

1 Quantifying the Influence of Surface-water Groundwater interaction on nutrient
2 flux in a lowland karst catchment

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16 **Abstract**

17 Nutrient contamination of surface and groundwaters is an issue of growing importance as the risks
18 associated with agricultural runoff escalate due to increasing demands on global food production. In
19 this study, the influence of surface-water groundwater interaction on the nutrient flux in a lowland
20 karst catchment was investigated with the aid of alkalinity sampling and a hydrological model. The
21 objective of the study was to determine the impact of ephemeral karst lakes (turloughs) on the
22 surface-water groundwater nutrient flux, and whether these lakes act as sources or sinks of nutrients
23 within the groundwater flow system. Water samples were tested from a variety of rivers, turloughs,
24 boreholes and springs at monthly intervals over three years. Alkalinity sampling was used to elucidate
25 the contrasting hydrological functioning between different turloughs. Such disparate hydrological
26 functioning was further investigated with the aid of a hydrological model which allowed for an
27 estimate of allogenic and autogenic derived nutrient loading into the karst system. The model also
28 allowed for an investigation of mixing within the turloughs, comparing observed behaviours with the
29 hypothetical conservative behaviour allowed for by the model. Within the turloughs, recorded nutrient
30 concentrations were found to reduce over the flooded period, even though the turloughs hydrological
31 functioning (and the hydrological model) suggested this would not occur under conservative
32 conditions. As such, it was determined that nutrient loss processes were occurring within the system.
33 Denitrification during stable flooded periods (typically 3-4 months per year) was deemed to be the
34 main process reducing nitrogen concentrations within the turloughs whereas phosphorus loss is
35 thought to occur mostly via sedimentation and subsequent soil deposition. The results from this study
36 suggest that, in stable conditions, ephemeral lakes can impart considerable nutrient losses on a karst
37 groundwater system.

38 **1 INTRODUCTION**

39 Global food production is predicted to increase by approximately 60% by 2050 (Alexandratos and
40 Bruinsma, 2012), thereby increasing the contamination risks associated with agricultural runoff of
41 raised nutrient concentrations in sensitive groundwater and surface-waters. Nutrient contamination of
42 groundwater has been reported across the world, for example: China (Zhang et al., 1996), Turkey
43 (Davraz et al., 2009), India (Rao and Prasad, 1997) and the United States (Domagalski and Johnson,
44 2012;Hudak, 2000), with such evidence contributing towards the introduction of the EU Nitrates
45 (91/676/EEC) and Groundwater (2006/118/EC) Directives.

46

47 In non-carbonate aquifers, nitrogen (N) and phosphorus (P) are subject to separate transport dynamics.
48 Nitrate (NO₃) is often found to be conservatively transported due to its high solubility and mobility
49 characteristics while P is retained due to its affinity to particulate matter (Weiskel and Howes, 1992).
50 In carbonate aquifers however, the existence of point recharge features, such as swallow or sink-holes,
51 provide direct access points for N and P into the aquifer. This allows contaminants to bypass the
52 protective soil cover associated with most diffuse recharge and enter the karst fracture/conduit
53 network with little or no attenuation (Coxon, 2011). Within the conduit system, a contaminant can
54 then be rapidly transmitted through an aquifer in ecologically significant quantities with very little
55 attenuation or chemical breakdown.

56

57 In the Republic of Ireland, carboniferous limestone covers approximately half of the land surface and
58 is often heavily karstified. Most of this limestone is lowland and coincides with productive
59 agricultural land (Drew, 2008) and as such, the influence of agricultural practices and nutrient loading
60 on karst is of particular importance. Current research into nutrient contamination in Ireland is of
61 additional significance as many catchments have failed to achieve the objectives set out by the first
62 management cycle of the EU Water Framework Directive (2000/60/EC), whereby all water bodies
63 were to have achieved at least ‘good’ water status by 2015 (in light of this, the objectives of the
64 Directive are to be reassessed for the second and third management cycles which end in 2021 and
65 2027 respectively).

66

67 While the hydrochemical processes in permanent lakes has been the subject of much research,
68 relatively little work has been carried out into the nutrient flux within ephemeral lakes and their
69 influence at a catchment scale. Ephemeral lakes, known as *turloughs* are a characteristic feature of the
70 Irish karst landscape. Their flooding results from a combination of high rainfall and consequently high
71 groundwater levels in topographic depressions in karst. Flooding typically occurs through
72 underground conduits and springs in autumn forming a lake for several months in winter which then
73 empties via swallow holes (or estavelles) in the springtime (Sheehy Skeffington et al., 2006). This

74 flooding promotes a biodiverse habitat as species have to adapt to survive the oscillation between
75 terrestrial to aquatic conditions. The turlough habitat is protected under the EU Water Framework
76 Directive (2000/60/EC) and designated as a priority habitat under Annex 1 of the EU Habitats
77 Directive (92/43/EEC). Numerous sites supporting ecological communities of national and
78 international importance have been designated as Special Areas of Conservation (SAC) and afforded
79 the highest level of protection available under EU conservational law.

80

81 Due to the protected status of turloughs within the study area of this project, as well as the protected
82 status of their eventual outlet at Kinvara Bay (part of Galway Bay complex SAC), it is important to
83 understand the nutrient processes which are occurring in the region. These processes are especially
84 important in the context of the likely future pressures on the catchment. Food Harvest 2020 is the
85 strategic plan to develop the Irish Agricultural Sector and is expected to lead to a 33% increase in
86 primary output across the country, compared to 2007-2009 averages (Department of Agriculture
87 Fisheries and Food, 2010). Such a plan would lead to substantial escalation in nutrient loading from
88 agricultural sources and thus poses a significant challenge to Ireland meeting the goals as set out by
89 the Water Framework Directive. The problem is exacerbated further with the likely increases in
90 rainfall intensity and frequency of storm events due to climate change which may encourage nutrients
91 to bypass the protective soil cover and enter the karst aquifer via point source features. Hence, the
92 objective of this research is to determine whether these protected temporary lakes are subject to the
93 same transformation processes as found in permanent lakes and to assess the impact of the turloughs
94 on the nutrient flux within the wider catchment, i.e. do the turloughs operate as sources or sinks of
95 nutrients to the catchment?

96

97 **2 AREA DESCRIPTION AND BACKGROUND**

98 The Gort Lowlands is a 480 km² catchment located in County Galway in the west of Ireland. The
99 eastern portion of the catchment is dominated by the Slieve Aughty Mountains and underlain by
100 Devonian Old Red Sandstone (Figure 1). The western portion of the catchment is mostly flat and
101 underlain by pure carboniferous limestone. Similar to the majority of karstic regions found within
102 Ireland, the catchment is primarily lowland (rarely rising above 30 m) and as such, the region is
103 subject to considerable interaction between ground and surface waters.

