

Article

Patterns and Drivers of Groundwater and Stream Nitrate Concentrations in Intensively Managed Agricultural Catchments

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Abstract: The environmental loss of nitrogen in agricultural landscapes has pervasive consequences, including human health implications, eutrophication, loss of habitat biodiversity and greenhouse gas emissions. The efficacy of mitigation strategies designed to control or prevent nitrate contamination of waterbodies requires an understanding of catchment scale pressures and processes. Groundwater and stream nitrate concentrations fluctuate over temporal scales ranging from the daily to the decadal. Identifying spatiotemporal trends and dominant drivers of nitrate in water is challenging as the drivers are intertwined. The effects of agronomic, meteorological and hydrogeological drivers on groundwater and stream nitrate were investigated over seven years in two well-drained agricultural catchments, dominated by tillage and grassland farming, respectively. A significant positive temporal trend in nitrate concentration was observed in the tillage catchment, whereas no long-term trend was observed in the grassland catchment. Agronomic, meteorological and hydrogeological factors were significantly related to temporal nitrate changes across both catchments. Clearly identifying the drivers influencing temporal changes in nitrate concentrations is critical to improving water quality. The study highlighted that to reduce groundwater nitrate levels in areas of high risk (thin soils, low clay content and shallow groundwater), nitrogen applications need to be reduced and/or tailored, particularly at times of restricted crop growth.

Keywords: nitrate; multiple regression; agronomy; soil moisture deficit; groundwater vulnerability

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1. Introduction

Groundwater discharge of nitrate (NO_3^-) into rivers, lakes and transitional waterbodies has negative environmental consequences [1]. The European Union Water Framework Directive (WFD; 2000/60/EC) stipulates that all member state waterbodies must achieve at least “Good status” within set reporting deadlines (2015, 2021, 2027). In the Republic of Ireland, the ecological status of surface waters is assessed by evaluating the relative abundance of sensitive versus non-sensitive aquatic organisms, surface water physico-chemistry and hydro-morphology. As of 2018, 47% of Irish rivers, 50% of lakes and 62% of transitional waterbodies were characterised by the EPA (Environmental Protection Agency) as below Good status [2]. Currently, there is no environmental quality standard for NO_3^- in rivers. Nitrogen is considered the primary limiting nutrient in transitional and coastal systems for which a standard of 2.6 mgN/L applies (Irish Surface Water Regulations, SI 77 of 2019). Between 2015 and 2018, 23% of Irish rivers had an annual average stream nitrate concentration in excess of 2.7 mgN/L [2]. In addition to biological impacts, the negative effects of elevated waterborne NO_3^- on human health [3] and greenhouse gas emissions [4,5] are well documented.

In Ireland, the Nitrates Directive (91/676/EEC) forms the basis for the agricultural programme of measures (POMs) to achieve Water Framework Directive goals. The Nitrates Action Programme (NAP) is implemented by the Good Agricultural Practice Regulations (SI 40/2020), while Water Framework Directive Programmes of Measures are enacted through the Water Framework Directive River Basin Management Plan. The focus of the Nitrates Directive is to prevent agriculturally derived NO_3^- from polluting European surface and groundwater.

Groundwater and stream water quality fluctuates over various temporal scales ranging from daily to seasonal, annual and decadal [6–9]. Identifying a temporal trend in water quality or an “underlying rate of change”, as opposed to short term fluctuations or noise in the data, is challenging [10], as the parameters which govern these temporal patterns are often related within a hydrologic system. Several authors have examined the link between climate and NO_3^- occurrence [11–13]. Net soil mineralisation of nitrogen (N) represents the balance between gross mineralisation and immobilisation [14]. Dry conditions and associated increases in soil moisture deficit (SMD) have been linked to increased N mineralisation with subsequent re-wetting, resulting in NO_3^- leaching losses to groundwater [15–17]. According to Leiros et al. [18], a positive linear correlation exists between soil organic matter content, temperature and net soil N mineralisation rates. Morecroft et al. [19] describe a link between enhanced soil N mineralisation and nitrification rates during summer drought periods in the UK and river NO_3^- concentrations. Leaching occurs when there is an accumulation of NO_3^- in the soil profile, which coincides with or is followed by a period of high drainage [20]. Bende-Michel et al. [21] describe a correlation between stream NO_3^- concentrations and patterns of source availability and contribution. Hydrologically inactive periods following spring applications of organic matter followed by mineralisation, drainage and mobilization were cited as dominant factors.

Agricultural activity is a significant pressure affecting the ecological status of 53% of Irish rivers [2]. Applications of nitrogen, via manures, fertilisers and stock excretion, to agricultural landscapes are essential to replenish soil nutrient levels and maintain and/or increase farm productivity. The type of agronomic practice and resultant N applications influences the likelihood, quantity and timing of N leaching to groundwater and subsequent transport to rivers [22]. N applied as inorganic N is immediately available for plant uptake; however, once in NO_3^- form it is also highly mobile and susceptible to leaching under appropriate soil and climatic conditions [23]. Organic N (from slurries, manures, livestock faeces) is less readily leached than inorganic fertiliser N but can become incorporated into soil organic matter [24]. If soil organic matter is subject to mineralisation, it can act as a protracted nitrate source to watercourses long after initial application.

The leaching of substantial quantities of NO_3^- to groundwater is often associated with intensive tillage farming, particularly in hydrogeologically susceptible catchments. In cropping systems, cultivation is typically carried out in between crop harvests, leading to increased rates of soil organic N mineralisation [25]. Cultivation often results in land being left fallow for prolonged periods; when this is coincident with high recharge, NO_3^- leaching losses can occur [26,27]. N leaching losses from grassland are typically lower than tillage when expressed as a percentage of total N inputs. Grassland systems have a greater proportion of each year spent under permanent grass cover, a longer growing season, a denser root system and a lack of autumn cultivation. In an Irish context, the N load applied to intensive grassland systems is considerably higher than tillage. As such, substantial N losses to groundwater occur from grassland agriculture in hydrogeologically susceptible catchments. FracLEACH refers to the quantity of dissolved N leached from soil to groundwater expressed as a proportion of the total N load applied at the land surface [28]. McAleer et al. [28] calculated FracLEACH according to the Intergovernmental Panel on Climate Change (IPPC) methodology in each of the study catchments presented herein. FracLEACH percentages of 41 and 44% were found at two arable hillslopes versus 21 and 14% at two grassland hillslopes.

While agronomic loading and meteorological drivers act to control the temporal load of NO_3^- leached to groundwater, the hydrogeological and hydrogeochemical setting of the catchment controls the response of water quality to the NO_3^- load. Catchment-specific soil/subsoil and geological parameters influence the timing of the groundwater and stream response to leached NO_3^- [29–31]. Denitrification is widely regarded as the dominant NO_3^- removal mechanism in groundwater [32]. McAleer et al. [28] and Jahangir et al. [33] described high bedrock groundwater denitrification rates in different geological settings. NO_3^- removal was correlated to aquifer permeability, availability of bacterial energy sources and groundwater oxygen concentration. Soil and subsoil denitrification can also be an important process for removing substantial quantities of leached NO_3^- . Soil and subsoil denitrification is promoted under saturated soil conditions [23], locally anaerobic conditions within soil microsites in particulate organic matter [34], organic-rich zones of low permeability sediments [35] and/or biofilms [36].

In permeable catchments, the dominant delivery pathway for nitrate is via shallow and deeper groundwater pathways [37]. Mellander et al. [38] demonstrated the close linkage between stream NO_3^- concentration and shallow groundwater concentrations in both study catchments presented herein, estimating a groundwater-stream flow contribution of 73% and 77% in the Grassland and Arable catchments, respectively. Subsurface hydrological pathways dominate and exert a significant influence on stream water quality, while hydraulic gradients indicate that both catchment streams are gaining [28].

The evolution of groundwater and stream water quality over time involves a complex interplay between agronomic practices, catchment meteorology, hydrogeology and hydrology. The aim of this study was to elucidate the factors contributing to long-term temporal groundwater and stream NO_3^- variation. The specific objectives of the study were:

- (1) to identify a discernible long-term trend in water quality over a six-hydrological year (seven calendar year) monitoring period in two distinct agronomic and hydrogeological settings.
- (2) to elucidate the hydrogeological, agronomic and meteorological factors that contributed to spatial and temporal trends.

2. Materials and Methods

2.1. Study Catchments

This study was undertaken in two intensively managed agricultural catchments: an arable catchment (11.6 km²) in the south-east of Ireland and a grassland catchment (7.6 km²) in the south-west (Figures 1 and 2). Both catchments are monitored within the Agricultural Catchments Programme (ACP) and were identified as susceptible to N losses to groundwater and stream receptors. Farmers within each catchment agreed to participate in the ACP and supply agricultural advisors with nutrient management records. The two catchments have been the subject of several detailed research projects, ranging in focus from agronomic [39,40] to hydrological and hydrogeological [28,38,41–43].

The grassland catchment is dominated by typically free draining soils (Table 1) and subsoils, varying in thickness. The bedrock formations identified in the catchment include the Castlehaven Formation, the Toe Head Formation and the Old Head Formation; all are Devonian fine- to medium-grained sandstones with minor siltstone and mudstone. The Geological Society of Ireland [44] describes the majority of the catchment as a Locally Important Aquifer with Bedrock that is Moderately Productive only in Local Zones. Groundwater vulnerability [45] in the catchment ranges from low to extreme, with evidence of bedrock outcropping at the surface along the margins of the stream and in the northwest of the catchment.

