



## Integrated assessment of agricultural nutrient pressures and legacies in karst landscapes

Fenton, O., Mellander, P-E., Daly, K., Wall, D. P., Jahangir, M. M. R., Jordan, P., Hennessey, D., Huebsch, M., Blum, P., Vero, S., & Richards, K. G. (2017). Integrated assessment of agricultural nutrient pressures and legacies in karst landscapes. *Agriculture, Ecosystems & Environment*, 239, 246 - 256. Advance online publication. <https://doi.org/10.1016/j.agee.2017.01.014>

[Link to publication record in Ulster University Research Portal](#)

**Published in:**  
Agriculture, Ecosystems & Environment

**Publication Status:**  
Published online: 30/01/2017

**DOI:**  
[10.1016/j.agee.2017.01.014](https://doi.org/10.1016/j.agee.2017.01.014)

**Document Version**  
Author Accepted version

**General rights**  
Copyright for the publications made accessible via Ulster University's Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**  
The Research Portal is Ulster University's institutional repository that provides access to Ulster's research outputs. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact [pure-support@ulster.ac.uk](mailto:pure-support@ulster.ac.uk).

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

3 O. Fenton<sup>a\*</sup>, P.-E. Mellander<sup>b</sup>, K. Daly<sup>a</sup>, Wall, D.P<sup>a</sup>, M.M.R. Jahangir<sup>c</sup>, P. Jordan<sup>d</sup>, D.  
4 Hennessey<sup>e</sup>, M. Huebsch<sup>f</sup>, P. Blum<sup>f</sup>, S. Vero<sup>g</sup>, K.G. Richards<sup>a</sup>

5 <sup>a</sup>*Teagasc, Environmental Research Centre, Johnstown Castle, Wexford, Co. Wexford,*  
6 *Ireland.*

7 <sup>b</sup>*Agricultural Catchments Programme, Teagasc, Environmental Research Centre, Johnstown*  
8 *Castle, Wexford, Co. Wexford, Ireland.*

9 <sup>c</sup>*Dept. Soil Science, Bangladesh Agricultural University, Mymensingh-2202*

10 <sup>c</sup>*School of Geography and Environmental Sciences, Ulster University, Coleraine, UK.*

11 <sup>e</sup>*Teagasc, Animal and Grassland Research and Innovation Centre, Moorepark, Fermoy, Co.*  
12 *Cork, Ireland.*

13 <sup>f</sup>*Karlsruhe Institute of Technology (KIT), Institute of Applied Geosciences (AGW), Kaiserstr.*  
14 *12, 76131 Karlsruhe, Germany.*

15 <sup>g</sup>*Department of Geology, Thompson Hall, Kansas State University, Manhattan, KS 66506*

16 \* Corresponding author. Tel.: +353 539171271; fax: +353 539142213.

17 E-mail addresses: [owen.fenton@teagasc.ie](mailto:owen.fenton@teagasc.ie) (O. Fenton), [per-erik.mellander@teagasc.ie](mailto:per-erik.mellander@teagasc.ie) (P.-E.

18 Mellander), [karen.daly@teagasc.ie](mailto:karen.daly@teagasc.ie) (Karen Daly), [david.wall@teagasc.ie](mailto:david.wall@teagasc.ie) (David Wall),

19 [mmrjahangir@gmail.com](mailto:mmrjahangir@gmail.com) (M.M.R. Jahangir), [p.jordan@ulster.ac.uk](mailto:p.jordan@ulster.ac.uk) (P. Jordan),

20 [deirdre.hennessey@teagasc.ie](mailto:deirdre.hennessey@teagasc.ie) (D. Hennessey), [manuela.huebsch@kit.edu](mailto:manuela.huebsch@kit.edu) (M. Huebsch),

21 [philipp.blum@kit.edu](mailto:philipp.blum@kit.edu) (P. Blum), [sara.vero@teagasc.ie](mailto:sara.vero@teagasc.ie) (S. Vero), [karl.richards@teagasc.ie](mailto:karl.richards@teagasc.ie)

22 (K.G. Richards).

