

1 **Integrated assessment of agricultural nutrient pressures and legacies in karst**
2 **landscapes**

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24 Landscapes typically deemed at risk from leached losses of nitrogen (N) and phosphorus (P)
25 are those with short subsurface hydrologic time lags. Due to the short time it takes nutrients
26 to move from a source to an area of concern, such sites are deemed perfect to test the efficacy
27 of programmes of measures as management changes. However, a small subset of these sites
28 can retain nutrients in soil/subsoil layers, which in turn are leached and can be either
29 attenuated (e.g. nitrate converted to gaseous forms or immobilised in soil and P can be
30 mineralised) or mobilised over time. This biogeochemical time lag can have long lasting
31 effects on water quality. In an intensive agricultural karst oxidised aquifer setting, the aim of
32 this study was to improve understanding of P and N inputs, retention, attenuation and
33 subsurface pathway distribution and to inform how similar sites can be managed in the future.
34 This was undertaken for the present site by integrating existing secondary and new primary
35 datasets for both N and P. Results showed that in the years pre-2000 slurry from an on-site
36 integrated pig production unit had been applied at rates of 33 t ha⁻¹ annually, which supplied
37 approximately 136 kg ha⁻¹ total N and approximately 26 kg ha⁻¹ total P annually. This
38 practice contributed to large quantities of N (Total N and NH₄-N) and elevated soil test P
39 (Morgan extractable P), present to a depth of 1 m. This store was augmented by recent
40 surpluses of 263 kg N ha⁻¹, with leached N to groundwater of 82.5 kg N ha⁻¹ with only 2.5 kg
41 N ha⁻¹ denitrified in the aquifer thereafter. High resolution spring data showed greatest
42 percentage loss in terms of N load from small (54-88%) and medium fissure pathways (7-
43 21%) with longer hydrologic time lags, with smallest loads from either large fissure (1-13%)
44 or conduit (1-10%) pathways with short hydrologic time lags (reaction time at the spring
45 from onset of a rainfall event is within hours). Although soils were saturated in P and in
46 mobile forms to 0.5 m, dissolved reactive P concentrations in groundwater remained low due
47 to Ca and Mg limestone chemistry. Depletion of the legacy store with no further inputs
48 (taking 25% of available mass of soil organic N as available in 1 m of soil/subsoil to be 75 kg
49 N ha⁻¹) would take approximately 50 years, with NO₃-N concentrations in the source area
50 dropping to levels that could sustain groundwater NO₃-N concentrations below admissible
51 levels within 9 years. Biogeochemical time lags (decades) are longer than hydrologic time
52 lags on this site (months to years). Future management should target farm surpluses that
53 maintain a legacy store at or below a soil organic N mass of ~ 20 kg N ha⁻¹. Incorporation of
54 biogeochemical and hydrologic time lag principles into future water quality regulations will
55 provide regulators with realistic expectations when implementing policies.

56

57 Keywords

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

59

60 1. Introduction

61 Large anthropogenic nutrient legacies connected to aquatic ecosystems which have
62 accumulated over decades, and inherent hydrologic and biogeochemical time lags (Basu et
63 al., 2012; Hamilton, 2011; Van Meter et al., 2016), can obscure correlations between the
64 implementation of conservation and water quality improvement (Bouraoui and Grizzetti,
65 2014). Hydrologic time lag refers to the duration required for average dissolved N in
66 groundwater reservoirs and unsaturated zones, to be transported from a source (such as a
67 fertiliser application area) to a receptor (a waterbody or abstraction point), through the
68 soil/subsoil/transition zone and bedrock medium (Sousa et al., 2013). The biogeochemical
69 time lag is caused by retention of N (typically organic) within the upper layers of soil/subsoil
70 and this is a long term source for mineralisation and nitrate leaching. Recent work by Van
71 Meter et al. (2016) has shown that accumulation of N in subsoil below plough layers leads to
72 legacies of N in soil and groundwater for many decades. International environmental
73 legislation has implicitly acknowledged the importance of “time lag”. For example, the
74 European Union (EU) Water Framework Directive (WFD, OJEC, 2000) initially targeted
75 ‘good’ qualitative status of all EU water bodies by 2015, irrespective of national or regional
76 meteorological or hydrologic conditions. In light of the burgeoning literature on time lag
77 (Fenton et al., 2011a, Sousa et al., 2013; Vero et al., 2014 and others) this deadline has been
78 revised to later reporting periods (2021). Nevertheless, there is still a temptation to forget
79 legacy and time lag considerations, in light of the legislative requirement to assign measures
80 to at-risk water bodies. It is likely, therefore, in these areas, that additional conservation
81 measures may be considered to those measures legislated, for example, within the EU
82 Nitrates Directive (NiD, OJEC, 1991).

