Integrated assessment of agricultural nutrient pressures and legacies in karst landscapes

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Abstract

Landscapes typically deemed at risk from leached losses of nitrogen (N) and phosphorus (P) are those with short subsurface hydrologic time lags. Due to the short time it takes nutrients to move from a source to an area of concern, such sites are deemed perfect to test the efficacy of programmes of measures as management changes. However, a small subset of these sites can retain nutrients in soil/subsoil layers, which in turn are leached and can be either attenuated (e.g. nitrate converted to gaseous forms or immobilised in soil and P can be mineralised) or mobilised over time. This biogeochemical time lag can have long lasting effects on water quality. In an intensive agricultural karst oxidised aquifer setting, the aim of this study was to improve understanding of P and N inputs, retention, attenuation and subsurface pathway distribution and to inform how similar sites can be managed in the future. This was undertaken for the present site by integrating existing secondary and new primary datasets for both N and P. Results showed that in the years pre-2000 slurry from an on-site integrated pig production unit had been applied at rates of 33 t ha^{-1} annually, which supplied approximately 136 kg ha^{-1} total N and approximately 26 kg ha^{-1} total P annually. This practice contributed to large quantities of N (Total N and NH_4-N) and elevated soil test P (Morgan extractable P), present to a depth of 1 m. This store was augmented by recent surpluses of 263 kg N ha^{-1}, with leached N to groundwater of 82.5 kg N ha^{-1} with only 2.5 kg N ha^{-1} denitrified in the aquifer thereafter. High resolution spring data showed greatest percentage loss in terms of N load from small (54-88%) and medium fissure pathways (7-21%) with longer hydrologic time lags, with smallest loads from either large fissure (1-13%) or conduit (1-10%) pathways with short hydrologic time lags (reaction time at the spring from onset of a rainfall event is within hours). Although soils were saturated in P and in mobile forms to 0.5 m, dissolved reactive P concentrations in groundwater remained low due to Ca and Mg limestone chemistry. Depletion of the legacy store with no further inputs (taking 25% of available mass of soil organic N as available in 1 m of soil/subsoil to be 75 kg N ha^{-1}) would take approximately 50 years, with NO_3-N concentrations in the source area dropping to levels that could sustain groundwater NO_3-N concentrations below admissible levels within 9 years. Biogeochemical time lags (decades) are longer than hydrologic time lags on this site (months to years). Future management should target farm surpluses that maintain a legacy store at or below a soil organic N mass of ~ 20 kg N ha^{-1}. Incorporation of biogeochemical and hydrologic time lag principles into future water quality regulations will provide regulators with realistic expectations when implementing policies.

Keywords

nitrogen; phosphorus; time lag; agriculture; water; soil

1. Introduction

Large anthropogenic nutrient legacies connected to aquatic ecosystems which have accumulated over decades, and inherent hydrologic and biogeochemical time lags (Basu et al., 2012; Hamilton, 2011; Van Meter et al., 2016), can obscure correlations between the implementation of conservation and water quality improvement (Bouraoui and Grizzetti, 2014). Hydrologic time lag refers to the duration required for average dissolved N in groundwater reservoirs and unsaturated zones, to be transported from a source (such as a fertiliser application area) to a receptor (a waterbody or abstraction point), through the soil/subsoil/transition zone and bedrock medium (Sousa et al., 2013). The biogeochemical time lag is caused by retention of N (typically organic) within the upper layers of soil/subsoil and this is a long term source for mineralisation and nitrate leaching. Recent work by Van Meter et al. (2016) has shown that accumulation of N in subsoil below plough layers leads to legacies of N in soil and groundwater for many decades. International environmental legislation has implicitly acknowledged the importance of "time lag". For example, the European Union (EU) Water Framework Directive (WFD, OJEC, 2000) initially targeted 'good' qualitative status of all EU water bodies by 2015, irrespective of national or regional meteorological or hydrologic conditions. In light of the burgeoning literature on time lag (Fenton et al., 2011a, Sousa et al., 2013; Vero et al., 2014 and others) this deadline has been revised to later reporting periods (2021). Nevertheless, there is still a temptation to forget legacy and time lag considerations, in light of the legislative requirement to assign measures to at-risk water bodies. It is likely, therefore, in these areas, that additional conservation measures may be considered to those measures legislated, for example, within the EU Nitrates Directive (NiD, OJEC, 1991).