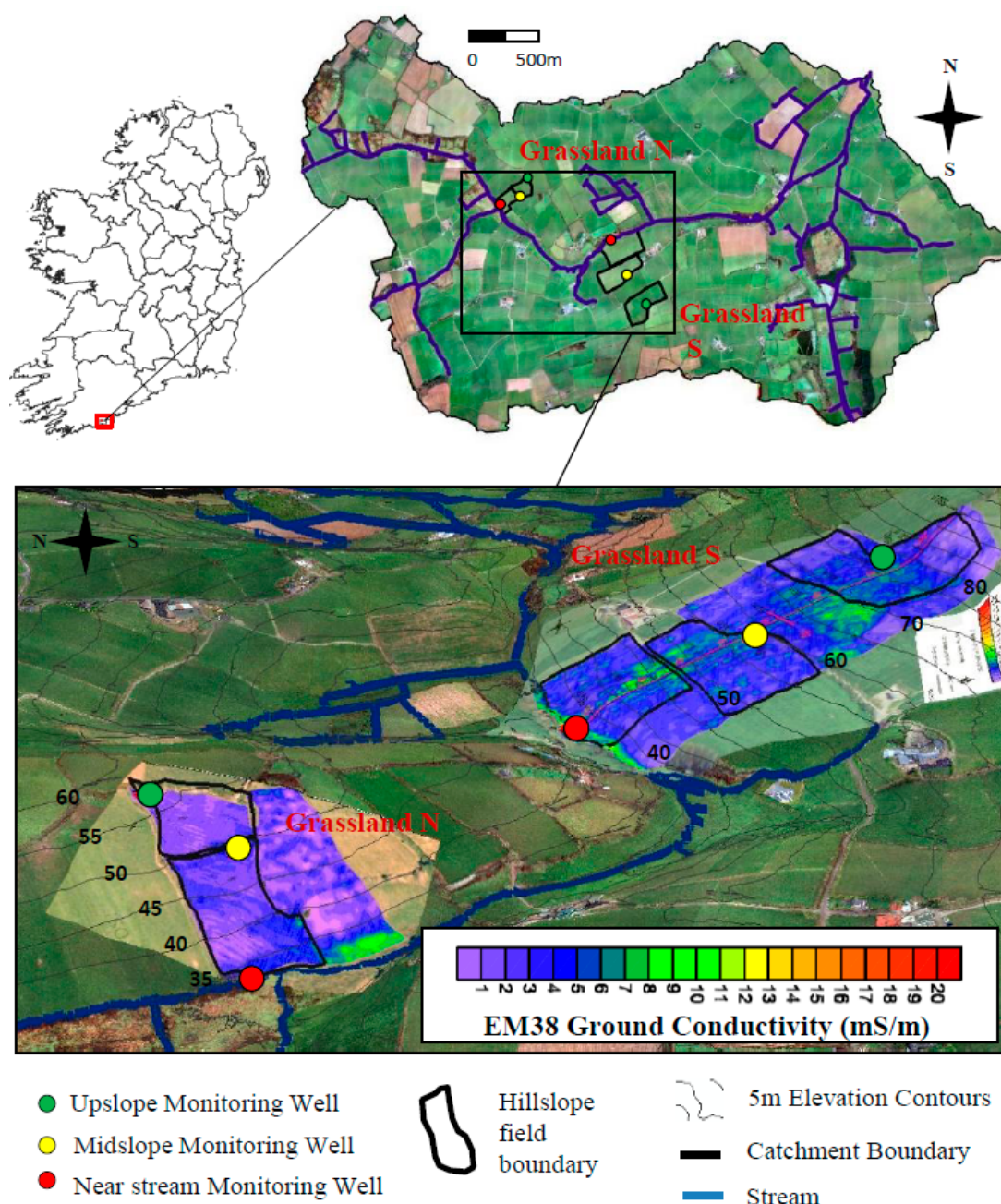


Figure 1. Grassland catchment area, hillslope field boundaries & monitoring wells and orthoimagery/electromagnetic ground conductivity (EM38) survey digitally grafted onto a catchment digital elevation model. High EM38 ground conductivity represents less permeable overburden, i.e., clay and/or waterlogged soil. The black field boundaries represent the areas where field specific agro-nomic information was available.

Table 1. Soil physical and soil chemical properties.

Site	Soil Type (WRB)	Sand (%)	Silt (%)	Clay (%)	Textural Class	Bulk Density (g/cm ³)	pH	Total C (%)	Total N (%)
Arable	Cambisol	38	35	27	Loam	1.14	6.7	2.95	0.29
Grassland	Cambisol	46	37	17	Loam	1.2	6.5	3.84	0.37

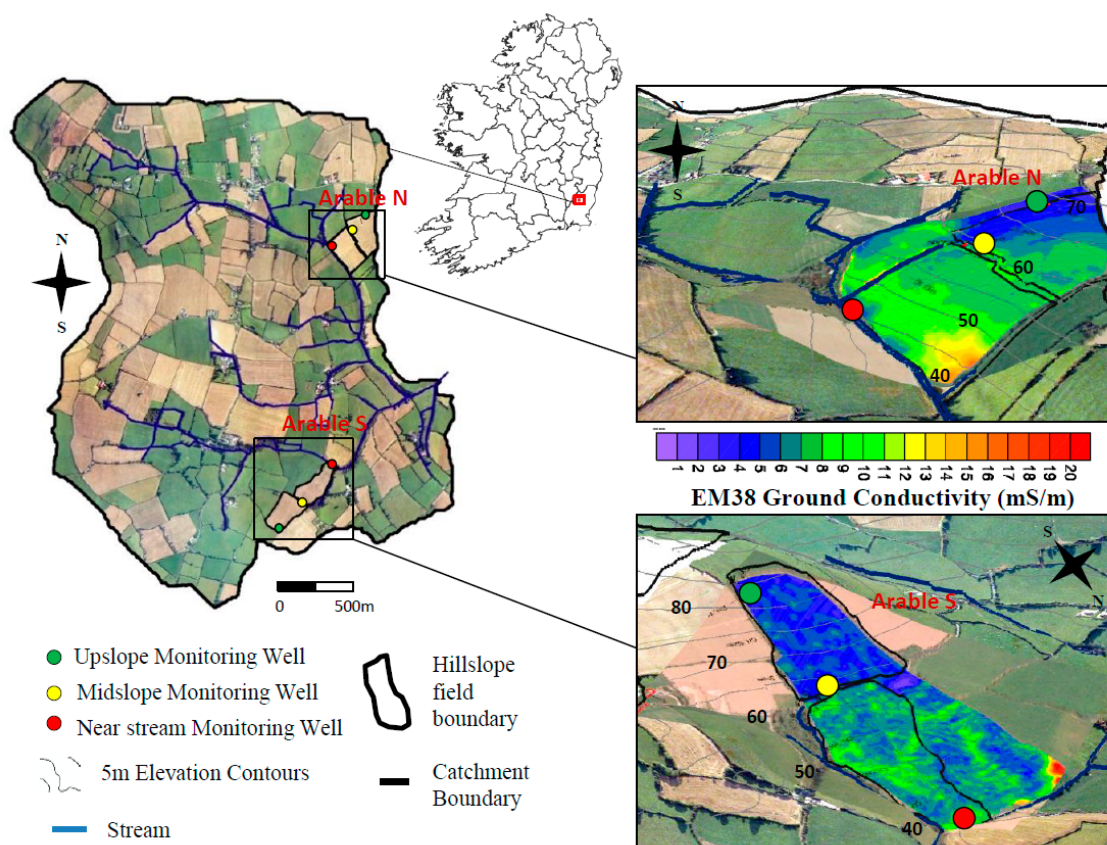


Figure 2. Arable catchment area, hillslope field boundaries, monitoring wells and orthomimagery/electromagnetic ground conductivity (EM38) survey digitally grafted onto a catchment digital elevation model. The black field boundaries represent the areas where field specific agronomic information was available.

The arable catchment is characterised by typically free draining soils (Table 1) and subsoils. Two dominant bedrock formations underlie the arable catchment: the Ballylane Formation and the Oaklands Formation; both formations comprise Ordovician siltstones and slates. The Oaklands formation is a Poor Aquifer with bedrock which is Generally Unproductive except for Local Zones [46]. The Ballylane Formation is a Locally Important Aquifer, with Moderate Productivity in Local Zones [46]. Groundwater vulnerability ranges from moderate to extreme; the majority of the catchment is highly vulnerable, with extreme vulnerability and outcropping of bedrock along the outer margins of the catchment.

The EPA conducts an ongoing Water Framework Directive monitoring programme in Ireland, whereby river water quality is assessed with reference to ecological criteria, hydromorphology and physico-chemical water quality [47]. The grassland catchment stream is a third order waterbody, described as the East Cruary_010. While the ecological status of the stream has not been measured, the stream discharges directly to the Argideen Estuary. The ecological status (2013–2018) of the estuary is Poor and winter losses of dissolved inorganic nitrogen are cited as a significant issue [47]. Agriculture and urban wastewater are the significant issues affecting the status of the estuary [47]. In both the grassland and arable catchments, elevated stream NO_3^- concentrations and the resultant N load losses to transitional waterbodies are a likely contributor to the Poor estuarine status described. The arable catchment stream is a third order tributary of the Slaney River, which is a sixth order river. The ecological status of the arable catchment tributary has not been classified by the EPA. The section of the Slaney River into which the arable catchment stream discharges (SLANEY_150), however, was characterised as Good status in 2013–2018 (EPA, 2019) [47]. While the Slaney River is characterised as Good ecological

status, the Slaney Estuary, into which the river discharges, has Poor status. Winter losses of dissolved inorganic nitrogen (nitrate, nitrite and ammonium) are cited as the significant issue affecting the estuary, with agriculture described as the most significant pressure.

2.2. Monitoring Infrastructure and Data Collection

Each of the study catchments contains two instrumented hillslopes of varying length and geometry, chosen to be representative of the upstream sub-catchments; the four hillslopes are described as *Grassland N*, *Grassland S*, *Arable N* and *Arable S*. The N and S notation simply denotes geographical location within each catchment (north versus south). Multilevel monitoring wells were installed at the top, middle and bottom of each hillslope (Figures 1 and 2). Twelve piezometers in total were targeted to intercept shallow groundwater pathways between 2 and 19 metres below ground level (m BGL). Screened sections ranged in length between one and four metres and intersected subsoil, fractured bedrock and bedrock layers (Table 2).

Table 2. Groundwater monitoring points used in the study: location, depth and lithology.