83

84 Demonstration and documentation (e.g. Kronvang et al., 2016) of conservation
85 measure implementation and successes that have improved water quality is encouraged and

86 this impact is most likely to be picked up on well drained sites (highly permeable soil and
87 underlying limestone or similarly permeable geology), as a correlation between farm
88 management and water quality can be quickly interpreted. This is due to soil hydrogeologic
89 characteristics that are conducive to intensive agriculture and also short hydrologic time lags
90 for nutrient transfer (Huebsch et al., 2013). However, a sub-set of these sites can also have a
91 legacy store of nutrients with differential sequestration and mobilisation dynamics and there
92 is a lack of understanding of controls on nutrient depletion trajectories (Van Meter and Basu,
93 2015).

94

95 Mapping of N and P vertical risk areas (Blicher-Mathiesen et al., 2014), which
96 anticipate nutrient specific attenuation factors, aims to divide a landscape into functional land
97 management parcels (Baily et al., 2012; Fenton et al., 2011b; O’Sullivan et al., 2015). Some
98 areas act as natural attenuation areas and should be maintained as such (e.g. denitrification
99 hotspots or flow sinks for N or specific soil chemistries that offer P attenuation due to high
100 binding energies and sorption capacities (Daly et al., 2015) and that can occur in sections of
101 drainage ditches (Shore et al., 2015), whereas other areas are considered mere delivery
102 points. Tesoriero et al. (2013) examined the vulnerability of streams in different catchments
103 to legacy nitrate pollution and found that high concentrations may be sustained for decades,
104 which were decoupled from present day farm management. A clear definition of legacy
105 effects by Bain et al. (2012) highlights this storage component (e.g. for N see Worrall et al.,
106 2015; for P see Jarvis et al., 2014) and the complex distribution of elements of this storage for
107 reactive nitrogen (N_r) and P amongst different hydrological flow paths. Where the storage
108 component is isolated below the rooting zone in the subsoil, and yet connected to a receptor
109 through surface springs or through surface-groundwater interactions, the water quality and
110 ecological impacts can be prolonged (Hamilton, 2011).

111

112 The present study focuses on intensively grazed dairy farm sites under permanent
113 pasture, e.g. characterised by well-drained soil/subsoil (moderate to high permeability)
114 underlain by high permeability bedrock (weathered and fractured karst) and dominated by
115 subsurface pathways in terms of P and N. On a similar site in terms of N, Huebsch et al.
116 (2013) showed that consideration of a hydrologic time lag, inferred past and documented
117 present N-loadings, local weather conditions and hydrogeological, pedological, geological
118 site characteristics and management changes were all significant factors that influenced
119 spatial and temporal trends of nitrate concentration over 12 years. Mellander et al. (2013),
120 focussing on P, postulated that P attenuation associated with soil chemistry, depth to bedrock
121 and retention within a karst aquifer ensured emergent spring water was below an ecological
122 impairment threshold. A revised intrinsic groundwater vulnerability assessment was used to
123 produce a specific P vulnerability assessment that used the soil and hydrogeological P
124 buffering potential of the landscape as key assumptions in moderating P export to the
125 emergent spring. Jarvie et al. (2014) also found that up to about 90% of the annual soluble P
126 flux was retained rather than diluted in a karst terrain in mid-continental USA, but
127 highlighted the potential for slow release of legacy P to surface waters.

128

129 To consider the need for future mitigation interventions on free-draining, intensive
130 agricultural land, the aim of this study was to develop an improved understanding of P and N
131 inputs, storage, attenuation and subsurface pathway distribution on a grassland site and to
132 consider how similar legacy sites can be managed into the future. The first objective, using an
133 integrated approach, was to collate and interpret existing secondary and additional primary
134 datasets to interpret all aspects of the nutrient continuum from source (inputs) to delivery.
135 The second objective was to assess the likely efficacy of present programmes of measures to

136 mitigate subsurface losses originating from legacy sources. In addition perspectives of
137 management/implications of the results are also discussed.

138

139 2. Materials and methods

140 *2.1 Study site*

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

152

153 Insert Fig 1.

154

155 *2.2. Secondary datasets*

156 All secondary datasets were used to initially characterise the site. Attributes such as
157 the type, source and purpose of these data are itemised in Table 1. In addition, data from a
158 perennial spring on site were examined previously by Huebsch et al. (2015) (Fig 1). In
159 summary, a pump house and lagoon (23 m²), is equipped with a Corbett trapezoidal flume
160 used to measure discharge from the lagoon with a calibrated water level recorder (Diver;
161 0.000 m to 10.000 m). A double wavelength spectrophotometer (5 mm path length) sensor
162 (NITRATAX plus sc, Hach Lange GmbH, Germany; Huebsch et al., 2015) measured NO₃-N
163 concentrations (0.000 to 25.000 mg L⁻¹). Both instruments measured at a 15 minute resolution

164 and were used to calculate NO₃-N flux from 27 November 2011 to 25 March 2013. Huebsch
165 et al. (2015) summarised that storm events altered nitrate concentrations significantly, i.e.
166 with rapidly decreasing or increasing concentrations. The response in the karst indicated a
167 strong dependent on nutrient source, whether mobilisation and/or dilution occurred, and on
168 the pathway taken.