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<sup>-1</sup> annually, which supplied  
37 approximately 136 kg ha<sup>-1</sup> total N and approximately 26 kg ha<sup>-1</sup> total P annually. This  
38 practice contributed to large quantities of N (Total N and NH<sub>4</sub>-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<sup>-1</sup>, with leached N to groundwater of 82.5 kg N ha<sup>-1</sup> with only 2.5 kg  
41 N ha<sup>-1</sup> 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<sup>-1</sup>) would take approximately 50 years, with NO<sub>3</sub>-N concentrations in the source area  
50 dropping to levels that could sustain groundwater NO<sub>3</sub>-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<sup>-1</sup>. 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 m<sup>2</sup>), 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 NO<sub>3</sub>-N  
163 concentrations (0.000 to 25.000 mg L<sup>-1</sup>). Both instruments measured at a 15 minute resolution



164 and were used to calculate NO<sub>3</sub>-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 N<sub>2</sub>-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<sup>-1</sup> (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 (NH<sub>3</sub> 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<sup>-1</sup> 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<sup>-1</sup> (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 NO<sub>3</sub>-N L<sup>-1</sup> leached from the source zone, with an N depletion rate (yr) of 0.16 from  
194 the mass accumulation, recharge of 500 mm yr<sup>-1</sup>, 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<sup>-1</sup>) 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 NO<sub>3</sub>-N load and concentration to distinct pathways by using high  
212 frequency monitoring of discharge and NO<sub>3</sub>-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  $0.2 \text{ mm hr}^{-1}$  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<sup>-1</sup> annually) has supplied approximately 136 kg  
243 ha<sup>-1</sup> total N and approximately 26 kg ha<sup>-1</sup> 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 NH<sub>4</sub>-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<sup>-1</sup> for the topsoil agronomic depth (0-15 cm) and

255 7.7 to 43.7 mg L<sup>-1</sup> for subsoil depths to 0.5 m, well in excess of the agronomic maximum of 8  
256 mg L<sup>-1</sup> (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 NH<sub>4</sub>-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<sup>-1</sup>, 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<sup>-1</sup>. At depth 40-60 cm there was more NO<sub>3</sub>-N than NH<sub>4</sub>-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 (NO<sub>3</sub>-N drinking water quality maximum admissible concentration  
277 (MAC) of 11.3 mg NO<sub>3</sub>-N L<sup>-1</sup>) borehole mean NO<sub>3</sub>-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  $0.05 \text{ mg L}^{-1}$ . 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  $0.9 \text{ mg L}^{-1}$  (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  $\text{N}_2$  accounted for  $8 \text{ kg N}$   
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  $1.6 \times 10^{-5}$  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 NO<sub>3</sub>-N concentration data and therefore leached losses of 43 kg NO<sub>3</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>  
304 <sup>1</sup> in this area are likely. Hence, the predictions made in the study by Landig et al. (2010) i.e.  
305 18040 ± 2320 kg NO<sub>3</sub>-N ha<sup>-1</sup> yr<sup>-1</sup> (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 NO<sub>3</sub>-N. The total flux for 2012 was 215 kg NO<sub>3</sub>-N yr<sup>-1</sup>. Flow was < 1 l s<sup>-1</sup> for 71.4% of the  
308 period, with 22% of flow > 1 l s<sup>-1</sup> to 1.2 l s<sup>-1</sup>. With respect to NO<sub>3</sub>-N, 82% of the period was  
309 ≤ 11.3 mg L<sup>-1</sup>, 10.5 % was from 11.3 to 13 mg L<sup>-1</sup> 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 NO<sub>3</sub>-N load by adding results from three control planes covering the full  
313 extent of the site boundary with the river (1800 ± 100 kg NO<sub>3</sub>-N yr<sup>-1</sup>, 13200 ± 1900 kg NO<sub>3</sub>-  
314 N yr<sup>-1</sup> and 140 ± 30 kg NO<sub>3</sub>-N yr<sup>-1</sup>) and three springs through direct measurements (17<sup>th</sup>  
315 November 2008 representing maximum flow conditions, 600 ± 50 kg NO<sub>3</sub>-N yr<sup>-1</sup>, 1100 ± 120  
316 kg NO<sub>3</sub>-N yr<sup>-1</sup> and 1200 ± 120 kg NO<sub>3</sub>-N yr<sup>-1</sup> (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<sup>-1</sup>, 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<sup>-1</sup> 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<sup>-1</sup>) 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<sup>-1</sup>) 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 ( $4.1 \text{ mg } L^{-1}$ ), 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  $0.035 \text{ mg } L^{-1}$  or  $< 0.075 \text{ mg } L^{-1}$   
359 (95 %ile).