Demonstration and documentation (e.g. Kronvang et al., 2016) of conservation measure implementation and successes that have improved water quality is encouraged and this impact is most likely to be picked up on well drained sites (highly permeable soil and underlying limestone or similarly permeable geology), as a correlation between farm management and water quality can be quickly interpreted. This is due to soil hydrogeologic characteristics that are conducive to intensive agriculture and also short hydrologic time lags for nutrient transfer (Huebsch et al., 2013). However, a sub-set of these sites can also have a legacy store of nutrients with differential sequestration and mobilisation dynamics and there is a lack of understanding of controls on nutrient depletion trajectories (Van Meter and Basu, 2015).

Mapping of N and P vertical risk areas (Blicher-Mathiesen et al., 2014), which anticipate nutrient specific attenuation factors, aims to divide a landscape into functional land management parcels (Baily et al., 2012; Fenton et al., 2011b; O'Sullivan et al., 2015). Some areas act as natural attenuation areas and should be maintained as such (e.g. denitrification hotspots or flow sinks for N or specific soil chemistries that offer P attenuation due to high binding energies and sorption capacities (Daly et al., 2015) and that can occur in sections of drainage ditches (Shore et al., 2015), whereas other areas are considered mere delivery points. Tesoriero et al. (2013) examined the vulnerability of streams in different catchments to legacy nitrate pollution and found that high concentrations may be sustained for decades, which were decoupled from present day farm management. A clear definition of legacy effects by Bain et al. (2012) highlights this storage component (e.g. for N see Worrall et al., 2015; for P see Jarvis et al., 2014) and the complex distribution of elements of this storage for reactive nitrogen (N_r) and P amongst different hydrological flow paths. Where the storage component is isolated below the rooting zone in the subsoil, and yet connected to a receptor through surface springs or through surface-groundwater interactions, the water quality and ecological impacts can be prolonged (Hamilton, 2011).

The present study focuses on intensively grazed dairy farm sites under permanent pasture, e.g. characterised by well-drained soil/subsoil (moderate to high permeability) underlain by high permeability bedrock (weathered and fractured karst) and dominated by subsurface pathways in terms of P and N. On a similar site in terms of N, Huebsch et al. (2013) showed that consideration of a hydrologic time lag, inferred past and documented present N-loadings, local weather conditions and hydrogeological, pedological, geological site characteristics and management changes were all significant factors that influenced spatial and temporal trends of nitrate concentration over 12 years. Mellander et al. (2013), focussing on P, postulated that P attenuation associated with soil chemistry, depth to bedrock and retention within a karst aquifer ensured emergent spring water was below an ecological impairment threshold. A revised intrinsic groundwater vulnerability assessment was used to produce a specific P vulnerability assessment that used the soil and hydrogeological P buffering potential of the landscape as key assumptions in moderating P export to the emergent spring. Jarvie et al. (2014) also found that up to about 90% of the annual soluble P flux was retained rather than diluted in a karst terrain in mid-continental USA, but highlighted the potential for slow release of legacy P to surface waters.

To consider the need for future mitigation interventions on free-draining, intensive agricultural land, the aim of this study was to develop an improved understanding of P and N inputs, storage, attenuation and subsurface pathway distribution on a grassland site and to consider how similar legacy sites can be managed into the future. The first objective, using an integrated approach, was to collate and interpret existing secondary and additional primary datasets to interpret all aspects of the nutrient continuum from source (inputs) to delivery. The second objective was to assess the likely efficacy of present programmes of measures to mitigate subsurface losses originating from legacy sources. In addition perspectives of management/implications of the results are also discussed.

2. Materials and methods

2.1 Study site

As a case study for the overall aim, this study was conducted at the Dairygold Research Farm, Teagasc, Animal and Grassland Research and Innovation Centre, Moorepark, Fermoy, Co. Cork, Ireland (52°09′N; 8°16′W). The permanent intensive grass based dairy farm in south-central Ireland (97 ha farmed) is split into two elevation levels (intensively grazed grassland on the upper level and temporary flooded grassland on the lower level); there is also a piggery on site (Fig 1). The soil is sandy loam in texture to 0.5 m depth with gravels intermixed with coarse and fine sands to 10 m depth (well to excessively drained) underlain by grey limestone with fractures and caverns. A groundwater divide demarcates flow on site with a northern boundary running parallel to the present site and terminating at the junction between the River Funshion and the River Blackwater (Fig 1). This means that all spring flow on site is derived from within this area.

Insert Fig 1.