104

105 As demonstrated by previous tracer studies (Drew, 2003), the prevailing drainage direction in the
106 catchment is east to west, with recharge from the non-carbonate Slieve Aughty Mountains (hereafter
107 referred to as just ‘mountains’) flowing across the lowland karst towards a major intertidal spring at
108 Kinvara Bay (known as Kinvara West). This significant contribution of allogenic recharge into the

109 karst aquifer imparts the catchment with a distinctive hydrochemical flux as well as unique
110 hydrological and ecological characteristics.

111

112 Three main rivers run down the Mountains and into the carboniferous lowlands: the Owenshree
113 (SA1), the Ballycahalan (SA2) and the Owendalulleegh (SA3), which goes on to feed the Beagh River
114 (SA4). The rivers supply chemically-aggressive acidic waters derived from the peaty non-carbonate
115 catchments of the Mountains into the lowlands which have rapidly influenced karst development in
116 the region, and the development of a complex network of sinking streams, conduits and turloughs.

117

118 In the Gort Lowlands (Figure 1), turloughs form a key component of the hydrological regime, offering
119 a zone of temporary storage for water surcharging out of the active conduit network. Numerous
120 turloughs are present within the Gort Lowlands but five turloughs in particular (Blackrock, Coy,
121 Coole, Garryland and Caherglassaun) are known to be highly influential upon the active conduit
122 network (Gill et al., 2013b). The chemically-aggressive allogenic recharge entering the Lowlands has
123 contributed to the development of a complex conduit network with relatively high flow rates. The five
124 turloughs within the network are all relatively eutrophic and deep in comparison to other turloughs
125 around Ireland and are underlain by non-alluvial mineral soil types (of relatively low CaCO₃
126 concentration) compared to the organic and marly soil types generally associated with turloughs of
127 longer periods of inundation (Kimberley et al., 2012).

128

129 Turloughs can be divided conceptually into three groups: diffuse flow-through, river flow-through and
130 surcharge tank systems (Figure 2) (Naughton et al., 2012; Gill et al., 2013a). The majority of
131 turloughs in Ireland are thought to behave as diffuse flow-through systems with the flux of water
132 through the turlough from the surrounding epikarst entering and exiting relatively slowly (Figure 2a).
133 In the Gort Lowlands however, the developed conduit system results in turloughs operating more akin
134 to *river flow-through* and *surcharge tank* systems (Gill et al., 2013a; Gill et al., 2013b). In *river flow-*
135 *through* systems (Figure 2b), water is also constantly flowing through the turlough similar to *diffuse*
136 *flow-through* systems (Figure 2a), however water volumes tend to be larger with higher discharge
137 rates. These turloughs also tend to show much more ‘flashy’ flooding behaviour as they are directly
138 linked to a river - Blackrock and Coole turloughs (see Figure 1) being examples of such types. In
139 *surcharge tank* systems the turlough can be viewed as a pressure release point along an underground
140 pipe network, providing overflow storage for the excess groundwater that cannot be accommodated
141 due to insufficient hydraulic capacity of the conduit network - Coy, Garryland and Caherglassaun
142 being examples of this type of system. *Surcharge tank* systems thus have a negligible flow through
143 component and can be considered to remain relatively undiluted once they have flooded. This has
144 been confirmed by a previous study (McCormack, 2014) which used multiple Electrical Conductivity

145 (EC) loggers placed within Coy turlough and found EC to spike during inflow events but remain
146 constant for the majority of the flooded season.

147

148 Most of the nutrient loading within the catchment is derived from agricultural and forestry sources.
149 Nutrients enter the aquifer via allogenic point sources, such as the three rivers draining the Mountains,
150 or by autogenic diffuse mechanisms within the lowlands. Each mechanism providing a
151 hydrochemically distinct input. Allogenic recharge is characterised by relatively low alkalinity water
152 (due to the non-carbonate bedrock) and moderate nutrient concentrations because of the relatively
153 low-intensity agriculture in the uplands. In the lowlands, the carbonate bedrock results in much higher
154 alkalinity levels and the higher agricultural intensity (mainly pasture for cattle) causes corresponding
155 higher nutrient concentrations (particularly for N) within the diffuse groundwater.

156

157 The Gort Lowlands catchment has been hydrologically modelled using Infoworks CS (Wallingford
158 Software, Wallingford, UK), a hydraulic modelling package more often used to model urban drainage
159 networks. The model simulates the hydraulic behaviour of a pipe network under varying conditions of
160 rainfall, land use, inflows etc. and represents the catchment as a complex network of pipes (conduits),
161 tanks (turloughs) and subcatchments (diffuse/epikarst). Internal storage within the system was
162 represented using five ponds with the same stage–volume characteristics as the surveyed turloughs.
163 The model was originally calibrated by Gill et al. (2013a) and was subsequently recalibrated due to
164 the availability of additional data (McCormack et al., 2014). For the recalibrated model (which was
165 used for this current study), the model efficiency, or r^2 , was assessed over the period 2010-2013 using
166 the Nash–Sutcliffe criterion based on the volumes in each turlough. Values of r^2 for all turloughs were
167 calculated as 0.81, 0.89, 0.96, 0.97 and 0.96 for Blackrock, Coy, Coole, Garryland and Caherglassaun
168 respectively. The use of this model to predict catchment hydrodynamics and submarine groundwater
169 discharge has been discussed previously by Gill et al. (2013a) and McCormack et al. (2014). For this
170 study, the model was adapted to simulate the movement of nutrients within the system (see Figure 3
171 for a schematic illustration of the model).

172

173 **3 METHODOLOGY**

174 The objective of the study was to determine the impact of temporary karst lakes (turloughs) on the
175 surface-water groundwater nutrient flux, and whether these lakes act as sources or sinks of nutrients
176 within the groundwater flow system This was carried out using the following strategy:

177

- 178 • Alkalinity (a useful indicator of recharge origin) was used as a hydrochemical method to
179 validate the hydraulic conceptualisation of the turloughs (surcharge tank, flow through etc).

- 180 • Following this, the hydraulic model was used to simulate the behaviour of nutrients passing
181 through the karst system assuming conservative conditions. Modelled and observed nutrient
182 behaviour within the turloughs were then compared, and any differences taken as indicative
183 of non-conservative nutrient processes within the turloughs.
- 184 • If a turlough is found to behave non-conservatively, the various possible processes (e.g.
185 dilution, sedimentation, denitrification etc.) are assessed to discern the likely cause.

186

187 **3.1 Hydrometry**

188 Turlough water levels were monitored using Mini-Diver[®] DI501 and DI502 monitors (Schlumberger
189 Water Services) placed at the lowest point in each turlough. Compensation for the variation in
190 prevailing air pressure was made using a BaroDiver[®] (DI500) which was installed at ground level
191 near Coy turlough. The locations of the diver platforms were surveyed via GPS which allowed the
192 water depth readings to be referenced against Ordnance Datum.