360

361 On 26<sup>th</sup> October 2012 DRP spring concentrations were negligible and total P  
362 concentrations were  $0.007$  to  $0.01 \text{ mg } L^{-1}$  pointing to a particulate source. On 22<sup>nd</sup> 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 ( $>180 \text{ mg } L^{-1}$ ) 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 NO<sub>3</sub>-N concentrations (control paddocks with no  
378 inputs) of 7.91 mg L<sup>-1</sup>; with a maximum of 39.01 mg L<sup>-1</sup> and a minimum of 0.00 mg L<sup>-1</sup>. 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<sup>-1</sup> (Range 0.12 to 282.5  
381 mg N L<sup>-1</sup>).

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<sup>-1</sup>, which is at  
388 the low end of the range for lowland springs in Ireland (5-250 m h<sup>-1</sup>; Drew, 2008). There is  
389 evidence of a quick discharge response to rainfall events - ~ 7 hours. Typically in all events  
390 the NO<sub>3</sub>-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 NO<sub>3</sub>-N concentration some time later with the maximum NO<sub>3</sub>-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 NO<sub>3</sub>-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 NO<sub>3</sub>-N concentration changed across  
418 events (Fig. 3). Proportionally and quantitatively the highest loss of NO<sub>3</sub>-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 ( $13.1 \text{ mg L}^{-1}$ ) and highest concentration of transfer pathway was in the large fissure flow of  
425 Event III ( $14.7 \text{ mg L}^{-1}$ ). 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  $15 \text{ mg L}^{-1}$ , with an assumed in-field denitrification rate of  $7.6 \text{ g N m}^3 \text{ day}^{-1}$   
479 <sup>1</sup> (other laboratory studies have recorded much lower denitrification rates of  $3.5 \text{ g NO}_3\text{-N m}^3$   
480  $\text{d}^{-1}$  (Healy et al., 2014)), a structure of  $712.5 \text{ m}^3$  would be needed to bring concentrations to  
481 zero, or  $175.5 \text{ m}^3$  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  $10.7 \text{ mg L}^{-1}$ .  
483 To bring these conditions to zero the bioreactor would only need to be  $54 \text{ m}^3$ . Setting the  
484 price of  $1 \text{ m}^3$  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 NO<sub>3</sub>-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<sup>-1</sup>.

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 NO<sub>3</sub>-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<sup>-1</sup>) figure increased  
510 from 1998 (average NO<sub>3</sub>-N concentration of 13 mg L<sup>-1</sup>) to 2008 (16.5 mg L<sup>-1</sup>), 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 NO<sub>3</sub>-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 NO<sub>3</sub>-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<sup>-1</sup>) 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



542 Acknowledgements

543 Thank you to all the farm staff in Moorepark and the technical staff in Johnstown  
544 Castle for the soil and water analysis. A special word of thanks goes to Simon Leach who  
545 helped with Fig 1. The authors wish to thank Teagasc for funding Sara Vero under the Walsh  
546 Fellowship Scheme.