169

170 *2.2 Primary datasets*

171 All primary datasets were developed (though additional field work, collating
172 unpublished data or re-analysis of existing data) to form further understanding of the site.
173 These data are itemised in Table 2. More specifically, the farm N balance including
174 attenuation was based on the amount of N input into the farm, recycled within and exported
175 (output) from the farm. Total N input included fertilizer N, concentrates (feed other than
176 grass), atmospheric deposition and biological N₂-N fixation (BNF) (Scholefield et al., 1991;
177 Ryan et al., 2011). The amount of N input by animal excreta and output by grazed grass and
178 silage was estimated to be equal and, therefore, was not accounted for in the N balance.
179 Nitrogen input by concentrate feed was calculated by multiplying the total amount of
180 concentrate by its crude protein (CP) content and dividing by 6.25 (balances rations for CP
181 rather than specifically for amino acids) (McDonald et al., 1995). The quantity of
182 atmospheric N deposition was estimated as 8 kg ha⁻¹ (Ryan et al., 2006). Total N surplus was
183 calculated by subtracting total output from total input (Scholefield et al., 1991). Total N to be
184 leached to groundwater was calculated considering N losses via volatilization (NH₃ emission),
185 accumulated in soil and losses by denitrification in the vadose zone (Jahangir et al., 2012;
186 Ryan et al., 2011).

187

188 Biogeochemical time lags were estimated using the formulae presented in van Meter
189 and Basu (2015) with the following input parameters: an approximation of 300 kg N ha⁻¹ as
190 the mass of the legacy N store for the first 1 m of soil/subsoil was estimated. With only 25%
191 of this figure likely to be mineralised i.e. 75 kg N ha⁻¹ (initial mass of the soil organic N) and
192 utilising ceramic cup average nitrate data for the whole farm as our initial concentration i.e.
193 35.36 mg NO₃-N L⁻¹ leached from the source zone, with an N depletion rate (yr) of 0.16 from
194 the mass accumulation, recharge of 500 mm yr⁻¹, saturation of 0.5 and porosity of 0.3.

195

196 Hydrologic time lags were estimated by firstly investigating unsaturated travel time to
197 10 m using site specific soil/subsoil physical data from Kramers et al. (2013) and converting
198 this to soil hydraulic data in RETC (Table 3). Daily meteorological data from a local synoptic
199 station were used as outlined in Vero et al. (2014). Nodes were placed at 1, 5 and 10 m,
200 representing depth to bedrock ranges on site. Initial breakthrough (IBT), centre of mass
201 (COM) and total exit (Exit) of a conservative tracer (dispersivity of 1/10th total profile depth,
202 with initial breakthrough and total exit assumed at threshold concentrations of 0.01 mmol
203 cm⁻¹) in days after start of simulation was estimated. An atmospheric upper boundary
204 condition allowing surface runoff and a free-draining lower boundary condition were used as
205 in Jaques et al. (2008). A third-type/Cauchy upper boundary condition was applied
206 (Konikow, 2011; Šimůnek et al., 2013).

207

208 Data collected at the perennial spring during the study of Huebsch et al. (2014) were
209 analysed further for the saturated component of the hydrologic time lag. For total hydrologic
210 time lag the unsaturated and saturated components can be added together. This work allowed
211 for the apportionment of NO₃-N load and concentration to distinct pathways by using high
212 frequency monitoring of discharge and NO₃-N concentration in the emerging spring