193

194 Two tipping bucket ARG100 rain gauges (Environmental Measurement Ltd., North Shields, UK)
195 were installed at the upper end of the catchment at Kilchreest, 70 meters above ordinance datum
196 (mAOD), and Francis Gap (250 mAOD). In addition, hourly rainfall and evapotranspiration data was
197 obtained from the Athenry synoptic weather station (approx. 20 km from the Gort Lowlands) run by
198 the national weather service, Met Éireann.

199

200 River gauging stations were located on the three primary rivers draining off the mountains, SA1, SA2
201 and SA3, with an additional station located on SA4 near the outlet of Lough Cutra. The gauges
202 consisted of a pressure transducer embedded into the river with the dataloggers set to collect data at
203 15 minute timesteps. Rating curves were developed for each gauging station (Figure 3) using the mid-
204 section velocity depth surveying method (Shaw, 2011).

205

206 **3.2 Hydrochemistry**

207 Monthly sampling was carried out at turloughs, rivers, springs and two upland sites (F and PE)
208 between March 2010 and March 2013, in addition to groundwater samples from boreholes and wells
209 within the carboniferous aquifer surrounding the turlough network (Figure 3). Water samples were
210 tested within 24 hours of collection. Samples were tested for alkalinity based on Standard Methods
211 (APHA, 1999) and Total Nitrogen (TN), nitrate (NO₃-N), nitrite (NO₂) and ammonium (NH₄) were
212 analysed using a Merck Spectroquant Nova 60 spectrophotometer and associated reagent kits. Quality
213 control (QC) was carried out using Merck Combicheck standards for each batch of monthly samples.

214 Total Phosphorus (TP) concentrations were determined by acidic persulphate digestion of samples at
 215 120°C and subsequent measurement of phosphate by colorimetry in accordance with the Standard
 216 Methods (APHA, 1999). Total Dissolved Phosphorus (TDP) concentrations were obtained similarly
 217 but with the added step of filtration directly after sampling using a 45 micron filter. QC was carried
 218 out for P by running a QC sample (0.025 mg l⁻¹ TP) with each batch of P analyses. All results were
 219 based upon duplicate samples that were collected and tested separately to rule out sampling error.

220

221 The one month sampling interval provided an approximation of their mean and maximum (observed)
 222 nutrient concentrations within the rivers. In the turloughs, the one month interval was deemed
 223 appropriate based on the findings of previous studies such as Gill (2010) who, in an attempt to
 224 optimise sampling methodologies, evaluated nutrient concentrations both spatially and temporally and
 225 found one month to be an adequate sampling interval. This one month interval has also been used as
 226 an established sampling technique for a variety of other ecohydrological turlough studies (Cunha
 227 Pereira, 2011; Cunha Pereira et al., 2010; Kimberley et al., 2012; Porst et al., 2012; Waldren, 2015).

228

229 3.3 Modelling

230 Along with modelling the hydraulic processes of a pipe network (Gill et al., 2013a), Infoworks CS
 231 also incorporates a water quality model which was used in order to evaluate the nutrient transport
 232 processes within the Gort Lowlands. The water quality model effectively runs in parallel with the
 233 hydraulic model; the calculated flows from the hydraulic model are used to calculate the associated
 234 output from the water quality model at each time-step. Each hydrochemical species can be modelled
 235 as being entirely dissolved or partially attached to sediment with the pollutants being treated as fully
 236 conservative. No interaction between pollutants and their environment was simulated, nor between
 237 one pollutant and another. The water quality model for the transport of dissolved nutrients carried out
 238 its calculations in two stages for each time step.

239

- 240 1. The *Network Model* calculates the concentration of dissolved pollutants at all nodes using the
 241 following conservation of mass equation:

$$\frac{dM_J}{dt} = \sum_i Q_i C_i + \frac{dM_{sJ}}{dt} - \sum_o Q_o C_o \quad (1)$$

242

243 where: M_J = Mass of dissolved pollutant in node J (kg)

244 Q_i = Flow into node J from link i (m³ s⁻¹)

245 C_i = Concentration in the flow into node J from link i (kg m⁻³)

246 M_{sJ} = Additional mass entering node J from external sources (kg)

247 Q_o = Flow from node J to link o ($\text{m}^3 \text{s}^{-1}$)
248 C_o = Concentration in the flow from node J to link o (kg m^{-3}).

249
250 2. The *Conduit Model* calculates the concentration of dissolved pollutants along each conduit
251 (represented as a conceptual link of defined length between two nodes in the network). The
252 governing equation describing the transport of dissolved pollutant (based on the conservation
253 of mass) is the following:

$$\frac{dC}{dt} + u \frac{dC}{dx} = 0 \quad (2)$$

254
255 where: C = Concentration (kg m^{-3})
256 u = Flow velocity (m s^{-1})
257 t = Time (s)
258 x = The spatial co-ordinate (m).

259

260 **4 RESULTS**

261 The results of alkalinity, total nitrogen, nitrate, total phosphorus and total dissolved phosphorus are
262 presented in Table 1.

263

264 **4.1 Alkalinity**

265 In the Gort Lowlands, alkalinity is particularly beneficial as an indicator of recharge origin due to the
266 substantial input of under-saturated allogenic recharge. By exploiting the distinct contrast between the
267 low alkalinity allogenic recharge and the saturated, high alkalinity autogenic recharge, insights can be
268 made into the likely source of water within the catchment.

269

270 **4.1.1 Surface-water**

271 Alkalinity concentrations within the turloughs were found to be quite variable. The predominant
272 process controlling their alkalinities is their hydrological functioning and the influx of water (from
273 conduit or diffuse sources). Other processes that are likely to alter a turlough's CaCO_3 concentration,
274 although to a lesser degree, include carbonate precipitation and dissolution.

275

276 Blackrock and Coy turloughs had mean alkalinities of 138.4 and $150.3 \text{ mg l}^{-1} \text{ CaCO}_3$ respectively.
277 These concentrations reflect the alkalinity of their primary source of water, SA1, which had a mean

278 alkalinity of 148.1 mg l⁻¹ CaCO₃. The alkalinities of Coole, Garryland and Caherglassaun turloughs
279 were slightly lower (114.4, 134.6 and 121.3 mg l⁻¹ CaCO₃) reflecting the lower concentration
280 contributions of SA2 (68.2 mg l⁻¹ CaCO₃) and SA3 (38.8 mg l⁻¹ CaCO₃) rivers. However, these
281 turloughs have noticeably higher concentrations than would be expected from a weighted mean
282 alkalinity based on the percentage flow contribution from the three rivers (71 mg l⁻¹ CaCO₃). Their
283 increased alkalinity, relative to what would be expected from the river inputs, can be attributed to
284 three factors. Firstly, these turloughs receive a minor influx of water from the more alkaline
285 Cloonteen River catchment to the south of the Gort Lowlands (see Figure 1), most significantly at
286 Garryland turlough. Secondly, as SA2 and SA3 rivers enter the limestone system under-saturated in
287 dissolved CaCO₃ their water is chemically aggressive and has a high dissolution potential. This is
288 likely to cause considerable solution of the limestone bedrock as they flow towards Coole. Thirdly, as
289 the river/conduit water moves through the catchment towards the lower three turloughs, it is being
290 diluted by the addition of high-alkalinity recharge from the diffuse groundwater.