547

548 References

- 549 Bain, D.J., Green, M.B., Campbell, J.L., Chamblee, J.F., Chaoka, S., Fraterrigo, J.M.,  
550 Kaushal, S.S., Martin, S.L., Jordan, T.E., Parolari, A.J., Sobczak, W.V., Weller, D.E.,  
551 Wollheim, W.M., Boose, E.R., Duncan, J.M., Gettel, G.M., Hall, B.R., Kumar, P.,  
552 Thompson, J.R., Vose, J.M., Elliott, E.M., Leigh, D.S., 2012. Legacy Effects in  
553 Material Flux: Structural Catchment Changes Predate Long-Term Studies. *BioSci.* 62  
554 (6), 575-584.
- 555 Basu, N.B., Jindal, P., Schilling, K.E., Wolter, C.F., Takle, E.S., 2012. Evaluation of  
556 analytical and numerical approaches for the estimation of groundwater travel time  
557 distribution. *J. Hydrol.* 475, 65-73.
- 558 Blicher-Mathiesen, G., H.E. Andersen, J. Carstensen, C.D. Børgesen, B. Hasler, and J.  
559 Windolf. 2014. Mapping of nitrogen risk areas. *Agri.Ecosyst. Environ.* 195, 149-160.
- 560 Bouraoui, F., Grizzetti, B., 2014. Modelling mitigation options to reduce diffuse nitrogen  
561 water pollution from agriculture. *Sci. Tot. Environ.* 468-469, 1267-1277.

562 Buckley, C., Wall, D.P., Moran, B., O'Neill, S., Murphy, P.N.C., 2016. Phosphorus  
563 management on Irish dairy farms post controls introduced under the EU Nitrates  
564 Directive. *Agri. Syst.* 142, 1-8.

565 Coxon, C., 2014. Water Quality in Irish Karst Aquifers. In: *Water Resource Management: the*  
566 *role of hydrogeology (Proceedings of 34th Annual Groundwater Conference, IAH*  
567 *Irish Group), Tullamore Offaly, 15-16 April 2014, International Association of*  
568 *Hydrogeologists (Irish Group), pp. 11-9-11-18.*

569 Daly, K., Styles, D., Lalor, S., Wall, D., 2015. Phosphorus sorption, supply capacity and  
570 availability in soils with contrasting parent material and chemical properties. *Eur. J.*  
571 *Soil Sci.* 66, 792-801.

572 Dingman, S.L., 2015. *Physical Hydrology 3rd ed.* Prentice Hall, Upper Sadle River, New  
573 Jersey, USA. ISBN 1-4786-1118-9.

574 Dodd, R.J., Sharpley, A.N., 2015. Conservation practice effectiveness and adoption:  
575 unintended consequences and implications for sustainable phosphorus management.  
576 *Nutr Cycl Agroecosyst*, DOI: 10.1007/s 10705-015-9748

577 Drew, D.P., 2008. Hydrogeology of lowland karst in Ireland. *Q. J. Eng. Geol. Hydrogeol.* 41,  
578 61-72.

579 European Commission, 1991. Council Directive (1991/676/EC). EC Directive of the  
580 European Parliament and of the Council of 12 December 1991 on the protection of  
581 waters against pollution caused by nitrates from agricultural sources. Brussels pp 1-8.

582 Environmental Protection Agency. 2008. *The Provision and Quality of Drinking Water in*  
583 *Ireland – A Report for the Years 2006–2007.* EPA, Wexford.

584 Fay, D., Kramers, G., Zhang, C, McGrath, D., Grennan, E., 2007. Soil Geochemical Atlas of  
585 Ireland, Teagasc and the Environmental Protection Agency, 120  
586 pp., <http://erc.epa.ie/safer/iso19115/display?isoID=105>

587 Fenton, O., Richards, K.R., Kirwan, L., Khalil, M.I., Healy, M.G. 2009. Factors affecting  
588 nitrate distribution in shallow groundwater under a beef farm in South Eastern  
589 Ireland, *J. Environ. Manage.* 90, 3135-3146.

