slopes to be common across seasons, significantly improved the model fit and increased the variance accounted for. This was more so for the WEPAi (F_{3383}=23.82, p<0.001, 16.4% variance accounted for) than for the NAOi (F_{3383}=18.71, p<0.001, 15.1% variance accounted for). However, it is unreasonable to constrain the slope of the models for season given the variability of the expression of the NAOi in weather during summer and winter. Also, allowing for separate slopes for each season gave a further significant improvement for the WEPAi (F_{3380}=3.45, p=0.017, 17.9% variance accounted for) but not for the NAOi

(F_{3380}=0.35, p=0.786, 14.7% variance accounted for). Secondly, because the data was obtained from 5 separate catchments, albeit under the same management regime, we anticipated that there will be some variation in the response between them and allowing for that variation may improve the model. This model~~,~~ allowed~~ing~~ for variation between catchments but~~,~~ was constrained to have a common slope, because there was no logical reason why the underlying relationships for monthly mean FI with either climate indices should vary between catchments~~ but allowed for different intercepts~~. Allowing different intercepts for each catchment means that the magnitude of the response could vary between the 5 field scale catchments as they were not all identical, and real-world environmental differences between the catchments, such as size, slope, presence or absence of livestock etc could lead to different outcomes. Comparing this model with the initial single line model (Figure 3) gave a highly significant improvement in model fit for both the NAOi (F_{4382}=11.58, p<0.001, 13.0% variance accounted for) and the WEPAi (F_{4382}=11.00, p<0.001, 10.8% variance accounted for). Thirdly, combining these two factors, and allowing both separate intercept and separate slope parameters for each season gave similar patterns of improvements in model fit as described previously where models did not allow for differences between catchments. Therefore, the best model for explaining mean monthly FI was as a function of the WEPAi, allowing for additive differences between catchments (separate intercepts) and both separate intercepts and separate slopes for each season (Figure 4a). The differences in both the intercepts and slopes between winter and summer were significant (intercept: t_{376}=7.86, p<0.001; slope: t_{376}=2.38, p=0.018), with the relationships for spring and autumn being intermediate between the two seasonal extremes.