291
292 Coy, Garryland and Caherglassaun are known to operate hydraulically as surcharge tank turloughs fed
293 via a single estavelle (with a degree of isolation from the main karst flows through the system) (Gill et
294 al., 2013b). Their hydrochemistry suggests that the low-alkalinity water brought in from the initial
295 flooding event remains within the turloughs and only slowly becomes enriched in bicarbonate over
296 time, most likely due to gradual recharge from the surrounding epikarst, as shown in Figure 4.
297 Blackrock and Coole turloughs, on the other hand, are seen to be directly influenced by river
298 concentrations, even during flooded periods, with dramatic reductions in alkalinity in response to a
299 flooding event. This pattern suggests that these turloughs can receive a significant amount of new
300 low-alkalinity water from their surface inputs while draining away the older higher alkalinity water
301 through their estavelles; i.e. acting predominantly as *river flow-through* systems, as opposed to the
302 *diffuse flow-through* from the surrounding epikarst.

303
304 The trend of increasing alkalinity over the flooding season as seen in the surcharge tank systems is
305 unusual for turloughs. Typical autogenically recharged turloughs tend to have much higher alkalinity
306 levels, due to the CaCO₃ rich waters that feed them, which does not increase over time (as they are
307 saturated) but tends to decrease (as observed by (Cunha Pereira, 2011)). Such losses in CaCO₃ from
308 turloughs have been attributed to the influx of water (saturated with CO₂) which comes into contact
309 with the air and gradually loses its CO₂ to the atmosphere, primarily from physiochemical processes
310 but also possibly biogenic processes (Coxon, 1994).

311

312 **4.1.2 Groundwater**

313 Groundwater alkalinity measured across the catchment generally varied between 300 and 400 mg l⁻¹
314 CaCO₃ but overall was found to be quite consistent (standard deviation ≤40 mg l⁻¹) with a mean value
315 of 365.1 mg l⁻¹ CaCO₃. The broad agreement and lack of variation between most groundwater
316 samples indicates the presence of a large diffuse/epikarst type aquifer with low transmissivity which
317 surrounds the active conduit network (McCormack et al., 2014).

318

319 **4.2 Nutrients**

320 The results of the NO₃, TN, total TDP and TP sample analysis are shown in Table 1. NO₂ and NH₄
321 were initially measured but were often near-to or below detection limits and as such, their
322 measurement was ceased.

323

324 **4.2.1 Surface-water: Rivers**

325 Values for TN in all rivers ranged between 0 and 3.9 mg l⁻¹ with a mean of 1.01 mg l⁻¹, whilst TP
326 concentrations ranged between 0 and 0.12 mg l⁻¹ with a mean value of 0.026 mg l⁻¹. Nutrient
327 concentrations in the rivers showed a high degree of variation, although a seasonal trend was apparent
328 with N and P highest in summer whereas lowest concentrations were in the winter for N and the
329 spring for P. Contrasting source/transport dynamics between N and P are apparent in the river nutrient
330 concentrations. Mean values of TN for each river were quite similar, ranging between 0.87 and 1.12
331 mg l⁻¹ whereas for TP, the rivers showed a wide range of mean values between 0.011 and 0.032 mg l⁻¹
332 (Table 1).

333

334 The lack of variation for N between all sampling locations, and the lack of variation for both N and P
335 between the upper and lower river sampling locations indicates that there is a minor but constant
336 addition of nutrients to the rivers from agricultural and forestry land-use practices as they travel down
337 through their catchments. Figures 5 and 6 show examples of nutrient variation for the SA1 River
338 (upper and lower sampling locations). The peak in P in July 2012 (Figure 6) (which was also seen to
339 a lesser extent in the other two rivers) occurs during the typical forestry fertilisation season of April to
340 August (Teagasc, 2013) and coincides with a period of heavy rainfall. Kilroy and Coxon (2005)
341 suggest that a response such as this could possibly reflect a hydrological switch where the catchments
342 change from a soil moisture deficit to a soil moisture surplus situation.

343

344 Nutrient load quantities in the rivers were estimated by combining the measured nutrient
345 concentration data with the observed flow data. Maximum observed TN loading for the SA1, SA2,

346 SA3 and SA4 rivers was found to be 46 kg hr⁻¹, 34 kg hr⁻¹ and, 23.9 kg hr⁻¹, 35.2 kg hr⁻¹ respectively
347 while TP loading was found to be 1.2 kg hr⁻¹, 4.1 kg hr⁻¹, 2.1 kg hr⁻¹ and 3.3 kg hr⁻¹ respectively.
348

349 **4.2.2 Surface-water: Turloughs**

350 Mean TN and TP concentrations for the turloughs were 1.12 mg l⁻¹ and 0.034 mg l⁻¹ with highest
351 concentrations recorded of 4.3 mg l⁻¹TN and 0.115 mg l⁻¹ TP. It should be noted that the mean TP
352 concentration lies just below 0.035 mg l⁻¹, the OECD threshold for TP in eutrophic lakes (OECD,
353 1982). Generally, the upper two turloughs (Blackrock and Coy) showed slightly higher N
354 concentrations and significantly higher P concentrations than the lower three turloughs. This is as
355 expected considering that the catchment of the upper two turloughs encompasses a greater proportion
356 of agricultural land than the lower three turloughs (Cunha Pereira, 2011). The upper turloughs also
357 tended to show mean concentrations greater than those of the SA1 River feeding them which suggest
358 that these turloughs are gaining nutrients from additional sources (see Discussion Section).

359
360 The lower mean nutrient concentrations in Coole, Garryland and Caherglassaun turloughs tended to
361 reflect the concentrations of the rivers feeding them. For example, mean concentrations of TN and TP
362 in Coole turlough were within $\pm 1\%$ of their primary source of water, the SA3 River. Nutrient
363 concentrations in Caherglassaun show similar values to Coole indicating a direct relationship between
364 these turloughs. However, Garryland turlough displays lower nutrient concentrations, most likely due
365 to the influx of water from the southern Cloonteen catchment as discussed previously. Figure 7 shows
366 the time-series of nutrient concentration data and turlough volume data across the 2011/2012 season.
367 For purposes of clarity, and as the flooding patterns in the five turloughs are quite similar, only the
368 average volume of the five turloughs is shown (as a percentage of maximum volume) rather than the
369 five individual time-series (for individual flooding patterns, see Figure 4). While the nutrient
370 concentrations in these plots are shown to be quite variable, a trend can be seen whereby nutrient
371 concentrations appear to decrease over the flooded period (between December and February/March).
372 This pattern is seen clearly seen for TN, NO₃ and TDP. However, a high TP concentration in
373 Blackrock during January 2012 does not conform to the trend, the reason for which is unclear. One
374 hypothesis is that the sample was influenced by point source contamination from an abattoir on the
375 south eastern edge of Blackrock Turlough. Nutrients are seen to increase (significantly in the case of
376 TN) after the main flood volumes have receded but with a small quantity of water still remaining.
377 These spikes could be due to the increased sensitivity of the turloughs to their river inputs during such
378 dry periods.