590 Fenton, O., Schulte, R.P.O., Jordan, P., Lalor, S.T.J., Richards, K.G., 2011a. Time lag: a  
591 methodology for the estimation of vertical and horizontal travel and flushing  
592 timescales to nitrate threshold concentrations in Irish aquifers, *Environ. Sci. Pol.* 14,  
593 419-431.

594 Fenton, O., Healy, M.G., Henry, T., Khalil, M.I., Grant, J., Baily, A., Richards, K.G., 2011b.  
595 Exploring the relationship between groundwater geochemical factors and  
596 denitrification potentials on a dairy farm in south east Ireland. *Ecol. Eng.* 37, 1304-  
597 1313

598 Fenton, O., Healy, M.G., Brennan, F., Jahangir, M.M.R., Lanigan, G.J., Richards, K.G.,  
599 Thornton, S.F., Ibrahim, T.G., 2014. Permeable reactive interceptors: blocking diffuse  
600 nutrient and greenhouse gases losses in key areas of the farming landscape. *J. Agric.*  
601 *Sci.* available on CJO2014. doi:10.1017/S0021859613000944

602 Hamilton, S.K., 2011. Biogeochemical time lags may delay responses of streams to  
603 ecological restoration. *Freshwater Biol.* 57, 43-57.

604 Hennessy, D., 2012. Effect of grazing season length and stocking rate on nitrate leaching.  
605 [http://www.teagasc.ie/publications/2012/1596/Teagasc\\_Technology\\_Updates\\_2007-](http://www.teagasc.ie/publications/2012/1596/Teagasc_Technology_Updates_2007-2012web.pdf)  
606 [2012web.pdf](http://www.teagasc.ie/publications/2012/1596/Teagasc_Technology_Updates_2007-2012web.pdf)

607 Horowitz, A.J., 2013. A review of selected inorganic surface water quality-monitoring  
608 practices: are we really measuring what we think, and if so, are we doing it right?  
609 Environ. Sci. Tech. 47, 2471-2486.

610 Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K.G., Jordan, P., Sawarieh,  
611 A., Blum, P., Goldscheider, N., 2015. Technical Note: Field experiences using  
612 UV/VIS sensors for high-resolution monitoring of nitrate in groundwater. Hydrol.  
613 Earth Syst. Sci. 19, 1589-1598.

614 Huebsch, M., Horan B., Blum P., Richards K.G., Grant J., Fenton O., 2013. Impact of local  
615 weather conditions and agronomic practices on groundwater nitrogen content in a  
616 karst aquifer on an intensive dairy farm in Southern Ireland. Agric. Ecosysts. Environ.  
617 179, 187-199.

618 Huebsch, M., Fenton, O., Horan, B., Hennessey, D., Richards, K.G., Jordan, P.,  
619 Goldscheider, N., Butscher, C., Blum, P., 2014. Mobilisation or dilution? Nitrate  
620 characteristics in karst springs. Hydrol. Earth Syst. Sci. 18, 4423-4435.

621 Irish Cooperative Organisation Society, 2015. Food Wise 2025 Environmmnetal Analysis  
622 Cooperation feedback Form.

623 Jahangir, M.M.R., Khalil, M.I., Johnston, P.M., Cardenas, L.M., Butler, M., Hatch, D.,  
624 Barrett, M., O'Flaherty, V., Richards, K.G., 2012. Denitrification potential in  
625 subsoils: A mechanism to reduce nitrate leaching to groundwater. Agric. Ecosysts.  
626 Environ. 147, 13-23.