2.2. Secondary datasets

All secondary datasets were used to initially characterise the site. Attributes such as the type, source and purpose of these data are itemised in Table 1. In addition, data from a perennial spring on site were examined previously by Huebsch et al. (2015) (Fig 1). In summary, a pump house and lagoon (23 m^2), is equipped with a Corbett trapezoidal flume used to measure discharge from the lagoon with a calibrated water level recorder (Diver; 0.000 m to 10.000 m). A double wavelength spectrophotometer (5 mm path length) sensor (NITRATAX plus sc, Hach Lange GmbH, Germany; Huebsch et al., 2015) measured NO_3-N concentrations (0.000 to 25.000 mg L^{-1}). Both instruments measured at a 15 minute resolution and were used to calculate NO_3-N flux from 27 November 2011 to 25 March 2013. Huebsch et al. (2015) summarised that storm events altered nitrate concentrations significantly, i.e. with rapidly decreasing or increasing concentrations. The response in the karst indicated a strong dependent on nutrient source, whether mobilisation and/or dilution occurred, and on the pathway taken.

2.2 Primary datasets

All primary datasets were developed (though additional field work, collating unpublished data or re-analysis of existing data) to form further understanding of the site. These data are itemised in Table 2. More specifically, the farm N balance including attenuation was based on the amount of N input into the farm, recycled within and exported (output) from the farm. Total N input included fertilizer N, concentrates (feed other than grass), atmospheric deposition and biological N_2-N fixation (BNF) (Scholefield et al., 1991; Ryan et al., 2011). The amount of N input by animal excreta and output by grazed grass and silage was estimated to be equal and, therefore, was not accounted for in the N balance. Nitrogen input by concentrate feed was calculated by multiplying the total amount of concentrate by its crude protein (CP) content and dividing by 6.25 (balances rations for CP rather than specifically for amino acids) (McDonald et al., 1995). The quantity of atmospheric N deposition was estimated as 8 kg ha^{-1} (Ryan et al., 2006). Total N surplus was calculated by subtracting total output from total input (Scholefield et al., 1991). Total N to be leached to groundwater was calculated considering N loses via volatilization (NH_3 emission), accumulated in soil and losses by denitrification in the vadose zone (Jahangir et al., 2012; Ryan et al., 2011).

Biogeochemical time lags were estimated using the formulae presented in van Meter and Basu (2015) with the following input parameters: an approximation of 300 kg N ha^{-1} as the mass of the legacy N store for the first 1 m of soil/subsoil was estimated. With only 25% of this figure likely to be mineralised i.e. 75 kg N ha^{-1} (initial mass of the soil organic N) and utilising ceramic cup average nitrate data for the whole farm as our initial concentration i.e. 35.36 mg NO_3-N L^{-1} leached from the source zone, with an N depletion rate (yr) of 0.16 from the mass accumulation, recharge of 500 mm yr^{-1}, saturation of 0.5 and porosity of 0.3.

Hydrologic time lags were estimated by firstly investigating unsaturated travel time to 10 m using site specific soil/subsoil physical data from Kramers et al. (2013) and converting this to soil hydraulic data in RETC (Table 3). Daily meteorological data from a local synoptic station were used as outlined in Vero et al. (2014). Nodes were placed at 1, 5 and 10 m, representing depth to bedrock ranges on site. Initial breakthrough (IBT), centre of mass (COM) and total exit (Exit) of a conservative tracer (dispersivity of 1/10th total profile depth, with initial breakthrough and total exit assumed at threshold concentrations of 0.01 mmol cm^{-1}) in days after start of simulation was estimated. An atmospheric upper boundary condition allowing surface runoff and a free-draining lower boundary condition were used as in Jaques et al. (2008). A third-type/Cauchy upper boundary condition was applied (Konikow, 2011; Šimůnek et al., 2013).

Data collected at the perennial spring during the study of Huebsch et al. (2014) were analysed further for the saturated component of the hydrologic time lag. For total hydrologic time lag the unsaturated and saturated components can be added together. This work allowed for the apportionment of NO_3-N load and concentration to distinct pathways by using high frequency monitoring of discharge and NO_3-N concentration in the emerging spring

(Mellander et al., 2013). Rainfall events (with total depth of 10 m) were separated from each other, if precipitation was less than 0.2 mm hr^{-1} within 24-hr in accordance with Kurz et al. (2005). The following events were examined: Event I, 11-15 November 2011; Event II, 16-18 November 2011; Event III (29 November-11 December 2011); Event IV, 3-20 January 2012. The method is similar to a hydrograph separation described by Dingman (2015), where hydrological pathways were identified as the segments between graphically identified inflection points along the recession limb of hydrographs. Here, instead of a hydrograph, the NO_3-N loadograph using the *Loadograph Recession Analysis* (LRA) method (Mellander et al., 2012a) was used to identify inflection points of source pathways. In order to separate flow pathways and transfer pathways the timing for the identified inflection points were used in the hydrograph and adapted to the loadograph, where in this case the inflection points were less clear. Individual transfer pathways were logarithmically separated from the start of the rising limb to the inflection points. The segments were assumed to represent the release of NO_3-N *via* different transfer pathways. These pathway loads could be quantified and were here interpreted to be transfer in conduit, large fissure, medium fissure and small fissure similar to Mellander et al. (2012b; 2013). The flow-weighted NO_3-N concentration was estimated for each pathway by dividing the transfer load with the discharge.