Grassland Catchment				
Hillslope Zone	<i>Grassland N</i>		<i>Grassland S</i>	
	^a Well screen	Lithology	^a Well screen	Lithology
Upslope	7–10	Bedrock	13–16	Bedrock
Midslope	4–7	^c Fractured rock	10.5–13.5	Bedrock
Near stream	2–3.5	^b Subsoil	4–7	^c Fractured rock
Arable Catchment				
Hillslope Zone	<i>Arable N</i>		<i>Arable S</i>	
	^a Well screen	Lithology	^a Well screen	Lithology
Upslope	12–15	Bedrock	16–19	Bedrock
Midslope	1–4	Bedrock	10.5–13.5	^c Fractured rock
Near stream	1–4	^b Subsoil	3.5–6.5	^c Fractured rock

^a Well screen: depth of top and bottom of well screen in m BGL. ^b Subsoil: refers to Quaternary deposits. ^c Fractured rock: enhanced permeability in the upper horizons due to weathering.

McAleer et al. [28] carried out a comprehensive hydrogeological and hydro chemical analysis of the groundwater in both study catchments, including the provision of detailed geological cross sections and measurements of hydraulic conductivity within each geological layer. Results indicated significant bedrock denitrification in low oxygen (<1–3.5 mg/L) conditions. Bedrock horizons that exhibited low dissolved oxygen and significant denitrification were omitted from the work presented herein. Instead, the investigation focusses on the shallow groundwater pathways, which are vulnerable to nitrate leaching and provide the bulk of streamflow. The average dissolved oxygen concentrations in the arable and grassland groundwater presented in this study were 5.8 and 9.5 mg/L, respectively.

Shallow groundwater and stream samples were collected every month over a seven-calendar year period (2010–2016). The samples were analysed for total oxidised nitrogen (NO_3^- and nitrite (NO_2^-)) by a Aquakem 600 Discrete Analyser (Aquakem 600 A, 01621 Vantaa, Finland), following the hydrazine reduction method. Figures 1 and 2 illustrate the location of the hillslopes within each catchment, monitoring well locations, orthoimagery and electromagnetic (EM) ground conductivity. EM ground conductivity measures the capacity of soil and subsoil to conduct an electrical current. The higher the conductivity, the more clay and organic particles in the soil. Clayey soils drain slowly and as such have a high relative moisture content, further increasing EM conductivity.

Each hillslope intersects with a stream at its base, which acts as a receptor for flow and hydro-geochemical processes. Both catchments are freely draining and represent high-risk areas to declining groundwater and surface water quality as a result of NO_3^- leaching and subsurface transport.

2.3. Agronomy

The Grassland catchment is dominated (83%) by permanent grassland, which is rotationally grazed from February to November and/or removed and ensiled as winter forage. The majority of the grassland area was utilised by intensive dairy production with an average (catchment) livestock density of 2.01 livestock units (LU) ha⁻¹ (equivalent to 171.5 kg organic N ha⁻¹). At least one-third of the catchment area is occupied by farmers that avail of the derogation under the E.U. Nitrates Directive to farm at livestock densities above 170 kg N ha⁻¹. In the arable catchment, 72% of the utilisable agricultural area is tillage. The tillage area breakdown is dominated by spring barley (48%), followed by winter barley (8.5%), winter wheat (7%) and winter oilseed rape (7%), with the remaining 1.5% tillage land area occupied by fodder beet, potatoes and maize. The ploughing and cultivation of the spring crops takes place between February and April, when soil conditions allow. The agricultural management timeframes in the grassland and arable catchments are presented in Table 3. All chemical fertiliser and organic N (manures and nitrogen deposited by grazing livestock) applications were recorded. The total quantity of organic nitrogen applied was divided by an availability factor (European Union Good Agricultural Practice for Protection of Waters Regulations, 2014). The total applied N was calculated as the sum of inorganic N and organic N.

Table 3. Agricultural management timeframes in the arable and grassland catchments.

Year	J	F	M	A	M	J	J	A	S	O	N	D
<u>Arable catchment</u>												
Ploughing—spring crops												
Sowing—spring crops												
Spring N fertilizer applications												
Ploughing—winter crops												
Sowing—winter crops												
Winter N fertilizer applications												
Tillage harvest												
Cover crops												
<u>Grassland catchment</u>												
Grazing grass												
Grassland N fertilizer application												
Grass Silage												
Slurry applications												
High application rates												
Lower application rates												

2.4. Meteorology

Local weather parameters were recorded at 10 min intervals throughout the monitoring period (2010–2016) by a weather station (BWS200, Campbell Scientific) located in the central lowlands of each study catchment. A secondary rain gauge (ARG-100) was positioned in the uplands of each catchment. The compiled weather parameters dataset included daily minimum, maximum and average values of temperature (°C), total rainfall (mm/day), 2 m wind speed (m/s) and solar radiation (W/m²).

Daily soil moisture deficit (SMD) was calculated for grassland and tillage scenarios using the Schulte et al. [48] and Premrov et al. [49] methods, respectively. These water mass balance models are modifications of the FAO-UNESCO reference crop evapotranspiration method [50] calibrated for Irish soil drainage conditions. Effective rainfall (mm/day) was calculated in daily time steps from total rainfall, evapotranspiration and SMD data.

2.5. Statistical Approach

Overall temporal trends in catchment NO₃⁻ concentrations were tested using a linear trend analysis. The General Linear Model procedure in Statistical Analysis System (SAS) version 9.4 was utilised as shown in previous studies [8]. The NO₃⁻ concentration data for

the trend analysis (2010–2016) were annualised: NO_3^- concentrations at each groundwater piezometer and hillslope stream sampling point were averaged over a calendar year, through which a temporal trend was fitted. Given the close linkage between stream NO_3^- concentration and shallow groundwater concentrations in both study catchments, the streams were included in the statistical analysis. In order to identify the drivers affecting catchment NO_3^- trends, a multiple linear regression approach with automatic parameter selection was undertaken. The effects of agronomic, meteorological and hydrogeological drivers (Table 4) on groundwater NO_3^- concentrations were estimated from 2010–2016.

Table 4. Agronomic, meteorological and hydrogeological variables interrogated in the regression.

Category	Explanatory variable	Unit	Description	Range (Grassland)	Range (Arable)
Agronomic variables	Inorganic N	(kg N ha^{-1})	Annual inputs of inorganic fertiliser	204–324	108–158
	Organic N		Annual inputs of slurry/manure	0–121	0–47
	Stocking N		Annual inputs of organic N from stock	92–194	0
	Total applied N		Total N application (chemical N + organic N + stocking N)	341–516	104–186
Meteorological variables	Total rainfall	(mm)	Total rainfall	1003.2–1535.2	845.0–1175.0
	SMD	(mm)	Soil moisture deficit.	0–72.9	0–43.7
	Effective rainfall	(mm)	Total rainfall—actual evapotranspiration—SMD	484.0–903.0	397.9–706.3
Hydrogeological variables	Watertable elevation	(maOD)	Monthly water table elevation above Ordnance Datum	25.4–65.2	38.8–85.1
	Ground elevation	(maOD)	Ground elevation of each piezometer above Ordnance Datum	25.8–70.8	39.8–85.4
	First rock appearance	(m BGL)	First rock appearance (m BGL)	1.4–7.3	2.8–4.0
	Piezometer top	(maOD)	Top of each piezometer well screen above Ordnance Datum	21.8–57.8	36.3–78.4
	Piezometer bottom	(maOD)	Bottom of each piezometer well screen above Ordnance Datum	18.8–54.8	33.3–74.4
	Well screen length	(m)	Length of aquifer screened by piezometer	1.5–3	3–4
	Total GW depth	(m)	Total depth of each piezometer from ground surface to bottom of screen	3.5–16	4–19
	EM ground conductivity	(ms/m)	EM 38 electrical conductivity at each piezometer location (Figures 1 and 2)	3–12	1–12

The responses in groundwater NO_3^- concentrations over a fixed six-month period of each hydrological year (October 1st to September 30th) were integrated at each piezometer and then regressed on driver variables that were averaged over a period preceding the measured NO_3^- response. The regression allowed two-way interactions between all driver variables of interest. Per catchment therefore, 36 integrated NO_3^- responses (six piezometers $\times$ six years) versus each integrated explanatory driver were simultaneously regressed with the piezometers providing the variation for the model. In all cases examined, the GLMSELECT procedure in SAS 9.4 (SAS, 2014) was used to select driver variables that were associated with the NO_3^- response. The final models were fitted with the MIXED procedure in SAS to make predictions and plots using the PLM and SGPLOT procedures.

The fixed six-month integration period of the groundwater NO_3^- response was October to March of each hydrological year; the response period was chosen to capture the main hydrologically active time of each year when groundwater was most vulnerable to NO_3^- leaching. This six-month integration period incorporated the mean travel time from soil surface to groundwater at the two hillslopes, which ranged from one month to thirteen months [51], and was similar to that used by Huebsch et al. [8]. The agronomic data was provided by the farmers on an annual basis; the explanatory driver integration period was,

therefore, one calendar year. In practice, however, the timings of application throughout a given year are demonstrated in Table 3. The hydrogeological parameters interrogated in the model were fixed variables. The length of the meteorological driver integration period varied from four to nine months. These integration periods were extended further back in time to see which driver period provided the best explanation of the groundwater NO_3^- responses.

To test for the effect of a delayed response of groundwater NO_3^- to explanatory drivers, a lag time of zero to five months was incorporated into the model. For a lag of one month, for example, the explanatory driver integration period would end one month before the beginning of the NO_3^- response period. The model interrogated all possible combinations of integration period and lag at each piezometer. There was no evidence that varying the lag time at each piezometer had any effect on the significance of the regression. The term “zero lag” is used with caution. Given that both the explanatory drivers and the NO_3^- responses were integrated over six-month periods, there exists an inherent lag of between zero and 12 months built into the model. Combining the maximum driver integration period of nine months, the maximum lag period of five months and the six-month NO_3^- integration period shows that the longest possible relationship between cause and effect interrogated during the multiple regression was 20 months. Table 5 illustrates the range of driver integration and lag periods, the best fit model driver periods and the NO_3^- response period.