627 Jahangir, M.M.R., Johnston, P., Khalil, M.I., Richards, K.G., 2012. Groundwater: A pathway  
628 for terrestrial C and N losses and indirect greenhouse gas emissions. Agric. Ecosysts.  
629 Environ. 159, 40-48.

630 Jahangir, M.M.R., Johnston, P., Khalil, M.I., Richards, K.G., 2012. Linking  
631 hydrogeochemistry to nitrate abundance in groundwater in agricultural settings in  
632 Ireland. *J. Hydrol.* 248, 212-222.

633 Jahangir, M.M.R., Johnston, P., Barrett, M., Khalil, M.I., Groffman, P., Boeckx, P., Fenton,  
634 O., Murphy, J. Richards, K.G., 2013. Denitrification and indirect N<sub>2</sub>O emissions in  
635 groundwater: hydrologic and biogeochemical influences. *J. Contam. Hydrol.* 152, 70-  
636 81.

637 Jarvie, H.P., Sharpley, A.N., Brahana, V., Simmons, T., Price, A., Neal, C., Lawlor, A.J.,  
638 Sleep, D., Thacker, S., Haggard, B.E., 2014. Phosphorus retention and remobilization  
639 along hydrological pathways in karst terrain. *Environ. Sci. Technol.* 48, 4860-4868.

640 Jordan, P., Menary, W., Daly, K., Kiely, G., Morgan, G., Byrne, P., Moles, R., 2005. Patterns  
641 and processes of phosphorus transfer from Irish grassland soils to rivers—integration  
642 of laboratory and catchment studies. *J. Hydrol.* 304, 20-34.

643 Kleinman, P.J.A., Sharpley, A.N., Withers, P.J.A., Bergström, L., Johnson, L.T., Doody,  
644 D.G., 2015. Implementing agricultural phosphorus science and management to  
645 combat eutrophication. *Ambio* 44, S297-S310.

646 Konikow, L.F., 2011. The secret to successful solute-transport modelling. *Ground Water.* 49  
647 (2), 144-159.

648 Kramers, G., Richards, K.G., Holden, N.M., 2009. Assessing the potential for the occurrence  
649 and character of preferential flow in three Irish grassland soils using image analysis.  
650 *Geoderma* 153 (3-4), 362-71.

651 Kronvang, B., Tornbjerg, H., Hoffmann, C.C., Poulsen, J.R., Windolf, J. 2016. Documenting  
652 success stories of management of phosphorus emissions at catchment scale: an

653 example from the Pilot River Odense, Denmark, *Water Sci. Technol.* DOI:  
654 10.2166/wst.2016.379

655 Kurz, I., Coxon, C., Tunney, H., Ryan, D., 2005. Effects of grassland management practices  
656 and environmental conditions on nutrient concentrations in overland flow. *J. Hydrol.*  
657 304 (1-4), 35-50.

658 Landig, F., Fenton, O., Bons, P., Hennessy, D., Richards, K.G., Blum, P., 2010. Estimation of  
659 nitrate discharge in a fractured limestone aquifer below a dairy farm in Ireland. *GQ10:*  
660 *Groundwater Quality Management in a Rapidly Changing World* (Proc. 7th  
661 International Groundwater Quality Conference held in Zurich, Switzerland, 13–18  
662 June 2010). IAHS Publ 342.

663 Lord I., Anthony S.G., 2002. Agricultural nitrogen balance and water quality in the UK. *Soil*  
664 *Use Manage.* 18(4), 363–369.

665 Martin, S.L., Hayes, D.B., Kendall, A.D., Hyndman, D.W., 2017. The land-use legacy effect:  
666 Towards a mechanistic understanding of time-lagged water quality responses to land  
667 use/cover. *Sci. Tot. Environ.* <http://dx.doi.org/10.1016/j.scitotenv.2016.11.158>

668 McCarthy, J., Delaby, L., Hennessy, D., McCarthy, B., Ryan, W., Pierce, K.M., Brennan, A.,  
669 Horan, B., 2015. The effect of stocking rate on soil solution nitrate concentrations  
670 beneath a free-draining dairy production system in Ireland. *J. Dairy Sci.* 98, 1-14.