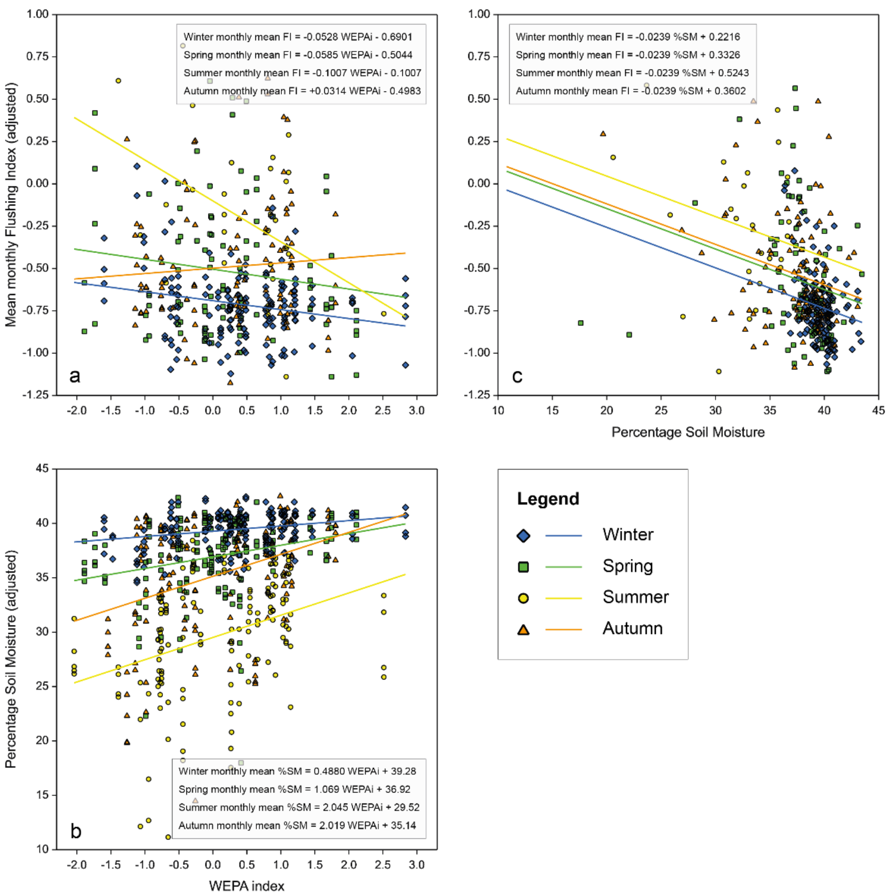


Figure 4. Best statistical model for (a) mean monthly FI, as a function of the WEPAi; (b) monthly mean soil moisture (%) as a function of the WEPAi; (c) monthly mean FI, as a function of the monthly mean soil moisture (%). All seasonal differences in parameter values have been adjusted for differences between the 5 field-scale catchments.

The seasonal differentiation of summer and winter FI, with summer FI elevated compared to that of winter, and with spring and autumn intermediate to these endmembers was the same as previously reported at this site for NO_3-N (Granger et al., 2023). This pattern has also been reported at other sites (Heathwaite and Bieroza, 2020) although not at others (Vaughan et al., 2017; Kincaid et al., 2020) and the catchment scale can be a relevant factor (Granger et al., 2023). In this study, while the actual slopes and intercepts of the models, fitted for the different seasons, are not particularly revealing as they simply reflect the conditions of this specific site over the study period, the significant difference in slope between winter and summer season is interesting. While for both seasons, a strongly positive WEPAi had a similarly strongly negative FI ($\approx$-0.75), the divergence between the seasons increases with an increasingly more negative WEPAi such that with a WEPAi of -2 the difference between summer and winter is $\approx$1, with a winter FI of $\approx$-0.5 and a summer FI of $\approx$+0.5. This seems likely due to the range of soil moisture conditions that each season may experience. In the winter, it is likely that the soil is at, or near, saturation all the time due to higher rainfall volumes and little or no evapotranspiration. This would mean that nearly all storm events would lead to a diluting FI response with low NO_3-N concentration rainwater having minimal interactions with what NO_3-N there was present in soil water. This low NO_3-N rainwater would then move rapidly over the saturated land surface and directly into drainage pathways causing a drop in NO_3-N concentrations. Even in months where the WEPAi was more positive, and rainfall was reduced, the overarching mechanism would not change dramatically as the soils would remain wet. In the summer, the ground conditions have more scope to vary, from very wet to very dry and so storm events could have very different FI responses as soils either wet up or dry within the same month, as different mechanisms for NO_3-N mobilisation predominate. Therefore, changes in the WEPAi potentially present themselves more dramatically in summer mean monthly FI. When very wet, the same dilution responses as occur in the winter should dominate, while drier soils would see storm event water move through the soil more, interacting with soil water and soil NO_3-N leading to flushing responses.