Table 5. Range of modelled driver and response integration periods over two hydrological years.

	Hydrological Year 1												Hydrological Year 2											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Agronomic drivers: Annualised per calendar year																								
Meteorological drivers:																								
Four-month driver integration																								
Nine-month driver integration																								
Six-month driver integration incorporating maximum lag																								
* Six-month driver integration (zero lag)																								
NO_3^- recharge (response) period																								

Green box shows the range of months over which agronomic drivers were annualised. Grey boxes (dark shade) show the range of integration periods tested for meteorological drivers within the model. Light grey box describes the maximum lag period trialed in the model. * Blue box shows the six-month integration period for meteorological drivers, which provided the best fit to the data. Red box shows the six-month integration period for the NO_3^- response in groundwater and streams.

Three multiple regression models were created: a joint model for catchments with catchment as an explanatory factor and a separate model for each catchment. The joint model datasets provided the regression with a wider range of results to identify trends and drivers. Interactions between all explanatory variables, including catchment as a factor, were tested. The only significant interactions that were found were two-way interactions involving catchment. In those cases, where required and practicable, separate models were fitted for each catchment. McAleer et al. [28] showed that the hydro-geochemical signature of both catchments differed substantially. Drivers that were not significant in the joint catchment model may be significant to a specific catchment only.

3. Results

3.1. Groundwater and Stream NO_3^- Concentrations

High level trends in groundwater and stream NO_3^- concentrations are shown in Figure 3 for both the grassland and arable catchments. A linear trend line was fitted through the mean annual groundwater and stream NO_3^- concentrations for each catchment.

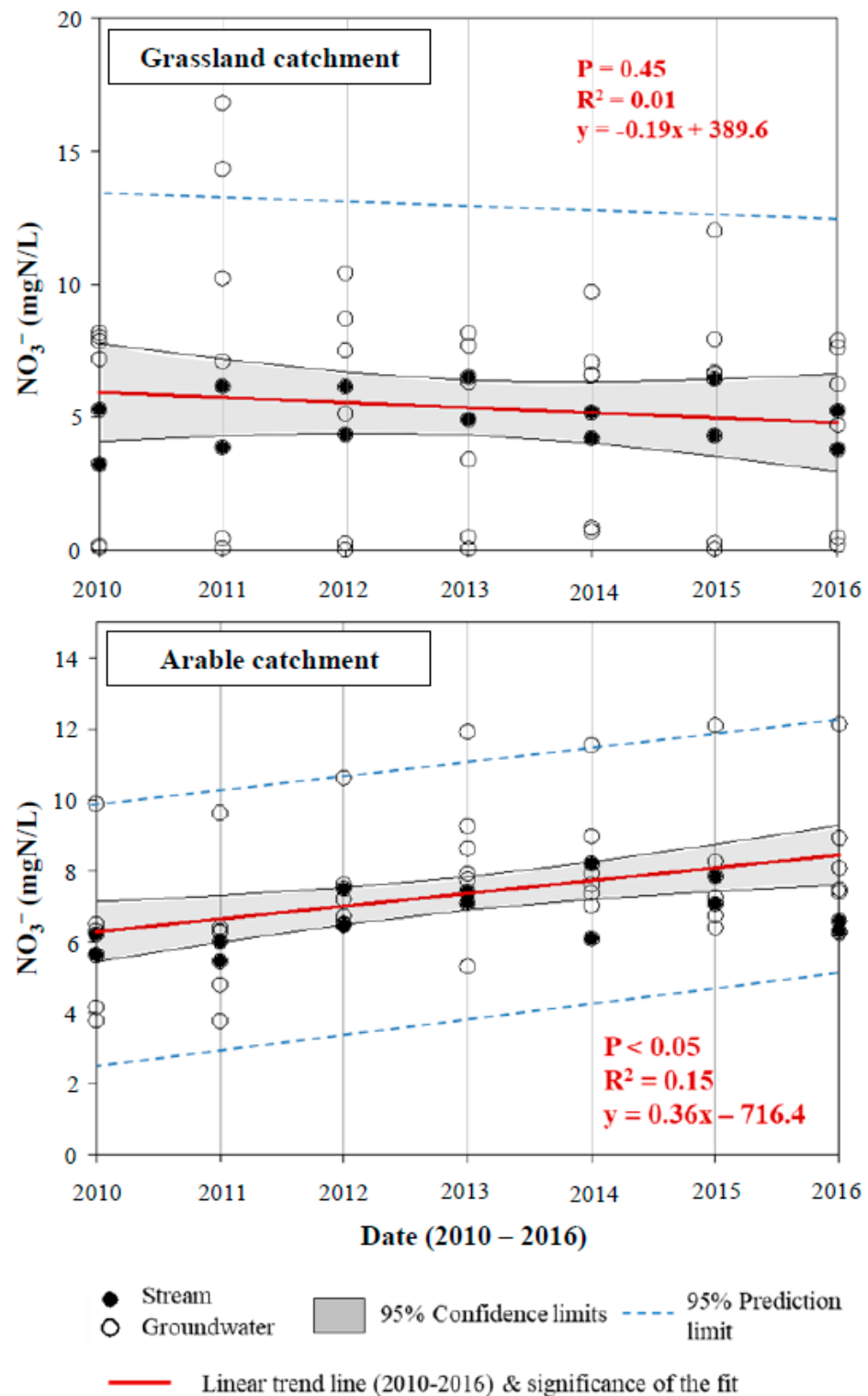


Figure 3. Grassland and arable catchment groundwater NO_3^- trends over time (2010 to 2016). The grassland catchment trend analysis includes all data from both the *Grassland N* and *Grassland S* hillslopes. The arable catchment trend analysis includes all data from both the *Arable N* and *Arable S* hillslopes. Open circles signify the mean annual groundwater NO_3^- concentration for each piezometer. Closed black circles represent the mean annual stream NO_3^- at the base of each hillslope. The trend line signifies the mean catchment NO_3^- concentration over time with the grey area representing the 95% confidence limits and the dotted lines signifying the 95% prediction limits.

Average annual groundwater NO_3^- concentrations (2010–2016) in the arable catchment were significantly greater ($p < 0.001$) than in the grassland catchment. Similarly, the average annual stream NO_3^- concentrations were also significantly higher ($p < 0.001$). Groundwater and stream NO_3^- concentration data from both catchments were compared against relevant environmental thresholds, including the European drinking water standard (DWS) of 11.3 mgN/L (Irish Drinking Water Regulations implementing the EU Drinking Water Directive (SI 122 of 2014)), the groundwater threshold value (GTV) of 8.46 mgN/L (Irish Groundwater Regulations implementing the EU Groundwater Directive (SI 366 of 2016)) and an estuarine water quality standard ($^{\text{est}}$ EQS) of 2.6 mgN/L (Irish Surface Water Regulations implementing the Water Framework Directive, SI 77 of 2019). The grassland catchment stream discharges directly to the Argideen Estuary, while the arable catchment stream flows into the River Slaney, which enters the Slaney Estuary. As such, the estuarine standard is deemed an appropriate threshold for stream water quality at each location.

In the grassland catchment, the spatiotemporal (2010–2016) mean groundwater NO_3^- concentration of 5.6 mgN/L was below the groundwater threshold value of 8.46 mgN/L. The average 2010–2016 stream NO_3^- concentration of 5.0 mgN/L exceeded the estuarine water quality standard of 2.6 mgN/L by a factor of almost two. Measured groundwater NO_3^- in the catchment showed variability over time and between hillslope locations and sample depths (coefficient of variation CV: 82%). Stream concentrations exhibited less temporal variation (CV: 30%). Despite substantial variability, particularly in groundwater NO_3^- , no statistically significant temporal trend was identified in the streams or groundwater of the Grassland catchment ($p = 0.45$).

The mean 2010–2016 groundwater NO_3^- concentration of 7.8 mgN/L in the Arable catchment was below the groundwater threshold value. The average stream NO_3^- concentration was 7.0 mgN/L and exceeded the estuarine threshold by factor of 2.7. Both groundwater and stream NO_3^- concentrations showed less temporal variability than the Grassland catchment with CVs of 27% and 19%, respectively. A significant, albeit weak, ($R^2 = 0.15$) positive trend was identified in the arable catchment, with NO_3^- concentrations significantly increasing over the seven-year period ($p < 0.05$).

High level trends, averaged both within and between the two study catchments, were shown in Figure 3. The higher resolution monthly distribution of shallow groundwater and stream NO_3^- from 2010 to 2016 at the Grassland hillslopes is illustrated in Figure 4. Stream and groundwater NO_3^- concentrations are plotted against N inputs, effective rainfall and soil moisture deficit (SMD). Patterns in groundwater NO_3^- were not synchronised between hillslopes or hillslope zones; to identify an overarching seasonality was difficult. In general terms, groundwater and stream NO_3^- concentrations appeared to be lower during summer months, with peaks typically occurring during winter and spring. Groundwater NO_3^- occurrence was highly variable in both space and time, ranging from 0 to 23.9 mgN/L; the 23.9 mgN/L value is an almost three-fold exceedance of the groundwater threshold value and over twice the drinking water standard of 11.3 mgN/L. Peak groundwater NO_3^- concentrations were measured in March 2011, following a rising pattern from October 2010 onwards, in the fractured bedrock and subsoil of the midslope and near stream monitoring wells of the *Grassland N* hillslope (Figure 4).

Following the March NO_3^- peaks, concentrations in the midslope and near stream zones typically declined throughout 2011 and 2012. In March 2011, a comparable peak (21.8 mgN/L) was also detected in the near-stream shallow groundwater of *Grassland N*. Smaller NO_3^- peaks in the near-stream shallow groundwater were measured in December 2011, February 2014 and May 2015. The high groundwater NO_3^- concentrations in the grassland catchment hillslopes corresponded to high stream NO_3^- , however, stream nitrate concentrations were substantially lower than shallow groundwater.