213 (Mellander et al., 2013). Rainfall events (with total depth of 10 m) were separated from each
214 other, if precipitation was less than 0.2 mm hr^{-1} within 24-hr in accordance with Kurz et al.
215 (2005). The following events were examined: Event I, 11-15 November 2011; Event II, 16-18
216 November 2011; Event III (29 November-11 December 2011); Event IV, 3-20 January 2012.
217 The method is similar to a hydrograph separation described by Dingman (2015), where
218 hydrological pathways were identified as the segments between graphically identified
219 inflection points along the recession limb of hydrographs. Here, instead of a hydrograph, the
220 $\text{NO}_3\text{-N}$ loadograph using the *Loadograph Recession Analysis* (LRA) method (Mellander et
221 al., 2012a) was used to identify inflection points of source pathways. In order to separate flow
222 pathways and transfer pathways the timing for the identified inflection points were used in
223 the hydrograph and adapted to the loadograph, where in this case the inflection points were
224 less clear. Individual transfer pathways were logarithmically separated from the start of the
225 rising limb to the inflection points. The segments were assumed to represent the release of
226 $\text{NO}_3\text{-N}$ *via* different transfer pathways. These pathway loads could be quantified and were
227 here interpreted to be transfer in conduit, large fissure, medium fissure and small fissure
228 similar to Mellander et al. (2012b; 2013). The flow-weighted $\text{NO}_3\text{-N}$ concentration was
229 estimated for each pathway by dividing the transfer load with the discharge.

230 3. Results and discussion

231 *3.1 Characterisation using secondary data*

232 In 2009, 2010, 2011 and 2012 annual rainfall was 1293, 869, 855 and 1097 mm,
233 respectively. Utilising the hybrid model of Schulte et al. (2005) for grassland in Ireland (see
234 Table 1), no runoff occurs on site and therefore infiltration on site was 673, 326, 364 and 578
235 mm for equivalent years. Irish soils have very low levels of P naturally other than reserves
236 that have been deposited by farming practices (animals, manures, fertilisers). The levels of
237 soil test P (bioavailable P) found in unfarmed soils is usually low as P present will largely be
238 bound to the soil in solid phase due to the relatively high levels of Fe, Al, and Mn in acid
239 soils and Ca in calcareous soils in Ireland. Legacy nutrients are evident to 1 m depth (both P
240 and N). In terms of past inputs using typical values, high rates of organic manure application
241 (slurry from the on-site integrated pig production unit had been applied to the upper levels of
242 the farm at typical application rates of 33 t ha⁻¹ annually) has supplied approximately 136 kg
243 ha⁻¹ total N and approximately 26 kg ha⁻¹ total P annually in the years pre-2000. Soil testing
244 of agricultural soils has seen a decline in the number of samples recording excessive P (from
245 24% in 1996 to 17% in 2015) with a concurrent increase in samples recording P deficiencies
246 (from 17% in 1996 to 31% in 2015). These trends are also reflected in declining P balances as
247 farmers are faced with the challenge of meeting a zero P balance requirement farm scale
248 under the current programme of measures i.e. the NiD. Ireland has a decreasing national P
249 surplus from 1990 to 2008 from 11 to 6 kg P ha.

250

251 This practice on the current site has contributed to large quantities of N (Total N and
252 NH₄-N) and elevated soil test P, (Morgan extractable P) present at all tested soil depths.
253 Firstly, in terms of P storage in the subsoil, data from Richards et al. (1998) showed that
254 Morgan's P ranged from 23.3 to 60.0 mg L⁻¹ for the topsoil agronomic depth (0-15 cm) and

255 7.7 to 43.7 mg L⁻¹ for subsoil depths to 0.5 m, well in excess of the agronomic maximum of 8
256 mg L⁻¹ (i.e. upper threshold of P Index 3, Morgan's). As some of this P is initially organically
257 bound there is potential for P movement downwards through the soil profile where it will be
258 mineralised. The parent material under these soils is deep limestone and if P makes its way
259 through the topsoil into the subsoil it is likely to be attenuated (precipitated) and stored as
260 calcium phosphates. Under the alkaline conditions that persist in the subsoil these calcium
261 phosphates are likely to be very stable.

262

263 In terms of N storage soil/subsoil testing showed NH₄-N concentrations for paddocks
264 receiving no fertilizer with high concentrations of 25.2, 10.0, 3.1, 0.9, and 0.8 mg kg⁻¹, for
265 successive depths (20 cm increments). Total N equivalents for these depths were 3.4, 8.8,
266 19.7, 8.8 and 7.7 mg kg⁻¹. At depth 40-60 cm there was more NO₃-N than NH₄-N, which
267 indicates mineralisation and a storage bank for potential leached losses.

268

269 Generic soil chemistry data points to a soil type that is typically high in Fe (Fay et al.,
270 2007; Selbie et al., 2015) and when associated with organic matter these compounds combine
271 to form amorphous forms of Fe-P (Daly et al., 2001). Whilst, Iron-rich soils have a strong
272 affinity for P with high P sorption capacities for P (Daly et al., 2015), amorphous forms of Fe
273 bound P can be soluble and mobile, as evidenced in elevated sub-surface water P
274 concentrations in an Irish ground-water fed catchment (Mellander et al., 2016).