379

380 **4.2.3 Groundwater**

381 The primary land use in the catchment is agriculture and as such, there are significant additional
382 sources of N and P. Mean groundwater concentrations across the catchment were recorded as 2.30 mg
383 l⁻¹ and 0.031 mg l⁻¹ for TN and TP respectively (Table 1) with overall mean N concentrations being
384 almost double those of surface water bodies while the overall mean P concentrations of the turloughs
385 and groundwater were shown to be similar. The results obtained from boreholes within the Gort
386 Lowlands showed a wide range of recorded results for N (0.2-10.4 mg l⁻¹ TN) with a standard
387 deviation of 0.92 mg l⁻¹ TN, although the mean concentrations at each borehole across the catchment
388 are within a similar range (between 1.2 and 3.3 mg l⁻¹). P showed a greater range of measured results
389 (0-0.58 mg l⁻¹ TP) with a standard deviation of 0.027 mg l⁻¹ TP, but more significantly, the mean
390 concentrations at each borehole showed large differences (between 0.005 and 0.072 mg l⁻¹ TP). These
391 results indicate that N was able to reach the groundwater relatively easily due to the high mobility and
392 solubility of NO₃, and more or less equalised across the catchment. P, on the other hand, being much
393 less mobile would only be likely to enter the groundwater in areas of extreme vulnerability (i.e.
394 through shallow and/or permeable subsoils). Thus, while the sources of P could be equally as
395 widespread, its ability to reach the groundwater is highly variable. However, once in the conduit
396 system, P is known to be transported conservatively with negligible attenuation (Mellander et al.,
397 2013; Kilroy and Coxon, 2005).

398

399 **4.2.4 Kinvara Springs**

400 Mean TN concentration for KW was measured as 1.05 mg l⁻¹ which reflected the mean concentrations
401 of the turloughs (1.12 mg l⁻¹ TN). P concentrations at the springs were among the lowest mean
402 concentrations found within the catchment (0.023 mg l⁻¹) suggesting the loss of P as water moves
403 through the karst system. These nutrient concentrations are in accordance with the findings of (Smith
404 and Cave, 2012) who suggest that Kinvara Bay is a source of N to the greater Galway Bay.

405

406 The nutrient loads leaving the Gort Lowlands system and discharging into the sea were calculated
407 using KW discharge and nutrient concentration data obtained by sampling at KW. The simulated
408 discharge at KW was estimated using the hydrological model which accounted for temporal tidal
409 effects and did not include any additional discharge from the un-modelled southern Cloonteen
410 catchment (see McCormack et al. (2014) for further detail). Using this methodology, the average daily
411 TN load was calculated as 788 kg day⁻¹ while the average daily TP load was 17.3 kg day⁻¹.

412

413 **4.3 Nutrient Modelling**

414 The hydraulic model was used to simulate the behaviour of nutrients passing through the karst system
415 acting as conservative tracers. These results have then been compared against the field sampling
416 results from the turloughs from which insights have been made as to the mobility and attenuation
417 behaviour of these nutrients.

418

419 **4.3.1 Nutrient Retention**

420 Nutrient transport through a highly karstified catchment such as the Gort Lowlands can be reasonably
421 assumed to act conservatively (once the nutrients have entered the conduit system). As such, making a
422 comparison between modelled and observed nutrient behaviours within the turloughs is a useful
423 technique to ascertain the magnitude of any non-conservative nutrient mechanisms taking place in
424 these groundwater dependent ecosystems.

425

426 Due to the limitations of monthly sampling in the rivers, a representative time series of observed
427 nutrient concentrations could not be established. As such, a hypothetical nutrient plume was used as
428 an input signal. The purpose of this pulse input signal is to predict how nutrients/contaminants would
429 behave after entering river flow-through and a surcharge tank turloughs. The hypothetical input
430 signal, presented in Figure 8, consists of mean observed TDP values in the rivers and a pulse of TDP
431 occurring in the SA1 River at the onset of the flooding season. While the simulations using this
432 hypothetical nutrient plume cannot be compared directly to observed behaviour, a comparison of
433 normalised simulation results with normalised observed results could be applied.

434

435 Blackrock turlough (Figure 9), a river flow-through turlough, shows a nutrient concentration peak-
436 recession type pattern where the concentration drops as the turlough is still filling. This pattern is
437 exhibited in both simulated and observed results and indicates a constant flux of water through the
438 turlough whether it is flooding or emptying. The simulated response of Coy, the surcharge tank type
439 turlough, is distinctly different to that of Blackrock. Once the contaminant has entered the water body,
440 the modelled concentration remains relatively unchanged (the small drop of concentration seen early-
441 on is due to the presence of a second swallow hole which only influences the turlough at a depth
442 above 10 m). Crucially however, the observed results in Coy also show a pattern of reducing
443 concentrations similar to that of Blackrock. The fact that this flow-through pattern, which is also seen
444 in the two other surcharge tank systems Garryland and Caherglassuan (Figure 7), is occurring in a
445 turlough which is known to have a minor flow-through component thus suggests that some non-
446 conservative nutrient removal/transformation processes must be occurring within these turloughs.

447 **4.3.2 Diffuse Contribution**

448 The contribution of modelled diffuse flow to the conduit network added approximately 35% to the
449 discharge from the catchment. By combining groundwater concentrations with the estimated diffuse
450 flow from each sub-catchment, a loading rate for each sub-catchment was determined. Diffuse influx
451 added between 48-112% (based on a mean groundwater concentration of 2.3 mg l^{-1} TN, SD of 0.92
452 mg l^{-1}). For P, the influx was lower but considerably more variable, adding between 5-65% (based on
453 a mean groundwater concentration of 0.0031 mg l^{-1} TN, SD 0.027 mg l^{-1} TN). While the estimate of
454 discharge from the sub-catchments may be sufficiently accurate to predict hydrological processes, the
455 significant variability of observed nutrient concentrations in groundwater hinder any precise
456 estimation of nutrient loading from diffuse sources, particularly for P.

457

458 **5 DISCUSSION**

459 Hydrologically, turloughs sit within a spectrum of different types ranging from diffuse flow-through
460 dominated to conduit dominated ephemeral lakes. The turloughs of the Gort Lowlands predominantly
461 fall under the conduit dominated category and are known to operate as river flow-through systems
462 (Blackrock and Coole), or surcharge systems (Coy, Garryland and Caherglassaun). Conceptually,
463 results from the flow-through turloughs reflect the hydrochemistry of their feeding rivers whereas the
464 surcharge tank turloughs can be isolated from any nutrient input (depending on the flood conditions).