The estuarine threshold of 2.6 mgN/L was exceeded on 96% of sampling occasions in the streams of both hillslopes. Temporal peaks in stream nitrate mostly closely reflected the temporal pattern of the near-stream shallow groundwater. Highest stream NO_3^-

concentrations typically occurred in October, November and January, however there were also large occasional peaks in May and July.

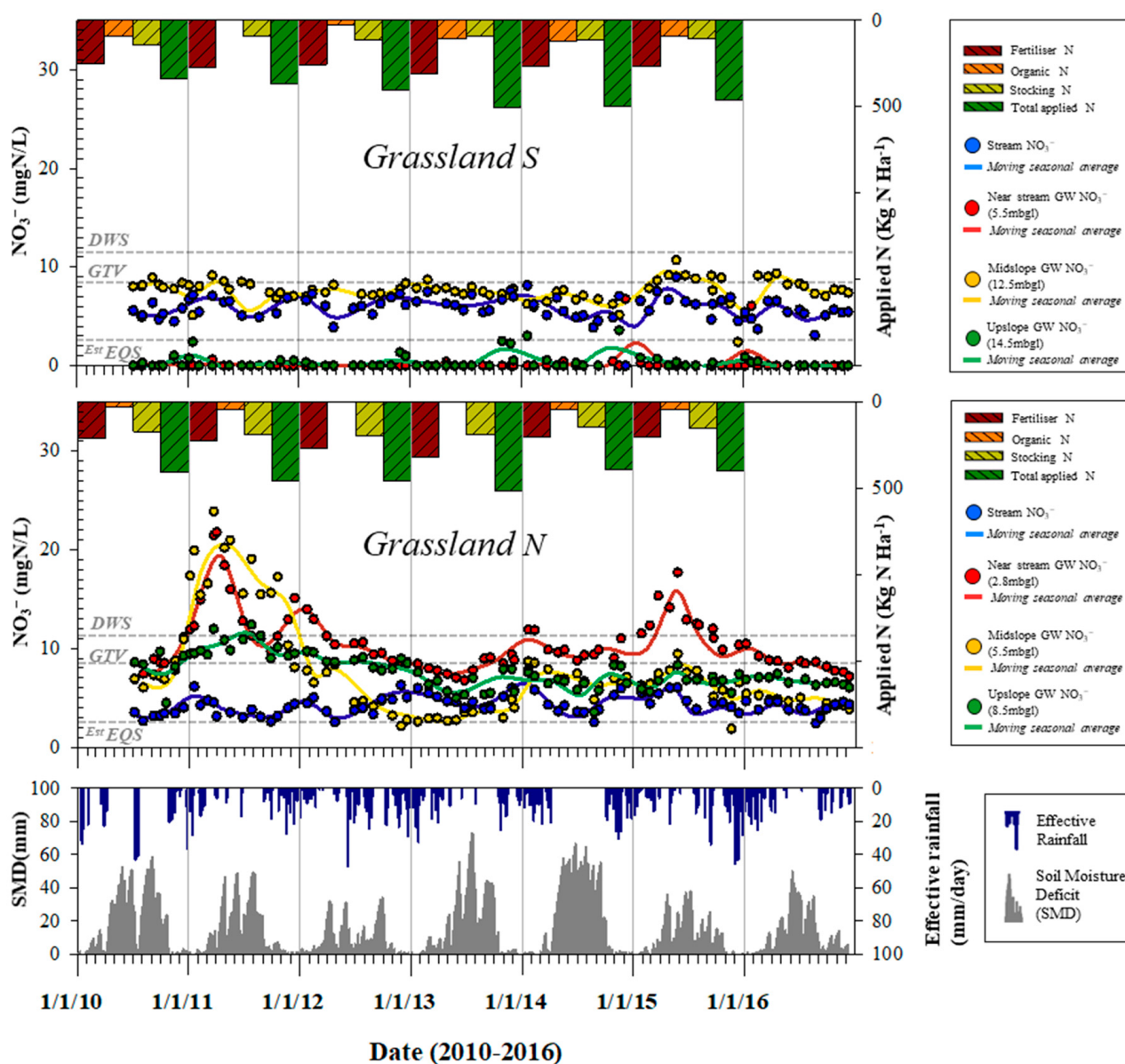


Figure 4. Grassland hillslope temporal trends in groundwater and stream NO_3^- , effective rainfall, soil moisture deficit and nitrogen application from 2010 to 2016.

The monthly distribution of shallow groundwater and stream NO_3^- from 2010 to 2016 at the arable catchment hillslopes (*Arable N* and *Arable S*) is illustrated in Figure 5. Groundwater NO_3^- occurrence was spatially more uniform as compared to the grassland catchment but exhibited temporal variation. The 2010–2016 average groundwater NO_3^- concentration of 8.83 mgN/L at the *Arable N* hillslope exceeded the groundwater threshold value of 8.46 mgN/L. The highest seven-year average groundwater NO_3^- concentration (11.2 mgN/L) was measured in the upslope shallow groundwater of the *Arable N* hillslope. NO_3^- concentrations occurred in March 2011, April 2013, October 2013, November 2014, October 2015 and October 2016.

The highest arable catchment groundwater NO_3^- concentration (18.6 mgN/L) occurred in the upslope zone (top of hillslope) of *Arable N* in October 2015. Corresponding concentrations in the midslope and near-stream shallow groundwater were 12.4 and

8.2 mgN/L, respectively. In the midslope zone, temporal peaks in NO_3^- typically mirrored the upslope zone, whereas in the near-stream groundwater, the highest concentrations typically occurred after the upslope groundwater peaks from December to February. At the *Arable S* hillslope, the spatial and temporal distribution of the groundwater NO_3^- was more uniform, both in space and time. In both the groundwater and the streams, the highest NO_3^- concentrations were typically observed in the months of September, October, November and December.

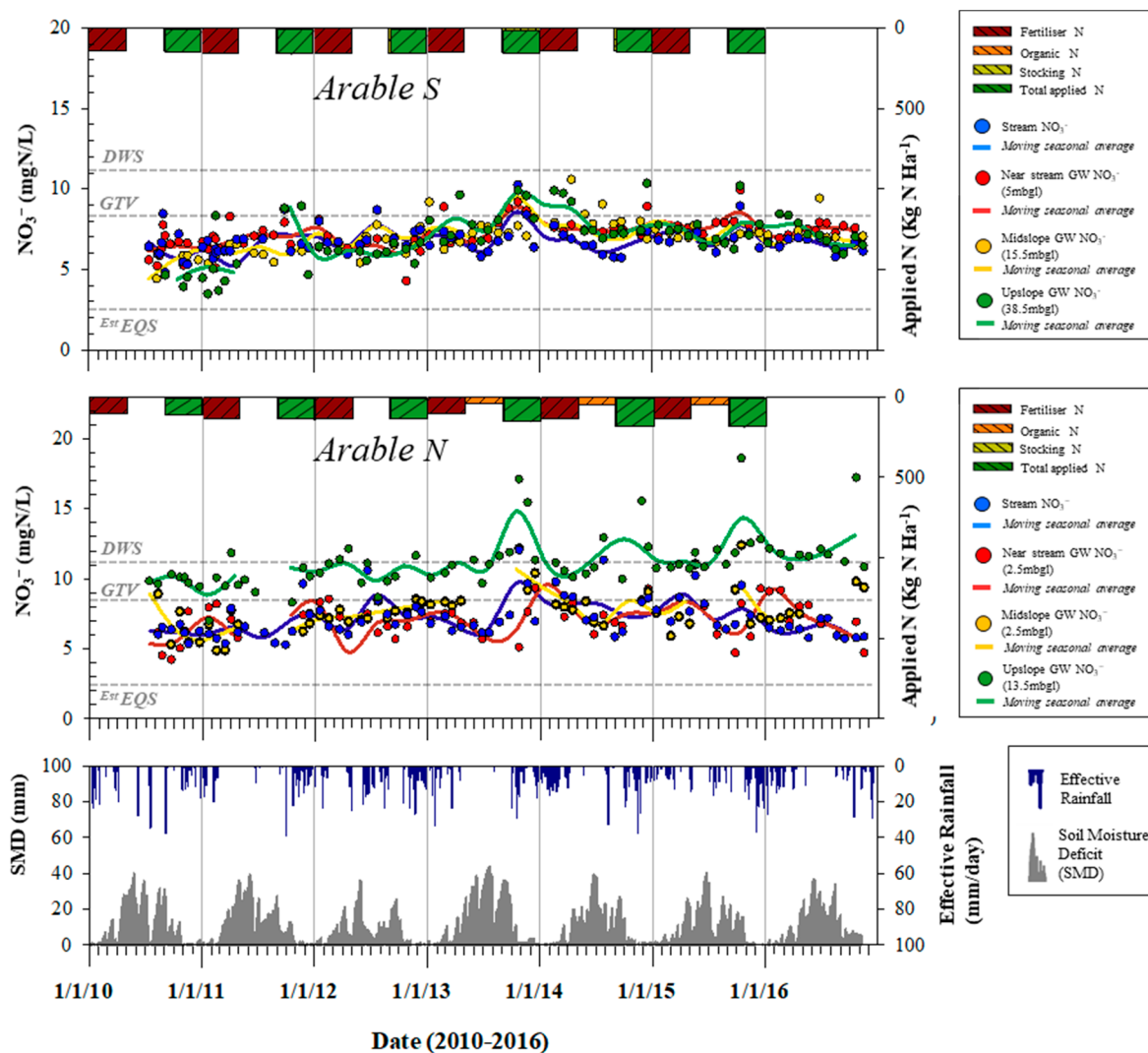


Figure 5. Arable hillslope temporal trends in groundwater and stream NO_3^- , effective rainfall, soil moisture deficit and nitrogen application from 2010 to 2016.

High groundwater NO_3^- concentrations corresponded to high stream NO_3^- . The estuarine standard of 2.6 mgN/L was exceeded substantially on all sampling occasions at both arable hillslopes throughout the monitoring period. The groundwater threshold value, which is over three times the estuarine standard, was exceeded on twelve occasions in the *Arable N* stream: twice in October, twice in November, twice in March with the remainder occurring in late winter and early spring. The GTV (8.46 mgN/L) was exceeded on five occasions in the *Arable S* stream: once in July, August and September and twice in October.