3. Results and discussion

3.1 Characterisation using secondary data

In 2009, 2010, 2011 and 2012 annual rainfall was 1293, 869, 855 and 1097 mm, respectively. Utilising the hybrid model of Schulte et al. (2005) for grassland in Ireland (see Table 1), no runoff occurs on site and therefore infiltration on site was 673, 326, 364 and 578 mm for equivalent years. Irish soils have very low levels of P naturally other than reserves that have been deposited by farming practices (animals, manures, fertilisers). The levels of soil test P (bioavailable P) found in unfarmed soils is usually low as P present will largely be bound to the soil in solid phase due to the relatively high levels of Fe, Al , and Mn in acid soils and Ca in calcareous soils in Ireland. Legacy nutrients are evident to 1 m depth (both P and N). In terms of past inputs using typical values, high rates of organic manure application (slurry from the on-site integrated pig production unit had been applied to the upper levels of the farm at typical application rates of 33 t ha^{-1} annually) has supplied approximately 136 kg ha^{-1} total N and approximately 26 kg ha^{-1} total P annually in the years pre-2000. Soil testing of agricultural soils has seen a decline in the number of samples recording excessive P (from 24% in 1996 to 17% in 2015) with a concurrent increase in samples recording P deficiencies (from 17% in 1996 to 31% in 2015). These trends are also reflected in declining P balances as farmers are faced with the challenge of meeting a zero P balance requirement farm scale under the current programme of measures i.e. the NiD. Ireland has a decreasing national P surplus from 1990 to 2008 from 11 to 6 kg P ha.

This practice on the current site has contributed to large quantities of N (Total N and NH_4-N) and elevated soil test P, (Morgan extractable P) present at all tested soil depths. Firstly, in terms of P storage in the subsoil, data from Richards et al. (1998) showed that Morgan's P ranged from 23.3 to 60.0 mg L^{-1} for the topsoil agronomic depth (0-15 cm) and

7.7 to 43.7 mg L^{-1} for subsoil depths to 0.5 m, well in excess of the agronomic maximum of 8 mg L^{-1} (i.e. upper threshold of P Index 3, Morgan's). As some of this P is initially organically bound there is potential for P movement downwards through the soil profile where it will be mineralised. The parent material under these soils is deep limestone and if P makes its way through the topsoil into the subsoil it is likely to be attenuated (precipitated) and stored as calcium phosphates. Under the alkaline conditions that persist in the subsoil these calcium phosphates are likely to be very stable.

In terms of N storage soil/subsoil testing showed NH_4-N concentrations for paddocks receiving no fertilizer with high concentrations of 25.2, 10.0, 3.1, 0.9, and 0.8 mg kg^{-1}, for successive depths (20 cm increments). Total N equivalents for these depths were 3.4, 8.8, 19.7, 8.8 and 7.7 mg kg^{-1}. At depth 40-60 cm there was more NO_3-N than NH_4-N, which indicates mineralisation and a storage bank for potential leached losses.

Generic soil chemistry data points to a soil type that is typically high in Fe (Fay et al., 2007; Selbie et al., 2015) and when associated with organic matter these compounds combine to form amorphous forms of Fe-P (Daly et al., 2001). Whilst, Iron-rich soils have a strong affinity for P with high P sorption capacities for P (Daly et al., 2015), amorphous forms of Fe bound P can be soluble and mobile, as evidenced in elevated sub-surface water P concentrations in an Irish ground-water fed catchment (Mellander et al., 2016).

Groundwater (NO_3-N drinking water quality maximum admissible concentration (MAC) of 11.3 mg NO_3-N L^{-1}) borehole mean NO_3-N concentrations for BH1, BH2, BH3, and BH4 were 17.8 ± 1.1 mg L^{-1}, 7.6 ± 0.3 mg L^{-1}, 9.0 ± 0.8 mg L^{-1}, and 17.7 ± 0.9 mg L^{-1}, respectively. Nitrite-N and NH_4-N equivalents were all below 0.05 mg L^{-1}. The water table remains from 25 to 30 m bgl with recharge from October, continuing until May or June. Nitrate-N produced by nitrification from fertilizers or manures may not have enough residence time to be biogeochemically processed. Both Fenton et al. (2009; 2011) and Jahangir et al. (2013) showed that lower rates of denitrification occur at higher saturated hydraulic conductivities (k_s). Herein there is high k_s at depth, resulting in high dissolved oxygen (DO) with high levels of DON (0.92-3.5 mg L^{-1}) and a high mean redox potential (Eh) of 176 mV. From 2010-2011, groundwater pH on site was approximately 6 (slightly acidic indicating dissolution), mean DOC was 0.9 mg L^{-1} (highest concentrations occurred in December-January and lowest in August-September). Jahangir et al. (2013) estimated leached N losses to groundwater to be 82 kg NO_3-N ha^{-1} yr^{-1} including actual on site denitrification rates, ammonia volatilization and microbial assimilations. However, as a reactive process of transport, this NO_3-N can be disintegrated further with 4% of the N being reduced through denitrification. Jahangir et al. (2012) estimated about 10% of the total dissolved N in groundwater was other than NO_3-N. Of this, DON and denitrified N_2 accounted for 8 kg N ha^{-1} yr^{-1}.