465

466 **5.1 Alkalinity**

467 Alkalinity results supported the conceptual hydraulic models for the catchment. Blackrock and Coole
468 turloughs showed signs of flow-through behaviour as evidenced by quick drops in alkalinity during a
469 flooded period. Coy, Garryland and Caherglassaun, on the other hand, showed no such behaviour
470 (which would conform to their conceptual models as surcharge tanks). The most noticeable trend,
471 particularly for the surcharge tank turloughs, was the increase in alkalinity across the flooding season.
472 As mentioned in Section 4.1.1, this could be attributed to gradual recharge from the surrounding
473 epikarst during recession due to a hydrological gradient between the turlough and its surrounding
474 epikarst.

475

476 **5.2 Nitrogen**

477 The typical pattern of N in the turloughs is peak concentrations occurring in early-winter (coinciding
478 with peaks or near-peaks in water levels) followed by a reduction in concentrations (and load)
479 throughout the spring and summer. This pattern is also reported in numerous permanent water bodies
480 in Ireland such as Lough Bunny (Pybus et al., 2003) and Lough Carra (King and Champ, 2000) as

481 well as in Scotland (Petry et al., 2002) and Wales (Reynolds et al., 1992). The trend is usually
482 explained by reduced effective rainfall and increased plant and microbial N-uptake in the catchments
483 during the growing season (late spring to early autumn) and the reverse process occurring in the late
484 autumn and winter (Cunha Pereira, 2011;Kaste et al., 2003). This pattern would thus be expected of
485 Blackrock and Coole turloughs (as they should reflect the N of the water feeding them), and indeed
486 the results generally supported this. Interestingly however, the trend can also be seen in Coy,
487 Garryland and Caherglassaun turloughs. This suggests that N is being lost from these turloughs by
488 alternative processes.

489

490 Losses of N from lakes are typically explained by three main processes: (a) net loss with outflowing
491 water (i.e. flow-through), (b) permanent loss of inorganic and organic nitrogen-containing compounds
492 to the sediments, and (c), reduction of NO_3 to N_2 by bacterial denitrification and subsequent return of
493 N_2 to the atmosphere (Wetzel, 2001). These processes are of additional importance within the Gort
494 Lowlands as the limiting nutrient in these turloughs has been shown to be N rather than P (Cunha
495 Pereira et al., 2010). An additional complication for N cycling in turloughs is the shift from flooded
496 and dry phases which result in fluctuation between aerobic and anaerobic soil conditions.

497

498 For many turloughs in Ireland, which operate more as diffuse flow-through systems, the most likely
499 explanation for a decline of N concentration is due to an equivalent decline in N concentration from
500 the inflowing water. Mass balance calculations carried out by Naughton (2011) showed that in order
501 for dilution to be the main process responsible for lowering TN concentrations, excessively high
502 levels of turnover were required during the recession period. While some degree of flow-through
503 behaviour must inevitably be occurring, other N reduction processes are also likely to be taking place.
504 This outflow/dilution concept is a suitable partial explanation for the behaviour of Blackrock and
505 Coole turloughs which are closely related to their respective river inputs. This concept however does
506 not explain the reduction of N in the surcharge tank turloughs. While these surcharge tank turloughs
507 do experience some dilution from diffuse water (as shown by alkalinity measurements), the incoming
508 water would be more likely to increase N concentration rather than reduce it. Thus, internal reduction
509 processes must also be taking place within these turloughs.

510

511 In many permanent lakes, sedimentation can be a major source of N loss as a result of permanent
512 internment of partially decomposed biota and inorganic and organic nitrogen compounds adsorbed to
513 organic particulate matter in the sediments (Wetzel, 2001). However, it is primarily organic nitrogen
514 that is lost to sediments as dissolved forms of N such as ammonium and nitrate are hardly adsorbed by
515 sediment particles and do not normally precipitate to insoluble forms in the sediment (Scheffer, 1998).
516 Within turloughs N in the water column is primarily found in an inorganic form. As such, the effect of
517 sedimentation on the Gort Lowlands turloughs should be limited.

518

519 Denitrification can cause significant loss of N in lakes. For it to take place, the key condition required
520 is anoxic conditions. Due to this condition, denitrification is an unlikely cause of N loss in most
521 turloughs as they tend to show dissolved oxygen (DO) levels near saturation ($>10 \text{ mg l}^{-1}$) (Cunha
522 Pereira, 2011). As most turloughs are shallow with average depths between 1 – 3 m (Naughton,
523 2011), DO levels can be assumed to remain high throughout the turlough water column. The turloughs
524 of the Gort Lowlands however are deeper, typically reaching depths greater than 10 m. These
525 turloughs are also more eutrophic which would encourage a ‘clinograde’ oxygen profile whereby DO
526 levels reduce with depth due to oxidative processes. In lakes where this ‘clinograde’ oxygen profile
527 occurs, oxygen consumption is most intense at the sediment-water interface, where the accumulation
528 of organic matter and bacterial metabolism are greatest (Wetzel, 2001). Thus the sediment surface is
529 the most important site for denitrification (Scheffer, 1998). Analysis of soil samples from the Gort
530 Lowland turloughs by (Kimberley and Waldren, 2012) found that elevated concentrations of available
531 forms of N and P in the lower turlough zones may be the result of anaerobic conditions, which
532 suggests that denitrification could occur within the turloughs of the Gort Lowlands.

533

534 Reddy and DeLaune (2008) state that denitrification rates in lakes vary between $34 \text{ and } 57 \text{ mg N m}^{-2}$
535 day^{-1} . Looking at the example of Caherglassaun over the 2011-2012 flooding season, that would
536 suggest a removal of 755–1266 kg N via denitrification between sampling points A and B (one month
537 apart) highlighted in Figure 10. The actual amount of N removed can be calculated as follows:

- 538 • N load at point A is 3121 kg ($1.1 \text{ mg l}^{-1} \times 2,837,295 \text{ m}^3$). N load at point B is 1724 kg.
- 539 • Supposing that N was removed by outflow only, the concentration should stay at 1.1 mg l^{-1}
540 while the volume reduces to $2,463,700 \text{ m}^3$. So the N load at point B would be 2710 kg.
- 541 • Thus 986 kg N ($2710-1724$) has been removed by non-conservative processes.

542 This value (986 kg) sits comfortably between the denitrification values as predicted for Caherglassaun
543 based on the denitrification rates of Reddy and DeLaune (2008) which suggests that denitrification is
544 a plausible cause of N removal during this period. It should be noted that this calculation is only made
545 possible by the fact that the turlough was in recession for the entire period between points A and B.
546 This allowed for the transformation processes to be isolated from any dilution effects as the turlough
547 did not receive significant inflow during this period.