3.2. Meteorology and Agronomy

The yearly totals of rainfall, effective rainfall, annual maximum accumulated SMD and the percentage of each year with a SMD in excess of 5 mm at the grassland catchment are presented in Table 6. The mean effective rainfall over the seven-year monitoring period was

691 mm/year. The highest annual effective rainfall total (903.0 mm/year) was measured during the 2015 calendar year. The winter of 2014/15 had highest seasonal effective rainfall total: December 2015 was the wettest month recorded during the study period. The greatest proportions of the year with a SMD more than 5 mm were measured in 2011 (55.9%) and 2014 (49.9%). The year of 2014 also exhibited the greatest number of consecutive days with SMD > 0 mm (177 days), occurring between April and September (Figure 4).

Table 6. Grassland catchment annual totals (2010–2016) of rainfall and effective rainfall, maximum accumulated SMD and the percentage of each year with a SMD in excess of 5 mm. The chemical N, organic N, stocking N and total available N inputs to the land surface from 2010 to 2016 are also included.

Year	2010	2011	2012	2013	2014	2015	2016
Catchment Meteorology							
Rainfall (mm/year)	1012.7	1029.2	1129.4	1003.2	1175.6	1468.0	1011.8
SMD (max)	58.3	49.1	34.4	72.9	66.4	37.8	49.7
% of year with a SMD > 5 mm	55.9	46.3	35.5	48.2	49.9	43.0	45.5
Effective rainfall (mm/year)	554.3	494.8	716.0	484.0	632.4	903.0	484.4
Catchment Agronomy							
^b <i>Grassland N</i>							
Inorganic N (kg N ha ^{−1})	211.3	225.2	266.9	323.7	203.5	203.5	^a nd
Organic N (kg N ha ^{−1})	28.1	44.9	0.0	0.0	44.9	44.9	^a nd
Stocking N (kg N ha ^{−1})	172.0	192.0	194.0	192.0	145.0	151.0	^a nd
Total available N (kg N ha ^{−1})	411.4	462.1	460.9	515.7	393.5	399.5	^a nd
^c <i>Grassland S</i>							
Inorganic N (kg N ha ^{−1})	252.0	276.1	255.9	307.3	264.8	267.7	^a nd
Organic N (kg N ha ^{−1})	89.9	0.0	30.0	106.3	121.3	91.4	^a nd
Stocking N (kg N ha ^{−1})	142.7	91.7	116.7	91.7	112.7	104.3	^a nd
Total available N (kg N ha ^{−1})	340.6	367.8	402.6	505.3	498.8	463.4	^a nd

^a nd: Land management data were unavailable for 2016. ^b *Grassland N* & ^c *Grassland S*: Hillslope annual N application figures are an average of available field specific data.

At the *Grassland N* hillslope, inorganic N inputs were variable throughout the monitoring period. The largest quantity of fertiliser (323.7 kg N ha^{−1}) was applied in 2013, while the lowest amounts (203.5 kg N ha^{−1}) were applied in 2014 and 2015. Organic N was spread in the form of cattle slurry in all years except 2012 and 2013, with relatively uniform rates. The highest whole farm stocking rates of 172–194 kg N ha^{−1} occurred between 2011 and 2013. Total applied N (inorganic N + organic N + stocking N) typically increased from 2010 to 2013 with lower totals thereafter. Both fields at the *Grassland N* hillslope were ploughed in 2010. At the *Grassland S* hillslope, highest inorganic N applications were in 2013. Organic N was spread in the form of cattle slurry, with application rates typically exceeding the *Grassland N* hillslope. Conversely, stocking N was lower in *Grassland S* compared to *Grassland N*. Total available N increased from 340.6 to 505.3 kg N ha^{−1} between 2010 and 2013, remaining high in 2014 and 2015. Typically, one to two silage cuts are taken per year with four to eight months of grazing.

The annual dataset of rainfall, effective rainfall, maximum SMD and the percentage of each year with SMD in excess of 5 mm is presented in Table 7 for the arable catchment. The highest annual effective rainfall (706.3 mm/year) was recorded in 2014; this was coincident with the highest total rainfall, the lowest percentage of the year with a SMD greater than 5 mm and the lowest accumulated SMD. December 2015 was the wettest month during the seven-year monitoring period. The greatest proportions of the year with a SMD in excess of 5 mm were measured in 2015 (46.6%), followed by 2013 (43.4%). The largest SMD of 43.7 mm occurred during July of 2013. The year of 2013 also exhibited the greatest number of consecutive days with SMD > 0 mm (167 days) occurring between mid-April and the beginning of October (Figure 5).

Table 7. Arable catchment annual totals (2010–2016) of rainfall and effective rainfall, maximum accumulated SMD and the percentage of each year with a SMD in excess of 5 mm. The chemical N, organic N, stocking N and total available N inputs to the land surface from 2010 to 2016 are also included.

Year	2010	2011	2012	2013	2014	2015	2016
Catchment Meteorology							
Rainfall (mm/year)	942.1	845.0	1115.0	886.6	1175.0	1103.4	923.8
SMD (max)	36.8	40.4	39.3	43.7	36.2	39.2	39.8
% of year with a SMD > 5 mm	33.9	32.3	34.8	44.4	23.2	46.6	37.3
Effective rainfall (mm/year)	517.5	397.9	628.7	484.3	706.3	619.2	503.7
Catchment Agronomy							
^b <i>Arable N</i>							
Inorganic N (kg N ha ^{−1})	103.8	137.1	137.1	107.7	139.0	139.0	^a nd
Organic N (kg N ha ^{−1})	0	0	0	42.5	47.2	47.2	^a nd
Stocking N (kg N ha ^{−1})	0	0	0	0	0	0	^a nd
Total available N (kg N ha ^{−1})	103.8	137.1	137.1	150.2	186.2	186.2	^a nd
^c <i>Arable S</i>							
Inorganic N (kg N ha ^{−1})	144.5	156.6	158.3	151.3	144.5	155.5	^a nd
Organic N (kg N ha ^{−1})	0	0	0	0	0	0	^a nd
Stocking N (kg N ha ^{−1})	0	0	0	0	0	0	^a nd
Total available N (kg N ha ^{−1})	144.5	156.6	158.3	151.3	144.5	155.5	^a nd

^a nd: Land management data were unavailable for 2016. ^b *Arable N* & ^c *Arable S*: Hillslope annual N application figures are an average of available field specific data.

At the *Arable N* hillslope, inorganic N inputs ranged from 103.8 kg N ha^{−1} in 2010 to 139.0 kg N ha^{−1} in 2016. Organic slurry was not applied between 2010 and 2012; therefore, total available nitrogen inputs were equal to fertiliser inputs and ranged from 103.8 to 137.1 kg N ha^{−1}. The addition of pig slurry from 2013 onwards resulted in an increase in total available N inputs to 150.2 kg N ha^{−1} in 2013 and 186.2 kg N ha^{−1} in 2014 and 2015. At the *Arable S* hillslope, no organic N was applied from 2010 to 2015; therefore, total available nitrogen was equal to inorganic N input. The quantity of applied fertiliser varied in each year. The highest application (158.3 kg N ha^{−1}) occurred in 2013, while the lowest quantity of N (144.5 kg N ha^{−1}) was applied in 2010 and 2014.

3.3. Multiple Regression Analysis

Visually comparing patterns in water quality, for example, between results from one monitoring well and one driver, provides anecdotal evidence of a potential impact. Using a statistical model allowed for 36 integrated NO₃[−] responses (six piezometers over six years) to be compared against 16 explanatory drivers simultaneously, while allowing for interactions between the explanatory drivers. This provides a greater level of confidence in determining what factors influence NO₃[−] losses. The discussion focuses on the significant agronomic, meteorological and hydrogeological drivers presented herein.

3.3.1. Joint Model for Catchments

Merging the datasets from the grassland and arable catchments provided the regression model with a wider range of results to identify trends and drivers of NO₃[−] occurrence. There was a significant effect of SMD, depth of each piezometer from ground surface to bottom of screen (total GW depth), depth to bedrock (first rock) and subsoil clay content (EM ground conductivity) on NO₃[−] occurrence across the two catchments ($R^2 = 0.58$, $p < 0.0001$).

(EQ1) $\text{Arable and Grassland catchment NO}_3^- = 20.67 + 0.09 (\text{SMD}) - 1.68 (\text{Total GW depth}) - 0.81 (\text{Piezometer bottom}) + 0.83 (\text{First Rock}) - 2.67 (\text{EM ground conductivity}) + 0.15 (\text{EM ground conductivity}^2)$ $R^2 = 0.58$, $p < 0.0001$)

An analysis of the F statistics of the regression indicated that no one explanatory variable dominated the prediction of groundwater NO₃[−]. EM ground conductivity ($p < 0.005$) and the total depth of each piezometer ($p < 0.01$) were negatively correlated with NO₃[−]. The

depth of first rock appearance at each well ($p < 0.05$) and SMD were positively correlated to groundwater NO_3^- ($p < 0.05$). SMD was integrated over six months preceding the fixed October to March NO_3^- explanatory period. Results indicated that groundwater NO_3^- decreases with increasing depth below ground level in both catchments. A significant interaction ($p < 0.005$) was identified between catchment and the total GW depth. The rate of change in NO_3^- with depth, however, was doubled in the grassland catchment as compared to the arable catchment.

3.3.2. Catchment Specific Model: Grassland Catchment

There was a significant effect of hydraulic conductivity, stocking N and inorganic N on groundwater NO_3^- occurrence in the Grassland catchment ($R^2 = 0.7$, $p < 0.0001$). EQ 2 describes the results of the Grassland catchment fit.

(EQ2) Grassland catchment $\text{NO}_3^- = 1.72 + 2.54$ (Hydraulic conductivity) + 0.03 (Stocking N) – 0.019 (Inorganic N) $R^2 = 0.7$, $p < 0.0001$

The F statistic indicated that the dominant factors affecting groundwater NO_3^- concentrations were hydraulic conductivity ($p < 0.0001$), stocking N ($p < 0.005$) and inorganic N ($p = 0.03$). Hydraulic conductivity and stocking N were positively correlated with groundwater NO_3^- , while inorganic N was negatively correlated.