671 McDonald, N.T., Watson, C.J., Lalor, S. T.J., Laughlin, R.J., Wall, D.P., 2014. Evaluation of  
672 soil tests for predicting nitrogen mineralisation in temperate grassland soils. *Soil Sci.*  
673 *Soc. Am. J.* 78, 1051-1064.

674 McDonald, N.T., Graham, S.F., Watson, C.J., Gordon, A., Lalor, S. T.J., Laughlin, R.J.,  
675 Elliott, C.T., Wall, D.P., 2016. Use of <sup>1</sup>H NMR to identify nitrogen and carbon

676 metabolites associated with mineralizable N in grassland soil, *Eur. J. Soil Sci.* doi:  
677 10.1111/ejss.12379.

678 McDonald, P., Edwards, R. A., Greenhalgh, J.F.D., Morgan, C.A., 1995. *Animal Nutrition*.  
679 5th ed. Addison Wesley Longman Ltd, Edinburgh Gate, Harlow, Essex, UK.

680 Mellander, P.-E., Melland, A.R., Jordan, P., Wall, D.P., Murphy, P.N.C., Shortle, G., 2012a.  
681 Quantifying nutrient transfer pathways in agricultural catchments using high temporal  
682 resolution data. *Environ. Sci. Pol.* 24, 44-57.

683 Mellander, P.-E., Jordan, P., Wall, D.P., Melland, A.R., Meehan, R., Kelly, C., Shortle, G.,  
684 2012b. Delivery and impact bypass in a karst aquifer with high phosphorus source and  
685 pathway potential. *Water Research.* 46, 2225-2236.

686 Mellander, P.-E., Jordan, P., Melland, A.R., Murphy, P.N.C., Wall, D.P., Meehan,  
687 S., Meehan, R., Kelly, C., Shine, O., Shortle, G., 2013. Quantification of phosphorus  
688 transport from a karstic agricultural watershed to emerging spring. *Environ. Sci.*  
689 *Technol.* 47, 6111-6119.

690 Mellander, P.-E., Jordan, P., Shore, M., McDonald, N., Wall, D.P., Shortle, G., Daly, K.,  
691 2016. Identifying contrasting controls and surface water signals from groundwater  
692 phosphorus flux. *Sci. Tot. Environ.* 541, 292-302.

693 O'Sullivan, L., Creamer, R.E., Fealy, R., Lanigan, G., Simo, I., Fenton, O., Carfrae, J.,  
694 Schulte, R.P.O., 2015. Functional Land Management for managing soil functions: a  
695 case-study of the trade-off between primary productivity and carbon storage in  
696 response to the intervention of drainage systems in Ireland. *Land Use Policy.* 47, 42-  
697 54.

698 Richards, K.G., Coxon, C., Ryan, M., 1998. Movement of phosphorus down the soil profile  
699 as indicated by morgan phosphorus values. Practical and innovative measures for the  
700 control of agricultural phosphorus losses to water. OECD Tuesday 16th June, Belfast,  
701 N. Ireland.

702 Ryan, W., Hennessy, D., Murphy, J.J., Boland, T.M., Shalloo, L., 2011. A model of nitrogen  
703 efficiency in contrasting grass-based dairy systems. *J. Dairy Sci.* 94, 1032-1044.

704 Ryan, M., Brophy, C., Connolly, J., McNamara, K., Carton, O.T., 2006. Monitoring of  
705 nitrogen leaching on a dairy farm during four drainage seasons. *Ir. J. Agric. Food Res.*  
706 45, 115-134.

707 Schipper, L.A., Robertson, W.D., Gold, A.J., Jaynes, D.B., Cameron, S.C., 2010.  
708 Denitrifying bioreactors: An approach for reducing nitrate loads to receiving waters.  
709 *Ecol. Eng.* 36,1532-1543.