548

549 When this same calculation is carried out over the same period for Garryland turlough, the Reddy and
550 DeLaune (2008) removal rate prediction is between 356-597 kg N but only 151 kg is removed from
551 Garryland. This lesser removal rate in Garryland may be related to the fact that the turlough is
552 occasionally linked with the southern Cloonteen catchment as well as Coole turlough depending on
553 water levels which would discourage the stable conditions required for denitrification. This is similar

554 to Coy, which over this particular period appears to show no denitrification at all. Again this may be
555 linked to instability at certain water levels as Coy is known to have an elevated swallow hole which
556 acts as an overflow at high water levels. As river flow through turloughs, Blackrock and Coole were
557 not considered for calculation as they are known to be unstable over flooded periods. Thus
558 Caherglassaun, which is the deepest and last turlough in the network, and consequently the most
559 stable, is predictably found to be the most likely site for denitrification to occur within the system.

560

561 The surcharge tank turloughs, particularly Caherglassaun, can therefore be considered as sinks of N
562 during the few months (typically 3-4 months) in which they are deep enough and stable enough for
563 denitrification to take place. The flow-through turloughs on the other hand are predominantly
564 influenced by dilution and tend to reflect their input. In certain situations however, these flow-through
565 turloughs can seemingly operate as nutrient sources. Mean observed concentrations in Blackrock
566 (1.32 mg l^{-1}) exceeded those measured in the river feeding it (1.03 mg l^{-1}) over the study period which
567 suggests a possible internal source of nutrients such as from grazing animals or the nearby abattoir.

568

569 **5.3 Phosphorus**

570 The major source of P to the turloughs is via river inputs. For the lower three turloughs (Coole,
571 Garryland and Caherglassaun), mean turlough P concentrations were a clear reflection of their river
572 input. The upper two turloughs, however, showed P levels in excess of their water source (SA1)
573 which suggests that these turloughs act as a source of P (or perhaps Blackrock is the source and Coy P
574 concentrations are only elevated by influx of Blackrock outflow). Similar to the discussion on N, the
575 cause of this elevated P could be due to the presence of an abattoir located next to Blackrock or due to
576 grazing during dry periods on both turloughs which would lead to increased nutrient concentrations at
577 the onset of flooding due to the release of soluble P from manure deposition. Another important factor
578 could be an artefact of the temporal resolution of sampling. Monthly sampling of turloughs was
579 deemed to be adequate to characterise the system as water is typically retained in the turloughs for
580 long periods. However, for the rivers, monthly sampling only offers a snapshot of concentrations at
581 the time of sampling. Thus any potential plumes of point source contamination in the rivers could be
582 missed by the river samples but would likely be accounted for in the turlough samples.

583

584 In terms of temporal variation, the turloughs appear to be similarly influenced by loss mechanisms for
585 P as for N (Figure 7). Unlike N, the P cycle in lakes has no gaseous loss mechanism, thus any P added
586 to the surcharge tank turloughs should remain within the system until drainage, but not necessarily the
587 water column (Reddy and DeLaune, 2008). One of the predominant mechanisms by which P is
588 transformed / removed from lake systems is sedimentation and subsequent accumulation and soil
589 deposition. If P has been sorbed onto particulate matter, it can settle and accumulate at the base of the

590 turlough, thus reducing the total P (TP) concentration of the water column, i.e. the flux of particulate
591 matter is generally from the water column to soil. This was confirmed by Keane (2010) who found
592 that turlough soils do not re-release significant P amounts back into the water column. Also, turloughs
593 with mineral soils (such as the Gort Lowlands turloughs) are more likely to accumulate P than
594 turloughs with organic soils (Waldren, 2015). As the P is retained in the soil, it can transfer from
595 available P pools into much larger immobile P pools and thus keep accumulating in the soil, a well-
596 documented phenomenon in ordinary agricultural soils. The sedimentation process would result in a
597 reduction of both TP and TDP species, as can be seen occurring in the turloughs. Indeed, this process
598 was somewhat evidenced by Kimberley and Waldren (2012) who found elevated P concentrations in
599 soil samples taken from the more saturated lower zones of turloughs. Thus, the pattern of reducing P
600 within the turloughs could be partially due to adsorption of P from a dissolved form to a particulate
601 form and subsequent sedimentation out of the water column into the soil. **However, further research is
602 required into the minerology of turlough soils and the relative importance of different P removal
603 mechanisms (adsorption, precipitation) under the prevailing hydrochemical conditions in this karst
604 area covered by glacially derived calcareous limestone till**

605

606 Aside for the trend of reducing concentrations over the flooded period, another pattern can be seen
607 whereby nutrients (N and P) are seen to increase (significantly for TN) once the flood has receded.
608 These spikes could be due to the increased sensitivity of the turloughs to their river inputs during dry
609 periods. During these periods, the turloughs have less capacity to dilute any incoming nutrient plumes
610 and so spikes in nutrient concentrations should be expected. Alternatively, it has been suggested
611 (Cunha Pereira, 2011) that such spikes might be due to the possible release of nutrients and organic
612 matter to the water column owing to the increased soil-water interactions.

613

614 **6 CONCLUSIONS**

615 The nutrient flux within a lowland karst catchment has been monitored over a three year period. The
616 allogenic nature of this catchment provides distinct hydrochemical characteristics, as demonstrated by
617 alkalinity results. The allogenicly fed river-conduit-turlough network displays relatively low
618 alkalinity concentrations compared to the more autogenic slow moving water found within the
619 surrounding epikarst/diffuse aquifer. Within the turloughs, alkalinity was able to easily distinguish
620 between the flow through turloughs (Blackrock, Coole) and the surcharge tank turloughs (Coy,
621 Garryland, Caherglassaun). Flow through turloughs displayed a distinct pattern whereby a significant
622 influx of fresh water could cause a noticeable change in hydrochemistry over time. This is in contrast
623 to the surcharge tank turloughs which showed stable alkalinity concentrations with a slow increase
624 over time due to the influx of diffuse recharge from the surrounding aquifer.

625

626 Unlike alkalinity, nutrient concentrations within the catchment are primarily influenced by
627 anthropogenic processes, i.e. agriculture. As a result, the nutrient flux within the catchment displayed
628 a greater degree of complexity, particularly as a result of the contrasting mobility traits of N and P. By
629 combining the hydraulic model with conservative nutrient concentrations, insights were gained into
630 how the turloughs should conceptually operate. This showed that while the flow through turloughs
631 behaved as expected with respect to nutrients, the surcharge tank turloughs can behave similarly to
632 permanent lakes under certain conditions. Under such conditions (long, deep and stable flooding), the
633 turloughs can operate as nutrient sinks within the catchment. These nutrient losses (i.e. non-
634 conservative behaviour) were attributed to be most likely due to the process of denitrification for N
635 and sedimentation for P.

636

637 As well as being nutrient sinks, the turloughs may also operate as nutrient sources due to manure
638 deposition from grazing animals during dry periods in the summer or via other point sources (such as
639 the abattoir located near Blackrock turlough, as well as on-site wastewater treatment systems, slurry
640 tanks etc.). These sources can be present in most turloughs, and results from this study suggest that
641 some turloughs may have gained considerable nutrient loads by such processes over the study period.
642 However, as these inputs can occur very rapidly, it is difficult to quantify without higher frequency
643 sampling of the turloughs and their inputs. It can thus be concluded that while not every turlough has
644 the potential to act as a nutrient sink every year, every turlough does have the potential to act as
645 nutrient source every year.