Landig et al. (2010) identified three distinctive fracture sets (Set A 078°/87°; Set B, 177°/59° and Set C, 349°/57°) on site. The median fracture spacing ranged from 0.27 to 0.43 m and effective hydraulic aperture ranged from 0.16 to 0.22 mm. A range of possible hydraulic conductivities were calculated, from $1.6 \text{ x } 10^{-5}$ to 6.4×10^{-5} m s^{-1}, with 30% of the total flux entering the nearby Funshion River (Fig 1) emanating from conduits. The 2012 spring flux equated to 2.2 kg NO_3-N ha^{-1} yr^{-1}, if the contribution area of the spring is the entire farm; however this area is likely to be much smaller at approximately 5 ha based on discharge and NO_3-N concentration data and therefore leached losses of 43 kg NO_3-N ha^{-1} yr^{-1} in this area are likely. Hence, the predictions made in the study by Landig et al. (2010) i.e. 18040 ± 2320 kg NO_3-N ha^{-1} yr^{-1} (54% of agronomic loadings) equates to 185 using an entire farm (97 ha). The total flux discharging from the spring during the 18 month period was 263 kg NO_3-N. The total flux for 2012 was 215 kg NO_3-N yr^{-1}. Flow was < 1 l s^{-1} for 71.4% of the period, with 22% of flow > 1 l s^{-1} to 1.2 l s^{-1}. With respect to NO_3-N, 82% of the period was ≤ 11.3 mg L^{-1}, 10.5 % was from 11.3 to 13 mg L^{-1} with the remainder above this concentration. For the entire farm using a discrete fracture network (DFN) model, derived from scanline samples in combination with a stream tube model, Landig et al. (2010) estimated total NO_3-N load by adding results from three control planes covering the full extent of the site boundary with the river (1800 ± 100 kg NO_3-N yr^{-1}, 13200 ± 1900 kg NO_3-N yr^{-1} and 140 ± 30 kg NO_3-N yr^{-1}) and three springs through direct measurements (17th November 2008 representing maximum flow conditions, 600 ± 50 kg NO_3-N yr^{-1}, 1100 ± 120 kg NO_3-N yr^{-1} and 1200 ± 120 kg NO_3-N yr^{-1} (same spring as in the current study).

3.2 Further characterisation

A detailed breakdown of the N balance is presented in Table 4 with a comparison provided with other dairy research farms. The big difference between these sites is the level of denitrification after leaching occurs to groundwater. The farm N balance for the present site shows that N input, N output, N surplus, N leached (to groundwater), N denitrified and N delivery to groundwater were 298, 35, 263, 148 (82.5), 2.5 and 145.5 kg N ha^{-1}, respectively. For the other sites in Table 4 denitrification ensures nitrate groundwater concentrations at these sites are consistently below MAC. Another comparison, on specialist dairy farms nationally (no import of slurries), the average farm gate N surplus was 168 kg N ha^{-1} in 2006

(Buckley et al., 2016). On this site which imported pig slurry, it is likely that the N and P surplus was higher than these levels in the years pre-2000. From an EU perspective van Grinsven et al. (2012) examined the implementation of the NiD in terms of N surplus and nitrate concentration across the northwest of the EU (Ireland, United Kingdom, Denmark, the Netherlands, Belgium, Northern France and Germany). Implementation of the NiD (since 1995) showed a major decrease of the soil N surplus), particularly in Belgium, Denmark, Ireland, the Netherlands and the United Kingdom, with a modest decrease of nitrate concentrations since 2000 in fresh surface waters in most countries. However, such decreases were less evident in groundwater due to time lags (Fenton et al. (2012) associated with nitrate in deep aquifers.