275

276 Groundwater (NO₃-N drinking water quality maximum admissible concentration
277 (MAC) of 11.3 mg NO₃-N L⁻¹) borehole mean NO₃-N concentrations for BH1, BH2, BH3,

278 and BH4 were $17.8 \pm 1.1 \text{ mg L}^{-1}$, $7.6 \pm 0.3 \text{ mg L}^{-1}$, $9.0 \pm 0.8 \text{ mg L}^{-1}$, and $17.7 \pm 0.9 \text{ mg L}^{-1}$,
279 respectively. Nitrite-N and $\text{NH}_4\text{-N}$ equivalents were all below 0.05 mg L^{-1} . The water table
280 remains from 25 to 30 m bgl with recharge from October, continuing until May or June.
281 Nitrate-N produced by nitrification from fertilizers or manures may not have enough
282 residence time to be biogeochemically processed. Both Fenton et al. (2009; 2011) and
283 Jahangir et al. (2013) showed that lower rates of denitrification occur at higher saturated
284 hydraulic conductivities (k_s). Herein there is high k_s at depth, resulting in high dissolved
285 oxygen (DO) with high levels of DON ($0.92\text{-}3.5 \text{ mg L}^{-1}$) and a high mean redox potential
286 (Eh) of 176 mV. From 2010-2011, groundwater pH on site was approximately 6 (slightly
287 acidic indicating dissolution), mean DOC was 0.9 mg L^{-1} (highest concentrations occurred in
288 December-January and lowest in August-September). Jahangir et al. (2013) estimated leached
289 N losses to groundwater to be $82 \text{ kg NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ including actual on site denitrification
290 rates, ammonia volatilization and microbial assimilations. However, as a reactive process of
291 transport, this $\text{NO}_3\text{-N}$ can be disintegrated further with 4% of the N being reduced through
292 denitrification. Jahangir et al. (2012) estimated about 10% of the total dissolved N in
293 groundwater was other than $\text{NO}_3\text{-N}$. Of this, DON and denitrified N_2 accounted for 8 kg N
294 $\text{ha}^{-1} \text{ yr}^{-1}$.

295

296 Landig et al. (2010) identified three distinctive fracture sets (Set A $078^\circ/87^\circ$; Set B,
297 $177^\circ/59^\circ$ and Set C, $349^\circ/57^\circ$) on site. The median fracture spacing ranged from 0.27 to 0.43
298 m and effective hydraulic aperture ranged from 0.16 to 0.22 mm. A range of possible
299 hydraulic conductivities were calculated, from 1.6×10^{-5} to $6.4 \times 10^{-5} \text{ m s}^{-1}$, with 30% of the
300 total flux entering the nearby Funshion River (Fig 1) emanating from conduits. The 2012
301 spring flux equated to $2.2 \text{ kg NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$, if the contribution area of the spring is the
302 entire farm; however this area is likely to be much smaller at approximately 5 ha based on

303 discharge and NO₃-N concentration data and therefore leached losses of 43 kg NO₃-N ha⁻¹ yr⁻¹
304 ¹ in this area are likely. Hence, the predictions made in the study by Landig et al. (2010) i.e.
305 18040 ± 2320 kg NO₃-N ha⁻¹ yr⁻¹ (54% of agronomic loadings) equates to 185 using an entire
306 farm (97 ha). The total flux discharging from the spring during the 18 month period was 263
307 kg NO₃-N. The total flux for 2012 was 215 kg NO₃-N yr⁻¹. Flow was < 1 l s⁻¹ for 71.4% of the
308 period, with 22% of flow > 1 l s⁻¹ to 1.2 l s⁻¹. With respect to NO₃-N, 82% of the period was
309 ≤ 11.3 mg L⁻¹, 10.5 % was from 11.3 to 13 mg L⁻¹ with the remainder above this
310 concentration. For the entire farm using a discrete fracture network (DFN) model, derived
311 from scanline samples in combination with a stream tube model, Landig et al. (2010)
312 estimated total NO₃-N load by adding results from three control planes covering the full
313 extent of the site boundary with the river (1800 ± 100 kg NO₃-N yr⁻¹, 13200 ± 1900 kg NO₃-
314 N yr⁻¹ and 140 ± 30 kg NO₃-N yr⁻¹) and three springs through direct measurements (17th
315 November 2008 representing maximum flow conditions, 600 ± 50 kg NO₃-N yr⁻¹, 1100 ± 120
316 kg NO₃-N yr⁻¹ and 1200 ± 120 kg NO₃-N yr⁻¹ (same spring as in the current study).