Given the importance of soil moisture in the mechanisms of NO_3-N delivery in our interpretation of the differences in seasonal response, it is prudent to examine this variable as a potential mediating factor in the relationships between the WEPAi and monthly mean FI. Monthly mean % soil moisture values were produced from soil moisture stations situated within each field-scale catchment. Over the study period, monthly means ranged from 40.1% in February (FP4) to 26.5% in June (FP13). A clear seasonal pattern of the highest soil moisture values occurring in the winter months, and the lowest in the summer months within all catchments can be clearly observed (Table S3). Simple linear regressions examining the mean monthly % soil moisture as a function of climate indices indicated a significant relationship; stronger for the WEPAi than for the NAOi, but again only explaining a relatively small percentage of the total variance (NAOi: t_{608}=3.11, p=0.002, 1.4% variance accounted for; WEPAi: t_{608}=7.21, p<0.001, 7.7% variance accounted for). There was no evidence for differences in intercepts between catchments (NAOi: F_{4604}=1.63, p=0.165; WEPAi: F_{4604}=1.74, p=0.140), but highly significant effects of allowing separate intercepts for each season (NAOi: F_{3605}=145.37, p<0.001, 42.4% variance accounted for: WEPAi: F_{3605}=148.92, p<0.001, 46.7% variance accounted for) and additionally for allowing separate slopes for each season (NAOi: F_{3602}=10.89, p<0.001, 45.1% variance accounted for; WEPAi: F_{3602}=4.65, p=0.003, 47.6% variance accounted for). Therefore, once again, the best fitting model for mean monthly % soil moisture was as a function of the WEPAi allowing for (non-significant) additive differences between catchments, and both separate intercepts and separate slopes for each season (Figure 4b).

The differences in both the intercepts and slopes between winter and summer were significant (intercept: t_{598}=20.76, p<0.001; slope: t_{598}=3.14, p=0.002), with the relationships for spring and autumn again being intermediate. This finding, that the WEPAi strongly and positively affects monthly mean soil moisture is not surprising given that a more positive WEPAi has been strongly linked to increased monthly rainfall totals (Granger et al., 2025). Also, the seasonal separation between winter and summer soil moisture is unsurprising given the differing rainfall totals in winter and summer. That the slopes between winter and summer differ significantly further indicates that the capacity for monthly mean soil moisture variability is greater in the summer than the winter when the ground conditions will nearly always be at or near saturation regardless of changes in the WEPAi. When the relationship between monthly mean soil moisture and monthly mean FI was examined, a highly significant relationship was found (t_{343}=7.71, p<0.001, 14.5% variance accounted for), far stronger than that seen for either the WEPAi or the NAOi as explanatory variables. There was significant evidence for differences in the intercepts between catchments (F_{4336}=6.09, p<0.001), and significant evidence for additional differences in intercept between seasons (F_{3336}=6.75, p<0.001), but no evidence for differences in slopes between seasons (F_{3333}=1.27, p=0.283). The best model accounted for 23.2% of the variance of the monthly mean FI (Figure 4c) and again, the difference between summer and winter was significant (intercept: t_{336}=3.94, p<0.001) with summer having the highest intercept and winter the lowest.

Adding a potential effect of the WEPAi to this model gave no additional effect (F_{1335}=0.69, p=0.408), with the percentage variance accounted for reducing slightly to 23.1%. In contrast, adding a potential effect of monthly mean soil moisture to the best model identified above for the effect of WEPAi, did produce a significant improvement in the fit (F_{1335}=16.80, p<0.001), increasing the percentage variance accounted for to 23.1%, as indicated for the above combined model. Therefore, the WEPAi has more effect on the monthly mean % soil moisture, which in turn exerts a greater effect on monthly mean FI than the WEPAi itself.

4. Conclusions

Nitrate losses from agricultural land remain a concern globally in the context of both private (loss of expensive nutrient additions) and public (water quality degradation and clean-up costs) goods. Most storm events measured from the grassland field-scale catchments occurred in the months between September to February, with the majority of these events exhibiting a negative, diluting, FI response. Over the March to August period, due to the decrease in rainfall totals over this period, far fewer storm events were recorded. The FI response of these events also changed with an increase in the proportion of storm events that exhibited a positive, flushing, FI although diluting events remained the common response.