3.3.3. Catchment Specific Model: Arable Catchment

There was a significant effect of total GW depth, total applied N and SMD on groundwater NO_3^- occurrence in the arable catchment ($R^2 = 0.8$, $p < 0.0001$). EQ 3 describes the results of the arable catchment fit.

(EQ3) Arable catchment $\text{NO}_3^- = 12.06 + 0.69$ (SMD) + 0.025 (Total applied N) – 1.25 (Total GW depth) + 0.02 (SMD²) + 0.083 (Total GW depth²) $R^2 = 0.8$, $p < 0.0001$

Total applied N and SMD were positively correlated with groundwater NO_3^- , indicating that increased N application and SMD resulted in higher average groundwater NO_3^- concentrations. Conversely, total GW depth was negatively correlated with groundwater NO_3^- . The negative linear term between GW depth and NO_3^- dominated over a depth range of zero to ten metres below ground level, after which the positive quadratic term kicks in.

4. Discussion

4.1. Groundwater and Stream NO_3^- Concentrations

In a European context, nitrate concentrations in Irish waters (2008–2015) were found to be amongst the lowest in the European Union [52]. In a national context however, groundwater and stream NO_3^- concentrations in the grassland and arable catchments were high. In 2018, over 80% of monitored Irish groundwater bodies had mean NO_3^- concentrations lower than the concentrations measured in the grassland and arable catchments [2]. Stream NO_3^- concentrations in the grassland catchment consistently exceeded the estuarine water quality standard of 2.6 mgN/L. In the arable catchment, average stream concentrations throughout the study period were more than double the estuarine water quality standard and showed a rising trend, placing the stream in the top 2% of catchments nationally, in terms of elevated stream NO_3^- . The data suggest that the current Good Agricultural Practice for the Protection of Water (GAP) regulations are not sufficient to manage N losses in hydrogeologically sensitive catchments, particularly where there is an estuarine receptor.

A significant, albeit weak, increasing trend in NO_3^- trend was identified in the arable catchment, over the seven-year study period. Despite substantial variability, particularly in groundwater NO_3^- , no statistically significant temporal trend was identified in the streams or groundwater of the grassland catchment. Identifying a temporal trend in water quality or an “underlying rate of change”, as opposed to short term fluctuations or noise in the data, is challenging. The absence of a strong temporal trend over the seven-year period in both catchments reflects the complexity of the hydrologic system and the interplay between the drivers effecting nitrate concentrations in the catchments.

Groundwater and stream NO_3^- concentrations fluctuate over temporal scales ranging from daily to seasonal, annual and decadal. Identifying spatiotemporal trends in water quality and the drivers, which determine those trends, is challenging as the drivers are often related to each other. The use of a multiple regression statistical approach allowed the significant drivers of stream and groundwater nitrate concentrations to be characterised, while also allowing the interactions and potential lags between drivers/responses to be scrutinised. During the regression analysis, the meteorological and agronomic driver integration periods were extended back in time to see which period provided the best explanation of the groundwater/stream NO_3^- responses. In addition, to test for the effect of a delayed response of NO_3^- concentrations to explanatory drivers, a lag time of zero to five months was tested within the model. Results indicated that a six-month driver integration period, followed directly by a six-month NO_3^- response period with no lag provided the best fit to the data. The relatively fast response between the dominant drivers and groundwater/stream NO_3^- concentrations in both catchments has implications for future management. Remedial measures at the land surface targeted to reduce N losses in both catchments are likely to have a measurable positive effect on water quality within a relatively short timeframe.

The statistical analysis highlighted that nitrate variability in each catchment was significantly related to agronomic, meteorological and hydrogeological factors. Together, these factors explained between 58 and 80% of nitrate variability over the monitoring period.

In the joint regression model for the catchments, 58% of the variation in groundwater and stream NO_3^- concentrations was explained by meteorological and hydrogeological parameters; this is significant in terms of categorising nutrient loss risk to agricultural catchments and has been recognised in the EPA's approach to Water Framework Directive implementation in Irish waterbodies [37,53,54]. The soil, subsoil and bedrock within a catchment can reduce the risk of diffuse NO_3^- losses to watercourses via denitrification. While this is positive and should be protected, in catchments where nitrate is currently causing an environmental issue, an increase in source loading may have a negative effect on water quality as whatever denitrification capacity those catchments have is insufficient to process the quantity of nitrogen being applied. Restoring denitrification capacity through the blocking of drains or installation of constructed wetlands within catchments could help to meet the estuarine water quality standards [55].

Attempting to marry agricultural productivity with environmental sustainability in nutrient sensitive catchments is a challenging task and requires additional measures, which go beyond the scope of the GAP regulations. To provide informed advice to stakeholders, an understanding of the catchment specific factors, which affect diffuse N losses to surface and groundwaters, is required. The introduction of the Local Authority Waters Programme (LAWPRO) and the Agricultural Sustainability Support and Advice Programme (2018) in Ireland provides bespoke support and advice to agricultural stakeholders to reduce the diffuse loss of nitrates to groundwater and streams in hydrogeologically vulnerable catchments.

4.2. Agronomic Factors

The results of the multiple regression analysis highlighted total applied N, inorganic N and stocking as statistically significant drivers of the observed groundwater and stream NO_3^- variation. In hydrogeologically sensitive catchments, therefore, where subsurface attenuation is not sufficient to reduce N losses adequately, an increase in the N load applied to the land surface results in an increase in groundwater and stream concentrations.

In the grassland catchment, although no positive temporal trend was detected in groundwater or stream NO_3^- during the seven-calendar year period, there existed substantial intra-year variation. The largest peak in groundwater NO_3^- (23.7 mgN/L) occurred in February of 2011; this may have resulted from a ploughing and re-seeding event in August 2010. Ploughing of permanent grassland has been cited as a major source of NO_3^- loss via soil organic matter mineralisation [56–58].

A positive correlation between stocking rate and NO_3^- concentrations was identified with a negative correlation between NO_3^- and inorganic N applications. The negative relationship between groundwater NO_3^- and inorganic N fertiliser inputs in the grassland catchment could be due to a reduction in N fertiliser application to the ploughed/reseeded field but higher N leaching from the ploughing event. This result highlights the difficulty and complexity involved in inferring statistical relationships between drivers and NO_3^- in complex catchments. Increased stream and groundwater NO_3^- concentrations in response to increased cattle numbers have been documented on a national scale since 2013 [2]. Ryden et al. [59] calculated that the amount of NO_3^- leached below a grass sward grazed by cattle was almost six times greater than that leached below a comparable cut sward. In contrast to cut grass systems, where a significant quantity of applied N is removed as silage [23], 85 to 90% of the N ingested by livestock is excreted as urine and faeces [60]. Urine, in particular, is highly concentrated in urea ($>1000 \text{ kgN ha}^{-1}$) [23]. Depending on the stocking rate, a significant proportion of a field may be covered by urine patches; chemical and organic N applications are spread indiscriminately over an entire paddock, including urine patches. Within an Irish dairy system, Dennis et al. [61] estimated that 14.1 and 20.7% of the soil surface was affected by urine at stocking rates of 2.0 and 2.94 livestock units ha^{-1} . This can lead to soil NO_3^- concentrations far in excess of grass requirements and results in NO_3^- leaching to groundwater. More precise nutrient management plans, which account for the highly concentrated N in urine patches, may help to avoid the doubling down of nutrients in portions of the field, which are above the grass requirement and, as such, leach to groundwater during favorable meteorological conditions. Reducing urine patch deposition by reducing the duration of grazing per day or the stocking rate at times of active recharge could further reduce leaching.

In the arable catchment, total applied N was identified as a significant driver of groundwater NO_3^- concentrations, with an increase in applied N resulting in an increase in NO_3^- . A significantly positive linear trend ($p < 0.05$) in average groundwater and stream NO_3^- over time was identified. In *Arable N*, total N applications increased from 103.8 to 186.2 kg N ha^{-1} from 2010 to 2016 due to an increase in organic N applied as slurry during the period with no reduction in inorganic N fertiliser. More precise nutrient management therefore offers an effective mitigation solution. While essential to replenishing soil nutrient levels and increasing farm productivity, a direct causality has been documented between inorganic and organic N fertiliser use and decreased water quality [62].

From 2013 to 2015, the highest concentrations of NO_3^- in the arable catchment were measured in October, November and December, the period after crop harvest. Over the study period, the land was left for green cover to naturally regenerate after crop harvest. It is likely that bare soil conditions or patchy green cover during the autumn and early winter period increased NO_3^- leaching to groundwater. In temperate climates, the period most prone to NO_3^- leaching is directly after the harvest [63]. In addition to a lack of N retention via crop cover [64], the autumn re-wetting period also represents a period of increased N mineralisation. The use of specially planted cover crops has been shown to decrease groundwater NO_3^- . Natural regeneration was found to reduce NO_3^- leaching when seed germination was stimulated by harrowing in autumn, but this was less effective than a planted mustard cover crop [65].

4.3. Meteorological Factors

In the grassland catchment, while no significant pattern was identified in the temporal trend analysis, substantial NO_3^- peaks occurred in the streams and groundwater. Large peaks in midslope and near-stream shallow groundwater were measured in February and March of 2011, following the ploughing event in August of 2010. In the six months preceding the March peak, two extended periods of SMDs occurred: 91 days between April and July and 48 days from July to September. During August (when ploughing occurred), SMD had accumulated to 31.3 mm. In March and April 2015, a second large peak in shallow groundwater NO_3^- was measured. The greatest number of consecutive

days with a measured SMD (177 days) was measured between April and September of 2014. This was followed by the wettest winter recorded during this study, in 2015. The 2010–2016 rising trend in groundwater and stream NO_3^- exhibited in the arable catchment was influenced by high NO_3^- concentrations in the 2013 and 2014 calendar years, with maximum NO_3^- concentrations measured during the winter recharge period (October and November). In the six months preceding these NO_3^- peaks, 182 consecutive days had a SMD, which accumulated to 43.7 mm. The prolonged period of high SMD conditions was followed by significant effective rainfall during the recharge period.