317

318 *3.2 Further characterisation*

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

327 (Buckley et al., 2016). On this site which imported pig slurry, it is likely that the N and P
328 surplus was higher than these levels in the years pre-2000. From an EU perspective van
329 Grinsven et al. (2012) examined the implementation of the NiD in terms of N surplus and
330 nitrate concentration across the northwest of the EU (Ireland, United Kingdom, Denmark, the
331 Netherlands, Belgium, Northern France and Germany). Implementation of the NiD (since
332 1995) showed a major decrease of the soil N surplus), particularly in Belgium, Denmark,
333 Ireland, the Netherlands and the United Kingdom, with a modest decrease of nitrate
334 concentrations since 2000 in fresh surface waters in most countries. However, such decreases
335 were less evident in groundwater due to time lags (Fenton et al. (2012) associated with nitrate
336 in deep aquifers.

337 However, since the introduction of the Good Agricultural practice rules (S.I. 378 of
338 2006) under the EU NiD, P inputs were constrained according the soil test P levels. Under
339 these rules no P could be applied to soils with P concentrations in excess of the agronomic
340 optimum levels and those that were at agronomic optimum levels (i.e. Morgan 's extractable
341 P 5-8 mg l⁻¹) were not allowed P applications to replace off-takes (i.e. maintained at P
342 balance). It was expected that these P management rules would draw down legacy soil P over
343 time or prevent excessive soil P build-up from occurring in future. Therefore in terms of
344 legacy P and vertical P transport on well drained sites appropriate conservation measures are
345 already in place.

346

347 Soil sampling data from sampling location 1 on the farm (Table 5), show that where
348 the Morgan's P level in the soil was very high (38 mg L⁻¹) the M3-A1/P ratio (2.07) was low,
349 with a low soil P sorption potential and high P availability under such conditions (Daly et al.,
350 2015). Where the Morgan's P concentration was less than the target agronomic range (5-8 mg

351 L⁻¹), at sampling location 2 (4.1 mg L⁻¹), the M3-Al/P ratio (16.9) was above the threshold
352 value of 11.7 where P is more strongly fixed with lower P solubility. These results suggest a
353 highly P saturated topsoil with high risk of P mobilisation in the presence of a hydrological
354 pathway. Although P concentrations in the source zone below the rooting zone are high, the
355 low resolution grab samples taken at different times from boreholes and the spring show very
356 low dissolved reactive P (DRP) concentrations (Maximum Admissible Concentration (MAC,
357 the nutrient conditions for meeting Good status required by EU WFD (SI 272 of 2009),
358 allows for mean molybdate reactive P (MRP) concentration of 0.035 mg L⁻¹ or < 0.075 mg L⁻¹
359 (95 %ile).

360

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

375

376 Leached N losses from the legacy store (down to 1 m) were captured on site in
377 ceramic cups at 0.9 m and showed average NO₃-N concentrations (control paddocks with no
378 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
379 average for all ceramic cups spread throughout the farm and every measurement date,
380 including immediately after ceramic cup insertion was 35.36 mg N L⁻¹ (Range 0.12 to 282.5
381 mg N L⁻¹).

382

383 The 1D-Hydrus numerical modelling, showed relatively slow migration of the tracer
384 to a depth of 10 m (Table 4). In a 0.7 m deep soil profile, Kramers et al. (2009) pointed to
385 some preferential pathways in this soil, which decreased with depth. On an adjacent site
386 Richards et al. (2005), showed matrix flow dominated with peak concentrations at 0.5 m
387 depth reached after 34-65 days. The average spring discharge on site was 5 m h⁻¹, which is at
388 the low end of the range for lowland springs in Ireland (5-250 m h⁻¹; Drew, 2008). There is
389 evidence of a quick discharge response to rainfall events - ~ 7 hours. Typically in all events
390 the NO₃-N concentration peaked (i.e. mobilisation) a few hours before discharge. During the
391 Huebsch et al. (2014) study an unpublished borehole (BH3) to spring uranine and optical
392 brightener (Tinopal) tracer experiment was conducted and showed highest peak concentration
393 at the spring after 11 h 26 min in a period of no rainfall. The zone of influence of the spring
394 in the current study was determined to be within the groundwater divide demarcated in Fig 1.
395 The tracer experiment also excluded connectivity with other springs in the area.

396

397 *3.3. Nitrate-N concentration and load across flow Events I-IV*

398 Flow event based information is presented in Table 6. Rainfall amount and
399 cumulative discharge during the flow event sequence follows a pattern, due to storage (e.g.
400 from Event II influencing Event III) within the system at any given time. This is more
401 applicable for Events I-III as they directly follow each other. Intermittent rainfall between
402 Event III and IV occurs below the 10 mm threshold. From a concentration perspective the
403 source appears constant and well connected to potential pathways with concentrations
404 approximating MAC, although decreasing for Event IV. As described by Huebsch et al.
405 (2014) during the four events examined - as rainfall intensified, discharge increased followed
406 by increased NO₃-N concentration some time later with the maximum NO₃-N concentration
407 reached earlier than the discharge peak. This was also the case for the events examined in the
408 present study.