Simple linear regression analysis found that the WEPAi appears to affect monthly mean NO_3-N FI more strongly than the NAOi. When differences between the 5 catchments and seasons were considered, it was found that there was a significantly different relationship between the summer FI response to the WEPAi and the winter response. Both seasons exhibited a negative response, with an increased WEPAi leading to a decreased, more diluting, FI. The main difference presented as a much steeper slope in the summer when compared to the winter indicating that the same positive change in WEPAi in the summer leads to a greater change in FI, towards a diluting response, than in the winter. When soil moisture was examined as a potential mediating factor in the relationship between climate indices and FI it was found that the WEPAi provided a better prediction of monthly mean soil moisture than the NAOi, allowing for differences between both catchments and season. There were ~~again~~ significant differences in intercept and slope between winter and summer responses with the slope of the summer response being steeper. This again indicates that the same positive change in the WEPAi leads to a greater increase in soil moisture content in the summer than in the winter. When examining the relationship between monthly mean soil moisture and monthly mean FI, this was found to be the best model for explaining variation in FI. The inclusion of the WEPAi did not improve the model and therefore could not be considered as mediating the effect of the WEPAi. The effects on FI present themselves most strongly in the summer rather than the winter, as soil moisture variability is much smaller in the winter than the summer, but most storm events in any given month are still likely to be negative FI, diluting events. Therefore, whilst NO_3-N export from the grassland field-scale catchments ~~can be~~were best predicted using a more local measure of soil moisture, this was only slightly better than models using ~~predicted using~~ the WEPAi, a measure calculated at a near global-scale. Where using the WEPAi over the slightly better measure of soil moisture is advantageous however is that soil moisture data is not widely available at the field scale and that the cost and maintenance of installing soil moisture monitoring networks would be prohibitive. ~~Prediction was slightly better with a local measure of soil moisture, although this variable requires substantially more resources for data collection. However, c~~Considerable variability remains around both relationships, indicating that other factors are involved which were not captured in our study. Furthermore, this study only examines one geographically localised dataset. To establish the predictive capabilities of the WEPAi on NO_3-N FI more widely, other datasets in different regions with differing environmental variables would need to be examined such that other environmental factors influencing NO_3-N export could be identified. The challenge here is then to build a dataset from a sufficiently diverse set of locations to be able to identify the key environmental variables influencing the responses. That said, given changing weather patterns and the need to build improved resilience for the water regulating services delivered by agricultural land, the work herein indicates that the WEPAi can provide a level of predictive capability for NO_3-N export at the field-scale. This work point to the challenge encapsulated in managing prolonged or changing periods of seasonal elevated soil moisture given its key role in linking climate patterns and NO_3-N export.

References

Agriculture and Horticulture Development Board, 2025. Nutrient Management Guide (RB209). https://ahdb.org.uk/nutrient-management-guide-rb209

Barraclough, D., 1989. A usable mechanistic model of nitrate leaching 1. The model. J. Soil Sci. 40, 543–554.

Bieroza, M.Z., Heathwaite, A.L., Mullinger, N.J., Keenan, P.O., 2014. Understanding nutrient biogeochemistry in agricultural catchments: the challenge of appropriate monitoring frequencies. Environ. Sci. Process. Impacts 16, 1676–1691.

Burns, D.A., Pellerin, B.A., Miller, M.P., Capel, P.D., Tesoriero, A.J., Duncan, J.M., 2019. Monitoring the riverine pulse: Applying high-frequency nitrate data to advance integrative understanding of biogeochemical and hydrological processes. Wiley Interdisciplinary Reviews-Water 6.

Butturini, A., Alvarez, M., Bernal, S., Vazquez, E., Sabater, F., 2008. Diversity and temporal sequences of forms of DOC and NO3-discharge responses in an intermittent stream: Predictable or random succession? J. Geophys. Res. (Biogeosci.) 113.

Carey, R.O., Wollheim, W.M., Mulukutla, G.K., Mineau, M.M., 2014. Characterizing Storm-Event Nitrate Fluxes in a Fifth Order Suburbanizing Watershed Using In Situ Sensors. Environ. Sci. Technol. 48, 7756–7765.

Castelle, B., Dodet, G., Masselink, G., Scott, T., 2017. A new climate index controlling winter wave activity along the Atlantic coast of Europe: The West Europe Pressure Anomaly. Geophys. Res. Lett. 44, 1384–1392.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling Eutrophication: Nitrogen and Phosphorus. Science 323, 1014–1015.