However, since the introduction of the Good Agricultural practice rules (S.I. 378 of 2006) under the EU NiD, P inputs were constrained according the soil test P levels. Under these rules no P could be applied to soils with P concentrations in excess of the agronomic optimum levels and those that were at agronomic optimum levels (i.e. Morgan 's extractable P 5-8 mg l^{-1}) were not allowed P applications to replace off-takes (i.e. maintained at P balance). It was expected that these P management rules would draw down legacy soil P over time or prevent excessive soil P build-up from occurring in future. Therefore in terms of legacy P and vertical P transport on well drained sites appropriate conservation measures are already in place.

Soil sampling data from sampling location 1 on the farm (Table 5), show that where the Morgan's P level in the soil was very high (38 mg L^{-1}) the M3-Al/P ratio (2.07) was low, with a low soil P sorption potential and high P availability under such conditions (Daly et al., 2015). Where the Morgan's P concentration was less than the target agronomic range (5-8 mg

L^{-1}), at sampling location 2 (4.1 mg L^{-1}), the M3-Al/P ratio (16.9) was above the threshold value of 11.7 where P is more strongly fixed with lower P solubility. These results suggest a highly P saturated topsoil with high risk of P mobilisation in the presence of a hydrological pathway. Although P concentrations in the source zone below the rooting zone are high, the low resolution grab samples taken at different times from boreholes and the spring show very low dissolved reactive P (DRP) concentrations (Maximum Admissible Concentration (MAC, the nutrient conditions for meeting Good status required by EU WFD (SI 272 of 2009), allows for mean molybdate reactive P (MRP) concentration of 0.035 mg L^{-1}or < 0.075 mg L^{-1} (95 %ile).

On 26th October 2012 DRP spring concentrations were negligible and total P concentrations were 0.007 to 0.01 mg L^{-1} pointing to a particulate source. On 22nd May 2013 concentrations were similar. Therefore, mobile P fractions that transfer below the soil layer are attenuated (precipitated) by Ca originating from the Karst system. The study by Jarvie et al. (2012) proposed that along the pathways of migration P flows through a “series of reactive conduits, mediating P flux transformations through retention and recycling of P, on a range of timescales from years to centuries”. At the present site, high alkalinity values in the spring-water samples (>180 mg L^{-1}) point towards the presence of dissolved Ca and Mg, derived from the Karst system. It is hypothesised on the present site that changes in the chemical environment from neutral to calcareous caused soluble P to precipitate out of solution in the presence of elevated levels of Ca and Mg. Batch experiments on Irish soils derived from limestone parent material demonstrated significantly lower P solubility in the presence of high Ca concentrations, compared to neutral non-calcareous soils at similar Morgan’s P (Daly et al., 2015).

Leached N losses from the legacy store (down to 1 m) were captured on site in ceramic cups at 0.9 m and showed average NO_3-N concentrations (control paddocks with no inputs) of 7.91 mg L^{-1}; with a maximum of 39.01 mg L^{-1} and a minimum of 0.00 mg L^{-1}. The average for all ceramic cups spread throughout the farm and every measurement date, including immediately after ceramic cup insertion was 35.36 mg N L^{-1} (Range 0.12 to 282.5 mg N L^{-1}).

The 1D-Hydrus numerical modelling, showed relatively slow migration of the tracer to a depth of 10 m (Table 4). In a 0.7 m deep soil profile, Kramers et al. (2009) pointed to some preferential pathways in this soil, which decreased with depth. On an adjacent site Richards et al. (2005), showed matrix flow dominated with peak concentrations at 0.5 m depth reached after 34-65 days. The average spring discharge on site was 5 m h^{-1}, which is at the low end of the range for lowland springs in Ireland (5-250 m h^{-1}; Drew, 2008). There is evidence of a quick discharge response to rainfall events - ~ 7 hours. Typically in all events the NO_3-N concentration peaked (i.e. mobilisation) a few hours before discharge. During the Huebsch et al. (2014) study an unpublished borehole (BH3) to spring uranine and optical brightener (Tinopal) tracer experiment was conducted and showed highest peak concentration at the spring after 11 h 26 min in a period of no rainfall. The zone of influence of the spring in the current study was determined to be within the groundwater divide demarcated in Fig 1. The tracer experiment also excluded connectivity with other springs in the area.

3.3. Nitrate-N concentration and load across flow Events I-IV

Flow event based information is presented in Table 6. Rainfall amount and cumulative discharge during the flow event sequence follows a pattern, due to storage (e.g. from Event II influencing Event III) within the system at any given time. This is more applicable for Events I-III as they directly follow each other. Intermittent rainfall between Event III and IV occurs below the 10 mm threshold. From a concentration perspective the source appears constant and well connected to potential pathways with concentrations approximating MAC, although decreasing for Event IV. As described by Huebsch et al. (2014) during the four events examined - as rainfall intensified, discharge increased followed by increased NO_3-N concentration some time later with the maximum NO_3-N concentration reached earlier than the discharge peak. This was also the case for the events examined in the present study.