409

410 *3.4 Flow paths and nitrate-N transfer pathways with Events I-IV*

411 Four types of flow and NO₃-N transfer pathways were identified by the separation
412 method conduit, large fissure, medium fissure and small fissure (Table 7 and Fig. 2) which is
413 in agreement with the number of flow compartments found by Landing et al. (2010). The
414 conduit and large fissure pathways were assumed to be quick-flow pathways and responded
415 relatively quickly to rainfall, whereas the small and medium fissure flow, were assumed to be
416 slower-flow pathways. Across the four analysed flow events all pathways were active but
417 their apportionment in terms of spring discharge and NO₃-N concentration changed across
418 events (Fig. 3). Proportionally and quantitatively the highest loss of NO₃-N was from the
419 small fissure pathway (54-88% and 1.3-10.5 kg respectively) for all flow events. This
420 pathway is likely to exhibit lower permeability and therefore higher attenuation capacity.
421 This was followed by the medium fissure pathway (7-21% and 0.1-2.4 kg) with the smallest

422 loads emanating from either large fissure (1-13% and 0.0-1.5 kg) or conduit (2-11% and 0.1-
423 1.4 kg) pathways. The highest event flow-weighted mean concentration was in Event III
424 (13.1 mg L^{-1}) and highest concentration of transfer pathway was in the large fissure flow of
425 Event III (14.7 mg L^{-1}). In terms of $\text{NO}_3\text{-N}$ concentration Event II and III breached MAC in
426 all pathways, whereas Events I breached MAC only in the quick-flow pathways. The $\text{NO}_3\text{-N}$
427 concentrations in Event IV remained below the MAC. The direction and magnitude of
428 discharge and $\text{NO}_3\text{-N}$ concentration hysteresis loops, following a rainfall event, provides
429 information on the $\text{NO}_3\text{-N}$ source availability. A clockwise direction typically means a
430 proximal source and an anticlockwise direction a distal source. The magnitude and clockwise
431 (proximal source as opposed to a more distal diffuse source) trajectory of the hysteresis loop
432 in Event II indicate that a substantial amount of $\text{NO}_3\text{-N}$ was available for transfer in the
433 conduits already at the start of that event.

434

435 While the highest loss (i.e. load) of $\text{NO}_3\text{-N}$ was in the slow-flow pathways in all
436 events (highest in Event IV small fissure flow), the highest flow-weighted mean
437 concentrations were in the quick-flow transfer pathways during the two high flow events
438 (Event II and III). As most of the $\text{NO}_3\text{-N}$ was lost via small fissures the transit time was
439 longer and $\text{NO}_3\text{-N}$ is likely to be more exposed to attenuation processes. This is important for
440 the south of Ireland as regionally important karst aquifers dominated by conduit flow are in
441 the west of Ireland whereas those dominated by diffuse flow (as in the present study) are in
442 the south of Ireland (Coxon, 2014). It is the south of Ireland that coincides with intensive
443 dairying.

444

445 *3.5 Implications*

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

464 An integrated or holistic characterisation has benefits for future management. In terms
465 of P losses on this site, zero P surpluses enforced under the NiD coupled with long term
466 sequestration within the system at depth will continue to manage losses, with no need for
467 further intervention. The work of Schulte et al. (2010) showed that for worst case scenarios of
468 high Total P and soil test P (Morgan's $P > 8 \text{ mg L}^{-1}$) starting points, average time to fall
469 below this concentration to agronomic optima was estimated at 7-15 years depending on the

470 field P balance. However, uncertainty analysis showed that variation across soil types was
471 high creating a wider range from 3 to >20 years.

472

473 From an N perspective one tempting option would be to remediate accessible
474 pathways e.g. spring discharges with finite ecologically engineered solutions. Taking the
475 example of an artificial nitrogen sink such as a woodchip denitrifying bioreactor (e.g. Fenton
476 et al., 2016; Schipper et al. 2010), which could be installed at the spring location to convert
477 nitrate to di-nitrogen gas based on the highest flow rate of $361 \text{ m}^3 \text{ day}^{-1}$ and the highest $\text{NO}_3\text{-N}$
478 N concentration of 15 mg L^{-1} , with an assumed in-field denitrification rate of $7.6 \text{ g N m}^3 \text{ day}^{-1}$
479 ¹ (other laboratory studies have recorded much lower denitrification rates of $3.5 \text{ g NO}_3\text{-N m}^3$
480 d^{-1} (Healy et al., 2014)), a structure of 712.5 m^3 would be needed to bring concentrations to
481 zero, or 175.5 m^3 to bring $\text{NO}_3\text{-N}$ concentration to MAC. In reality the bioreactor could be
482 smaller as the average flow was $39 \text{ m}^3 \text{ day}^{-1}$ and average $\text{NO}_3\text{-N}$ concentration 10.7 mg L^{-1} .
483 To bring these conditions to zero the bioreactor would only need to be 54 m^3 . Setting the
484 price of 1 m^3 of woodchip at 100 €. The total flux price equivalent of the nutrient value for
485 the entire 18 month period at the spring would be about 300 € (1.15 € per kg) and therefore it
486 would take 25 years to re-coup the cost of the $\text{NO}_3\text{-N}$ being lost.