Creed, I.F., McKnight, D.M., Pellerin, B.A., Green, M.B., Bergamaschi, B.A., Aiken, G.R., Burns, D.A., Findlay, S.E.G., Shanley, J.B., Striegl, R.G., Aulenbach, B.T., Clow, D.W., Laudon, H., McGlynn, B.L., McGuire, K.J., Smith, R.A., Stackpoole, S.M., 2015. The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. Can. J. Fish. Aquat. Sci. 72, 1272–1285.

Granger, S.J., Hawkins, J.M.B., Bol, R., White, S.M., Naden, P., Old, G., Bilotta, G.S., Brazier, R.E., Macleod, C.J.A., Haygarth, P.M., 2010. High temporal resolution monitoring of multiple pollutant responses in drainage from an intensively managed grassland catchment caused by a summer storm. W. Air Soil Pollut. 205, 377–393.

Granger, S.J., Upadhayay, H.R., Castelle, B., Collins, A.L., 2025. The influence of large-scale climate patterns on sediment loss from agricultural land-exploration using an instrumented field and catchment scale platform. Environmental Research Letters 20.

Granger, S.J., Upadhayay, H.R., Collins, A.L., 2023. Hydro-chemical responses at different scales in a rural catchment, UK, and implications for managing the unintended consequences of agriculture. Environ. Res. 228, 115826.

Hall, R.J., Hanna, E., 2018. North Atlantic circulation indices: links with summer and winter UK temperature and precipitation and implications for seasonal forecasting. Int. J. Clim. 38, E660–E677.

Harrod, T.R., Hogan, D.V., 2008. The soils of North Wyke and Rowden. Unpublished report to North Wyke Research, revised edition of original report by T.R. Harrod,

Soil Survey of England and Wales (1981). North Wyke Research, Okehampton, Devon.
Heathwaite, A.L., Bieroza, M., 2020. Fingerprinting hydrological and biogeochemical drivers of freshwater quality. Hydrol. Process. 35.

Heaton, T.H.E., Stuart, M.E., Sapiano, M., Sultana, M.M., 2012. An isotope study of the sources of nitrate in Malta's groundwater. J. Hydrol. 414, 244–254.

Jalón-Rojas, I., Castelle, B., 2021. Climate Control of Multidecadal Variability in River Discharge and Precipitation in Western Europe. Water 13, 257.

Kincaid, D.W., Seybold, E.C., Adair, E.C., Bowden, W.B., Perdrial, J.N., Vaughan, M.C.H., Schroth, A.W., 2020. Land Use and Season Influence Event-Scale Nitrate and Soluble Reactive Phosphorus Exports and Export Stoichiometry from Headwater Catchments. Water Resour. Res. 56, e2020WR02736.

Liu, W.L., Tian, S.Y., Youssef, M.A., Birgand, F.P., Chescheir, G.M., 2022. Patterns of long-term variations of nitrate concentration - Stream discharge relationships for a drained agricultural watershed in Mid-western USA. J. Hydrol. 614.

Marinos, R.E., Van Meter, K.J., Basu, N.B., 2020. Is the River a Chemostat?: Scale Versus Land Use Controls on Nitrate Concentration-Discharge Dynamics in the Upper Mississippi River Basin. Geophys. Res. Lett. 47.

Mellander, P.E., Jordan, P., Bechmann, M., Fovet, O., Shore, M.M., McDonald, N.T., Gascuel-Odoux, C., 2018. Integrated climate-chemical indicators of diffuse pollution from land to water. Scientific Reports 8, 944.

Monteith, D.T., Evans, C.D., Reynolds, B., 2000. Are temporal variations in the nitrate content of UK upland freshwaters linked to the North Atlantic Oscillation? Hydrol. Process. 14, 1745–1749.