3.4 Flow paths and nitrate-N transfer pathways with Events I-IV

Four types of flow and NO_3-N transfer pathways were identified by the separation method conduit, large fissure, medium fissure and small fissure (Table 7 and Fig. 2) which is in agreement with the number of flow compartments found by Landing et al. (2010). The conduit and large fissure pathways were assumed to be quick-flow pathways and responded relatively quickly to rainfall, whereas the small and medium fissure flow, were assumed to be slower-flow pathways. Across the four analysed flow events all pathways were active but their apportionment in terms of spring discharge and NO_3-N concentration changed across events (Fig. 3). Proportionally and quantitatively the highest loss of NO_3-N was from the small fissure pathway (54-88% and 1.3-10.5 kg respectively) for all flow events. This pathway is likely to exhibit lower permeability and therefore higher attenuation capacity. This was followed by the medium fissure pathway (7-21% and 0.1-2.4 kg) with the smallest loads emanating from either large fissure (1-13% and 0.0-1.5 kg) or conduit (2-11% and 0.1-1.4 kg) pathways. The highest event flow-weighted mean concentration was in Event III (13.1 mg L^{-1}) and highest concentration of transfer pathway was in the large fissure flow of Event III (14.7 mg L^{-1}). In terms of NO_3-N concentration Event II and III breached MAC in all pathways, whereas Events I breached MAC only in the quick-flow pathways. The NO_3-N concentrations in Event IV remained below the MAC. The direction and magnitude of discharge and NO_3-N concentration hysteresis loops, following a rainfall event, provides information on the NO_3-N source availability. A clockwise direction typically means a proximal source and an anticlockwise direction a distal source. The magnitude and clockwise (proximal source as opposed to a more distal diffuse source) trajectory of the hysteresis loop in Event II indicate that a substantial amount of NO_3-N was available for transfer in the conduits already at the start of that event.

While the highest loss (i.e. load) of NO_3-N was in the slow-flow pathways in all events (highest in Event IV small fissure flow), the highest flow-weighted mean concentrations were in the quick-flow transfer pathways during the two high flow events (Event II and III). As most of the NO_3-N was lost via small fissures the transit time was longer and NO_3-N is likely to be more exposed to attenuation processes. This is important for the south of Ireland as regionally important karst aquifers dominated by conduit flow are in the west of Ireland whereas those dominated by diffuse flow (as in the present study) are in the south of Ireland (Coxon, 2014). It is the south of Ireland that coincides with intensive dairying.

3.5 Implications

Reducing agriculture N surpluses by 40-53% across 8 catchments in Denmark has proven successful in decreasing N loads to estuaries in < 5 years. However, in the same study, two catchments and estuaries presented a time delay of decades, possibly due to oxic groundwater within associated aquifer types (i.e. chalk) (Windolf et al. (2012). Therefore for both P and N, conservation programmes, design and outcomes must always consider and adapt to hydrologic and biogeochemical time lag impacts. It will always be important to demonstrate changes in water quality trajectories and foster accountability with full implementation of measures. primary and secondary data presented herein should enable a framework to be developed, which will enable a clearer characterisation of any at risk site. It highlights the large amount of data and field work needed to characterise at risk sites. The results presented, show that a legacy store was present which is highly mobile and all subsurface pathways are active during rainfall events (dominated in terms of small fissure diffuse flow with long transit times). In terms of legacy P, there was high long term sequestration capacity due to limestone chemistry. In terms of N there was some limited attenuation possible. Future research should also consider sampling the storage component to greater depths as agronomic testing only goes to 0.1 m, with other studies typically not going beyond 1 m. This is an important consideration considering the slow matrix driven flow, which is 10 m in places.

An integrated or holistic characterisation has benefits for future management. In terms of P losses on this site, zero P surpluses enforced under the NiD coupled with long term sequestration within the system at depth will continue to manage losses, with no need for further intervention. The work of Schulte et al. (2010) showed that for worst case scenarios of high Total P and soil test P (Morgan's P > 8 mg L^{-1}) starting points, average time to fall below this concentration to agronomic optima was estimated at 7-15 years depending on the field P balance. However, uncertainty analysis showed that variation across soil types was high creating a wider range from 3 to >20 years.