487

488 Martin et al. (2017) have investigated the time lags involved between land use/cover
489 change and water quality change, documenting the large range of time scales involved. Van
490 Meter and Basu (2016) indicate how estimation of time lags is difficult due to an incomplete
491 understanding of controls on nutrient depletion trajectories after changes in land-use or
492 management practices. The simple model developed by Van Meter and Basu (2015)

493 incorporated biogeochemical and hydrologic time lags and showed that legacy effects added
494 to overall time lags above those of the hydrologic component alone.

495

496 The estimate of biogeochemical time lags using the input data documented in 2.2
497 showed that it would take 50 years for the legacy store (with no further inputs) to become
498 depleted. However, it would only take 9 years for the concentrations leaving the source area
499 to return to concentrations that would then dilute current groundwater NO₃-N concentrations
500 on site after the hydrologic time lag through the unsaturated zone. Therefore to manage the
501 site the mass of the soil organic N pool in the storage component must remain or drop below
502 20 kg N ha⁻¹.

503

504 By examining the N surplus and corresponding N leached to groundwater at the same
505 time point can be insightful (Table 4). Four scenarios are examined using farm N Input-
506 Output data, an annual effective drainage figure of 500 mm, the area of the farm i.e. 97 ha
507 and NO₃-N concentration in groundwater for 1998 (pre2000), 2008 (present scenario),
508 equilibrium (taking data from a nearby site used in Huebsch et al. (2012) after the store in the
509 first 1 m is depleted). The inorganic leached N to groundwater (kg N ha⁻¹) figure increased
510 from 1998 (average NO₃-N concentration of 13 mg L⁻¹) to 2008 (16.5 mg L⁻¹), even though
511 surpluses decrease (indicating a biogeochemical time lag). In a scenario, where equilibrium
512 had been reached (after 9 years of legacy store depletion), maintenance of current surpluses,
513 as in the study of Huebsch et al. (2012), would result in acceptable groundwater
514 concentrations. Here climate (Lord and Anthony, 2002) as in the Huebsch study would play a
515 major role in determining groundwater NO₃-N concentrations. Since attenuation in this
516 aquifer is low, concentrations emanating from the spring site discharging to the surface
517 waterbody are likely to be marginally lower than those in groundwater. For the present time,

518 strict adherence to the present set of conservation measures i.e. NiD, whilst controlling
519 annual surpluses to deplete those stored, mineralised and leached from the top 1 m of
520 soil/subsoil to groundwater is prudent.

521

522 4. Conclusions

523 The present study found biogeochemical time lags (decades) to be longer than hydrologic
524 equivalents (months to years). Retention of nutrients occurred in soil/subsoil layers to 1 m
525 depth. Despite high P saturated soils to 0.5 m the underlying Karst chemistry attenuated
526 groundwater and spring DRP to allowable concentrations. In terms of N, high levels of N
527 (organic forms) mineralised and then leached through the deep subsoil to bedrock at
528 approximately 10 m depth. Thereafter the greatest percentage of N loss in terms of load for
529 all flow events stemmed from the small fissure pathway (54-88%) (longest hydrologic time
530 lag), followed by the medium fissure pathway (7-21%) with the smallest loads emanating
531 from either large fissure (1-13%) or conduit (1-10%) pathways (shortest hydrologic time lag).
532 While the highest loss (i.e. load) of NO₃-N was in the slow-flow pathways in all events, the
533 highest flow-weighted mean concentrations were in the quick-flow transfer pathways during
534 the two high flow events. With no further surpluses, it was estimated that depletion of the soil
535 organic N legacy store in the top 1 m of soil/subsoil would take approximately 50 years, but
536 would take only 9 years (equivalent equilibrium N mass in the top 1 m of soil/subsoil would
537 reach 20 kg N ha⁻¹) for leached nitrate concentrations leaving this depth to drop to acceptable
538 levels. Future management must focus on depleting the N mass in this storage compartment.
539 Incorporation of biogeochemical and hydrologic time lag principles into future water quality
540 regulations will provide regulators with realistic expectations when implementing policies.

541

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547

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