The results suggest that a combination of nitrogen loading from agriculture, SMD and recharge can result in substantial NO_3^- leaching losses to groundwater. Dry conditions and associated elevated SMDs have been previously linked to NO_3^- mineralisation processes and NO_3^- leaching to groundwater [15–17]. Hart [65] and Schmidt et al. [66] reported increases in net mineralisation, nitrification rates and loss of mineral N below the rooting zone, related to summer drought and increased soil temperatures. Furthermore, during drought periods, plant roots die off, reducing the crop's ability to uptake both water and nutrients; this can lead to an accumulation of applied NO_3^- in the surface soil [67], which, when followed by high recharge, can lead to large NO_3^- leaching losses [26,27]. Tyson et al. [68] described significant increases in winter NO_3^- loss on a fertilized grassland site, citing the preceding summer's SMD as the dominant environmental driver. A similar grassland pattern was identified by Richards [69], where high SMD and low uptake of N by summer grass cover, followed by the re-wetting of soil, resulted in NO_3^- leaching. High cumulative SMD during dry periods enhances the lability of N.

While previous research reinforces the link between high SMD and enhanced N mineralisation, the presence of a SMD alone precludes significant NO_3^- leaching. If a soil has a moisture deficit, field capacity has not yet been reached and rainfall is unlikely to recharge the underlying aquifer. High intensity rainfall following a period of prolonged SMD causes field capacity to be exceeded, thus mobilising accumulated NO_3^- . While a landowner cannot control the weather, there are land management strategies which could help to minimise the effect of mineralisation and subsequent flushing of NO_3^- through the system. Nutrient management advice needs to be tailored for crop growing conditions as influenced by meteorological conditions, such as elevated SMD. McDonald et al. [70] advocate precision farming and highlight that NO_3^- supplied from soil N reserves through N mineralisation processes need to be accounted for when prescribing additional fertiliser N applications.

In the grassland catchment, frequent renewal of pasture swards could maximise the uptake of N and minimise N losses via mineralisation [58]. Grasslands often need renovation to improve sward quality and increase productivity [71], but this can result in elevated nitrate leaching, as seen at the *Grassland N* hillslope. The timing of sward renewal and method of renewal influence NO_3^- leaching [72]. Pasture renewal in springtime rather than autumn or using direct drilling methods could reduce leaching losses following reseeding [56,72]).

4.4. Hydrogeological Factors

While agronomic loading and meteorological drivers act to control the temporal load of NO_3^- leached to groundwater, the hydrogeological and hydro-geochemical setting of the catchment dictates the mobilisation, transport and transformation of NO_3^- thereafter. Hydrogeological factors exerted a significant effect on groundwater and stream NO_3^- occurrence. In both study catchments, depth of first rock appearance was positively correlated to NO_3^- concentrations. When rock is at or near the surface, that is, when the depth of first rock appearance is low, this reduces soil and subsoil denitrification potential. In Ireland, groundwater vulnerability is determined according to the thickness and permeability of the soils and subsoils, which can act as a protective filtering layer over groundwater. The greater the thickness and the lower the permeability of the soil and subsoil, the greater the attenuation capacity and protection offered to the underlying

aquifer. In both the grassland and arable catchments, the highest recorded concentrations of groundwater NO_3^- were measured in the most vulnerable parts of the hillslopes.

In both catchments, EM ground conductivity in the top 2 m of soil and subsoil was negatively correlated with NO_3^- . Low EM ground conductivity indicates either shallow bedrock or sandy, permeable overburden. High EM ground conductivity represents less permeable overburden, i.e., clay and/or waterlogged soil. The soil clay content is directly related to groundwater vulnerability with greater clay content reducing both permeability and vulnerability [43]. Weier et al. [73] described increased soil denitrification rates as soil texture became finer, soil water content and soil organic carbon concentrations increased. Parkin et al. [74] described a patchy distribution of “hot spots” and “hot moments” of subsoil denitrification. The patchiness was associated with localized zones with high particulate organic matter, most likely related to irregular distributions of animal excreta and organic manures applied in the land, and preferential pathways from the soil zone to the subsoil. Jahangir et al. [75] described higher rates of denitrification in the topsoil (25%) versus subsoil (4%). Subsoil denitrification was carbon limited and increased to 20% when there were sufficient electron donors. Craswell [76] demonstrated decreases in dissolved oxygen concentrations and increases in denitrification rates in a clay soil, following the saturation of the soil with water. The distribution of higher EM ground conductivity values in both catchments suggests that there exist lower permeability pockets of clayey soils and subsoils, particularly in the near-stream zones of the grassland and arable catchments.

Clague et al. [35] described seasonal denitrification at a gley soil site where the soil profile was periodically saturated near the ground surface. The presence of localized zones of decreased permeability in both the grassland and arable catchments in near-stream zones, coupled with a water table that rises close to the ground surface during high recharge, suggests that saturated clay rich soils may create conditions conducive to denitrification. High bedrock denitrification rates were measured in the deeper groundwater pathways of the grassland catchment, with comparatively low rates in shallow groundwater, soils and subsoils [28]. Low rates of denitrification were measured throughout the arable catchment where the aquifer was predominantly aerobic [28]. Although the soil and subsoils in both catchments are characterised as well drained, denitrification is possible under locally anaerobic conditions within soil microsites in particulate organic matter, organic-rich zones of low permeability sediments [35] and/or biofilms [36].

Premrov et al. [27] and Jahangir et al. [77] investigated the spatial and temporal occurrence of NO_3^- in groundwater underlying a spring barley catchment. Analogous to the arable catchment presented herein, the aquifer was aerobic, suggesting a limited capacity for groundwater denitrification. Annual N application was less than that of the arable catchment with an average annual N application of 115 kg N ha^{-1} . Premrov et al. [27] observed mean shallow (4 m BGL) groundwater concentrations of 22.4 mgN/L over a three-year period with a winter cover from natural regeneration. At the same site, Jahangir et al. [78] described mean groundwater NO_3^- concentrations of 11 mgN/L in Quaternary deposits and bedrock (4–30 m BGL). The mean shallow groundwater NO_3^- from 2010 to 2016 in the arable catchment of 7.8 mgN/L was 40% less than the results presented by Jahangir et al. [78] at a comparable depth. This suggests that despite low measured denitrification rates in the bedrock of the arable catchment, clayey soils and subsoils in the Quaternary deposits may have resulted in some NO_3^- attenuation.

A significant negative relationship between groundwater depth and NO_3^- was identified in both grassland and arable catchments. The rate of change in NO_3^- to depth, however, was double in the grassland catchment compared to the arable catchment, highlighting a greater capacity for NO_3^- removal via denitrification. In the grassland catchment, a negative correlation was also identified between NO_3^- and hydraulic conductivity (K_{sat}), which decreased with depth, resulting in higher groundwater denitrification and lower groundwater NO_3^- . High rates of bedrock denitrification have been directly measured in the grassland catchment by McAleer et al. [28]. Results support the relationship with K_{sat} identified by the multiple regression analysis and highlighted that near-stream zones signif-

icantly reduced groundwater NO_3^- . It is likely that the buffering capacity of the grassland catchment aquifer contributed to the lack of a significant temporal trend identified in the NO_3^- distribution.

While not directly measured, the results presented herein suggest that soil/subsoil denitrification may be possible, especially in the saturated clay rich deposits in both catchments. From a mitigation perspective, it is essential that these zones of NO_3^- removal are both preserved and enhanced where possible, particularly in catchments such as the grassland site, where large denitrification rates have been demonstrated under appropriate environmental conditions [28]. The importance of a well-designed agricultural drainage system is clear, providing greater crop and grass yield, extended grazing seasons and better availability of N in the soil. However, excessive land drainage and, in particular, direct tile drainage to streams can bypass near-stream NO_3^- removal zones. In addition, in situ remediation measures, such as constructed wetlands [53] and bioreactors, which use organic carbon rich media to enhance microbial reduction of NO_3^- to N gases [78], could further enhance NO_3^- removal, improve biodiversity and sequester carbon.

The drivers behind changes in groundwater and stream NO_3^- are complex and influenced by agricultural practices, site hydrology and meteorological factors. Simplistic relationships between temporal NO_3^- changes and one of these drivers could result in policy makers and land managers implementing measures that will be less effective. The hydrogeological setting of individual farms can be used to inform the location of hillslope zones vulnerable to N leaching. Mitigation strategies can be tailored to reduce nitrogen application where necessary on hydrogeologically vulnerable catchments with sensitive receptors, such as estuaries. Nitrogen use efficiency should be optimised to account for restricted crop or grass growth, such as high SMD conditions, while areas of natural N removal should be both protected and enhanced where possible.

5. Conclusions

Identifying trends in groundwater and stream nitrate is essential for policy makers, catchment scientists and farm managers alike. In this study, the trends in nitrate concentrations varied between catchments. A significant but weak positive temporal trend was observed in the tillage catchment, whereas no long-term trend was observed in the grassland catchment. The drivers which govern these trends are complex and often related to multiple pressures affecting water quality. This study found that agronomic (stocking rate and fertiliser inputs), meteorological (soil moisture deficit) and hydrogeological (hydraulic conductivity and groundwater depth) factors were significantly related to temporal nitrate changes across both catchments. When a nitrogen load is applied to the landscape, how the catchment responds to that load both spatially and over time is a function of hydrogeology and meteorology. Understanding the drivers which increase NO_3^- losses to groundwater and surface water enables catchment-specific mitigation strategies to be recommended. Future research should focus on improving nitrogen use efficiency, particularly under restricted crop growth (high SMD conditions). Accounting for hydrogeological setting during nutrient management planning is essential, while preservation/enhancement of natural nitrogen removal zones is advised. These measures can potentially contribute to reducing the load of nitrogen lost from agricultural land to groundwater and streams, while the efficacy of such measures should be trialed in research catchments such as the Agricultural Catchments Programme.

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