710 Scholefield, D., Lockyer, D.R., Whitehead, D.C., Tyson, K.C., 1991. A model to predict  
711 transformations and losses of nitrogen in UK pastures grazed by beef cattle. *Plant Soil*  
712 132, 165-177.

713 Schulte RPO, Diamond J, Finkle K, Holden NM, Brereton AJ., 2005. Predicting the soil  
714 moisture conditions of Irish grasslands. *Ir J Agric Food Res.* 44, 95-110.

715 Sharpley, A.N., Bergström, L., Aronsson, H., Bechmann, M., Bolster, C.H., Börling, K.,  
716 Djodjic, F., Jarvie, H.P., Schoumans, O.F., Stamm, C., Tonderski, K.S., Ulén, B.,  
717 Uusitalo, R., Withers, P.J.A. 2015. Future agriculture with minimized phosphorus  
718 losses to waters: Research needs and direction. *Ambio.* 44(2), 163-179.

719 S.I. no. 272 of 2009. European Communities Environmental Objectives (Surface Waters)  
720 Regulations 2009.



721 Šimůnek, J.D., J., Mallants, D., van Genuchten, M.Th., 2008. Modelling coupled water flow,  
722 solute transport, and geochemical reactions affecting heavy metal migration in a  
723 podzol soil. *Geoderma*, 145, 449-461.

724 Tesoriero, A.J., Duff, J.H., Saad, D.A., Spahr, N.E., Wolock, D.M., 2013. Vulnerability of  
725 Streams to Legacy Nitrate Sources. *Environ. Sci. Technol.* 47, 3623-3629.

726 van Grinsven, H.J.M., ten Berge, H.F.M., Dalgaard, T., Fraters, B., Durand, P., Hart, A.,  
727 Hofman, G., Jacobsen, B.H., Lalor, S.T.J., Lesschen, J.P., Osterburg, B., Richards,  
728 K.G., Techen, A.K., Vert`es, F., Webb, J., Willems, W.J., 2012. Management,  
729 regulation and environmental impacts of nitrogen fertilization in northwestern Europe  
730 under the Nitrates Directive: a benchmark study, *Biogeosciences*. 9, 5143–5160.

731 Van Meter, K.J., Basu, N.B., 2015. Catchment Legacies and Time Lags: A Parsimonious  
732 Watershed Model to Predict the Effects of Legacy Storage on Nitrogen Export. *PLoS*  
733 *ONE* 10(5): e0125971. doi:10.1371/journal.pone.0125971

734 Van Meter, K.J., Basu, N.B., Veenstra, J.J., Burras, C.L., 2016. The nitrogen legacy:  
735 emerging evidence of nitrogen accumulation in anthropogenic landscapes,  
736 *Environmental Research Letters*, Volume 11, Number 3

737 Vero, S.E., Ibrahim, T.G., Creamer, R.E., Grant, J., Healy, M.G., Henry, T., Kramers, G.,  
738 Richards, K.G., Fenton, O., 2014. Consequences of varied soil hydraulic and  
739 meteorological complexity on unsaturated zone time lag estimates. *J Contam.*  
740 *Hydrol.*170, 53-67.

741 Windolf, J., Blicher-Mathiesen, G., Carstensen, J., Kronvang, B. 2012. Changes in nitrogen  
742 loads to estuaries following implementation of governmental action plans in  
743 Denmark: A paired catchment and estuary approach for analysing regional responses

744 Catchment science and policy evaluation for agriculture and water quality, Environ.  
745 Sci. Policy 24, 24-33

746 Worrall, F., Howden, N.J.K., Burt, T.P., 2015. Evidence for nitrogen accumulation: the total  
747 nitrogen budget of the terrestrial biosphere of a lowland agricultural catchment.  
748 Biogeochem. 123, 411-428.