From an N perspective one tempting option would be to remediate accessible pathways e.g. spring discharges with finite ecologically engineered solutions. Taking the example of an artificial nitrogen sink such as a woodchip denitrifying bioreactor (e.g. Fenton et al., 2016; Schipper et al. 2010), which could be installed at the spring location to convert nitrate to di-nitrogen gas based on the highest flow rate of 361 m^3 day^{-1} and the highest NO_3-N concentration of 15 mg L^{-1}, with an assumed in-field denitrification rate of 7.6 g N m^3 day^{-1} (other laboratory studies have recorded much lower denitrification rates of 3.5 g NO_3-N m^{-3} d^{-1} (Healy et al., 2014)), a structure of 712.5 m^3 would be needed to bring concentrations to zero, or 175.5 m^3 to bring NO_3-N concentration to MAC. In reality the bioreactor could be smaller as the average flow was 39 m^3 day^{-1} and average NO_3-N concentration 10.7 mg L^{-1}. To bring these conditions to zero the bioreactor would only need to be 54 m^3. Setting the price of 1 m^3 of woodchip at 100 €. The total flux price equivalent of the nutrient value for the entire 18 month period at the spring would be about 300 € (1.15 € per kg) and therefore it would take 25 years to re-coup the cost of the NO_3-N being lost.

Martin et al. (2017) have investigated the time lags involved between land use/cover change and water quality change, documenting the large range of time scales involved. Van Meter and Basu (2016) indicate how estimation of time lags is difficult due to an incomplete understanding of controls on nutrient depletion trajectories after changes in land-use or management practices. The simple model developed by Van Meter and Basu (2015) incorporated biogeochemical and hydrologic time lags and showed that legacy effects added to overall time lags above those of the hydrologic component alone.

The estimate of biogeochemical time lags using the input data documented in 2.2 showed that it would take 50 years for the legacy store (with no further inputs) to become depleted. However, it would only take 9 years for the concentrations leaving the source area to return to concentrations that would then dilute current groundwater NO_3-N concentrations on site after the hydrologic time lag through the unsaturated zone. Therefore to manage the site the mass of the soil organic N pool in the storage component must remain or drop below 20 kg N ha^{-1}.

By examining the N surplus and corresponding N leached to groundwater at the same time point can be insightful (Table 4). Four scenarios are examined using farm N Input-Output data, an annual effective drainage figure of 500 mm, the area of the farm i.e. 97 ha and NO_3-N concentration in groundwater for 1998 (pre2000), 2008 (present scenario), equilibrium (taking data from a nearby site used in Huebsch et al. (2012) after the store in the first 1 m is depleted). The inorganic leached N to groundwater (kg N ha^{-1}) figure increased from 1998 (average NO_3-N concentration of 13 mg L^{-1}) to 2008 (16.5 mg L^{-1}), even though surpluses decrease (indicating a biogeochemical time lag). In a scenario, where equilibrium had been reached (after 9 years of legacy store depletion), maintenance of current surpluses, as in the study of Huebsch et al. (2012), would result in acceptable groundwater concentrations. Here climate (Lord and Anthony, 2002) as in the Huebsch study would play a major role in determining groundwater NO_3-N concentrations. Since attenuation in this aquifer is low, concentrations emanating from the spring site discharging to the surface waterbody are likely to be marginally lower than those in groundwater. For the present time, strict adherence to the present set of conservation measures i.e. NiD, whilst controlling annual surpluses to deplete those stored, mineralised and leached from the top 1 m of soil/subsoil to groundwater is prudent.

4. Conclusions

The present study found biogeochemical time lags (decades) to be longer than hydrologic equivalents (months to years). Retention of nutrients occurred in soil/subsoil layers to 1 m depth. Despite high P saturated soils to 0.5 m the underlying Karst chemistry attenuated groundwater and spring DRP to allowable concentrations. In terms of N, high levels of N (organic forms) mineralised and then leached through the deep subsoil to bedrock at approximately 10 m depth. Thereafter the greatest percentage of N loss in terms of load for all flow events stemmed from the small fissure pathway (54-88%) (longest hydrologic time lag), followed by the medium fissure pathway (7-21%) with the smallest loads emanating from either large fissure (1-13%) or conduit (1-10%) pathways (shortest hydrologic time lag). While the highest loss (i.e. load) of NO_3-N was in the slow-flow pathways in all events, the highest flow-weighted mean concentrations were in the quick-flow transfer pathways during the two high flow events. With no further surpluses, it was estimated that depletion of the soil organic N legacy store in the top 1 m of soil/subsoil would take approximately 50 years, but would take only 9 years (equivalent equilibrium N mass in the top 1 m of soil/subsoil would reach 20 kg N ha^{-1}) for leached nitrate concentrations leaving this depth to drop to acceptable levels. Future management must focus on depleting the N mass in this storage compartment. Incorporation of biogeochemical and hydrologic time lag principles into future water quality regulations will provide regulators with realistic expectations when implementing policies.

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