Musolff, A., Zhan, Q., Dupas, R., Minaudo, C., Fleckenstein, J.H., Rode, M., Dehaspe, J., Rinke, K., 2021. Spatial and Temporal Variability in Concentration-Discharge Relationships at the Event Scale. Water Resour. Res. 57.

Orr, R.J., Murray, P.J., Eyles, C.J., Blackwell, M.S.A., Cardenas, L.M., Collins, A.L., Dungait, J.A.J., Goulding, K.W.T., Griffith, B.A., Gurr, S.J., Harris, P., Hawkins, J.M.B., Misselbrook, T.H., Rawlings, C., Shepherd, A., Sint, H., Takahashi, T., Tozer, K.N., Whitmore, A.P., Wu, L., Lee, M.R.F., 2016. The North Wyke Farm Platform: effect of temperate grassland farming systems on soil moisture contents, runoff and associated water quality dynamics. Eur. J. Soil Sci. 67, 374–385.

Preedy, N., McTiernan, K., Matthews, R., Heathwaite, L., Haygarth, P., 2001. Rapid incidental phosphorus transfers from grassland. J. Environ. Qual. 30, 2105–2112.

Rodwell, M.J., Rowell, D.P., Folland, C.K., 1999. Oceanic forcing of the wintertime North Atlantic Oscillation and European climate. Nature 398, 320–323.

Royer, T.V., David, M.B., Gentry, L.E., 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. Environ. Sci. Technol. 40, 4126–4131.

Scholefield, D., Tyson, K.C., Garwood, E.A., Armstrong, A.C., Hawkins, J., Stone, A.C., 1993. Nitrate leaching from grazed lysimeters: effects of fertilizer input, field drainage, age of sward and patterns of weather. J. Soil Sci. 44, 601–613.

Smith, E.L., Kellman, L.M., 2011. Nitrate Loading and Isotopic Signatures in Subsurface Agricultural Drainage Systems. J. Environ. Qual. 40, 1257–1265.

Smith, R.V., Jordan, C., Annett, J.A., 2005. A phosphorus budget for Northern Ireland: inputs to inland and coastal waters. J. Hydrol. 304, 193–202.

Speir, S.L., Tank, J.L., Bieroza, M., Mahl, U.H., Royer, T.V., 2021. Storm size and hydrologic modification influence nitrate mobilization and transport in agricultural watersheds. Biogeochemistry 156, 319–334.

Turner, R.E., Rabalais, N.N., 2003. Linking landscape and water quality in the Mississippi river basin for 200 years. Bioscience 53, 563–572.

Ulén, B., Lewan, E., Kyllmar, K., Blomberg, M., Andersson, S., 2019. Impact of the North Atlantic Oscillation on Swedish Winter Climate and Nutrient Leaching. J. Environ. Qual. 48, 941–949.

Vaughan, M.C.H., Bowden, W.B., Shanley, J.B., Vermilyea, A., Sleeper, R., Gold, A.J., Pradhanang, S.M., Inamdar, S.P., Levia, D.F., Andres, A.S., Birgand, F., Schroth, A.W., 2017. High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. Water Resour. Res. 53, 5345–5363.

VSN International, 2022. Genstat for Windows 22nd Edition. VSN International, Hemel Hempstead, UK.

Webb, B.W., Walling, D.E., 1985. Nitrate behaviour in streamflow from a grassland catchment in Devon, U.K. Water Res. 19, 1005–1016.

West, H., Quinn, N., Horswell, M., 2019. Regional rainfall response to the North Atlantic Oscillation (NAO) across Great Britain. Hydrology Research 50, 1549–1563.

Woollings, T., Blackburn, M., 2012. The North Atlantic Jet Stream under Climate Change and Its Relation to the NAO and EA Patterns. J. Clim. 25, 886–902.

Zimmer, M.A., Pellerin, B., Burns, D.A., Petrochenkov, G., 2019. Temporal Variability in Nitrate-Discharge Relationships in Large Rivers as Revealed by High-Frequency Data. Water Resour. Res. 55, 973–989.

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