646

647

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652

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821 **Table 1: Ranges and mean values for alkalinity Nitrate (NO₃), Total Nitrogen (TN), Total Phosphorus**
 822 **(TP) and Total Dissolved Phosphorus (TDP) for turloughs, groundwater, selected rivers and Kinvara**
 823 **(grouped and individual) for the period between March 2010 and March 2013.**

	Alkalinity (mg l ⁻¹ CaCO ₃)		TN (mg l ⁻¹)		NO ₃ (mg l ⁻¹ NO ₃ -N)		TP (mg l ⁻¹)		TDP (mg l ⁻¹)	
	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>
Rivers	1-246	48.5	0-3.9	1.01	0-3.1	0.71	0.0037-0.121	0.026	0-0.066	0.018
SA1	15-246	148.1	0.2-3.4	1.03	0.1-1.5	0.55	0.014-0.113	0.027	0.006-0.044	0.016
SA2	12-205	68.2	0-3.1	1.12	0.1-1.6	0.68	0.015-0.102	0.032	0.008-0.064	0.024
SA3	2-92	38.8	0.1-3.5	1.09	0.1-3.1	0.66	0.012-0.087	0.039	0.007-0.049	0.020
F	1-42	16.5	0-3.7	0.87	0-2.4	0.53	0.005-0.021	0.011	0-0.014	0.007
PE	1-31	10.2	0.2-2.2	0.89	0-3	0.84	0.004-0.055	0.013	0-0.042	0.009
Turloughs	42-239	131.8	0.1-4.3	1.12	0-2.4	0.66	0.014-0.115	33.70	0.006-0.061	0.021
Blackrock	46-239	138.4	0.3-3	1.32	0.3-1.5	0.81	0.022-0.115	0.047	0.013-0.0061	0.029
Coy	58-220	150.3	0.3-3	1.11	0-2	0.57	0.025-0.064	0.042	0.006-0.0046	0.021
Coole	42-235	114.4	0.3-3.2	1.10	0.2-1.7	0.66	0.024-0.045	0.030	0.009-0.0032	0.020
Garryland	77-170	134.6	0.3-2.7	0.95	0.1-1.7	0.60	0.014-0.034	0.021	0.005-0.0025	0.016
Caherglassaun	77-235	121.3	0.1-4.3	1.11	0-2.4	0.65	0.019-0.036	0.027	0.008-0.0028	0.020
Groundwater	104-547	365.1	0.2-10.4	2.30	0-10.3	1.51	0-0.58	0.031	0-0.484.9	0.021
BH3	135-547	387.8	0.4-3.9	2.45	0.1-3.6	1.60	0.003-0.05	0.013	0-0.035	0.008
BH5	246-508	307.7	0.3-3.1	1.39	0-1.4	0.48	0.009-0.58	0.072	0.005-0.485	0.052
BH7	308-420	366.9	0.4-10.4	3.31	0-10.3	2.79	0.007-0.053	0.015	0.005-0.014	0.008
BH10	104-458	357.0	0.1-4.2	2.17	0.1-2.6	1.52	0-0.013	0.005	0.0006-0.010	0.004
BH11	269-362	313.6	0.2-2.4	1.24	0-2.9	0.69	0.005-0.13	0.033	0.004-0.021	0.007
BH12	123-439	375.5	0.3-5.2	2.95	0.2-3.8	1.97	0.008-0.047	0.019	0.002-0.029	0.007
BH14	162-458	375.5	1.1-5	2.91	0-3.4	1.75	0.033-0.082	0.053	0.031-0.065	0.042
BH15	369-481	425.7	0.2-3.1	1.31	0.1-1.9	0.68	0.031-0.08	0.052	0.029-0.058	0.042
BH16	316-462	376.0	0.3-5.5	2.96	0.2-4.3	2.15	0.011-0.039	0.019	0.009-0.034	0.017
Kinvara West (KW)	96-200	155.6	0.4-2.3	1.05	0.1-2.5	0.66	0.009-0.033	0.023	0.008.1-0.022	0.017

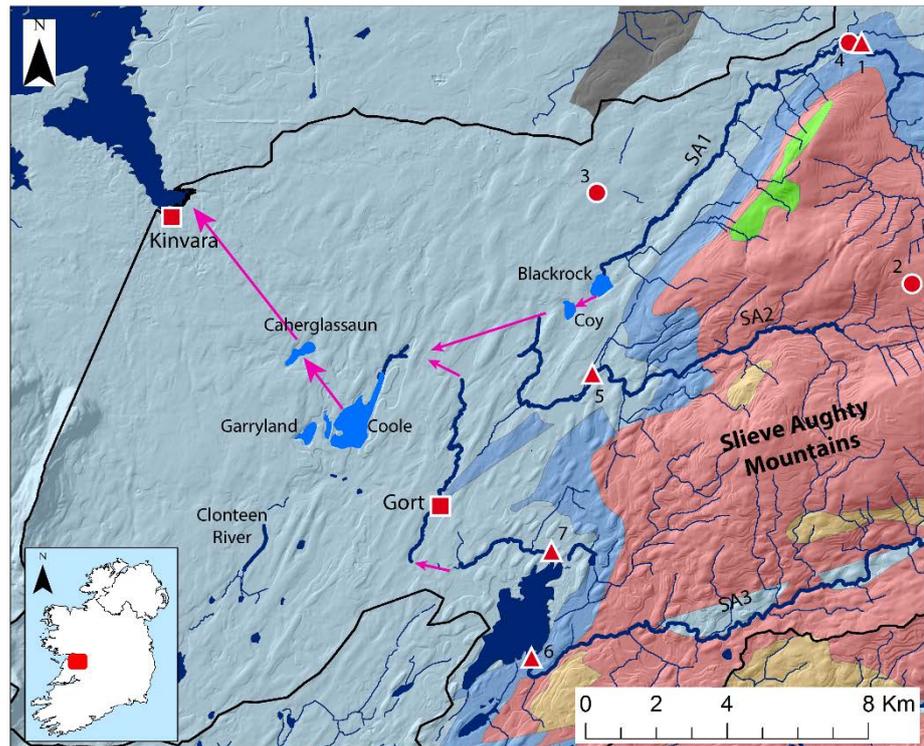
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Geology

-  Carboniferous Pure Bedded Limestones
-  Carboniferous Lower Impure Limestones
-  Devonian Old Red Sandstone
-  Silurian Metasediments and Volcanics
-  Ordovician Metasediments

Key

-  Lakes and Sea
-  Turloughs
-  Catchment
-  Rivers
-  Direction of Conduit Flow
-  Towns
-  **Rain Gauges**
1. Kilchreest
2. Francis Gap
3. Ardrahan
-  **River Gauges**
4. SA1
5. SA2
6. SA3
7. SA4



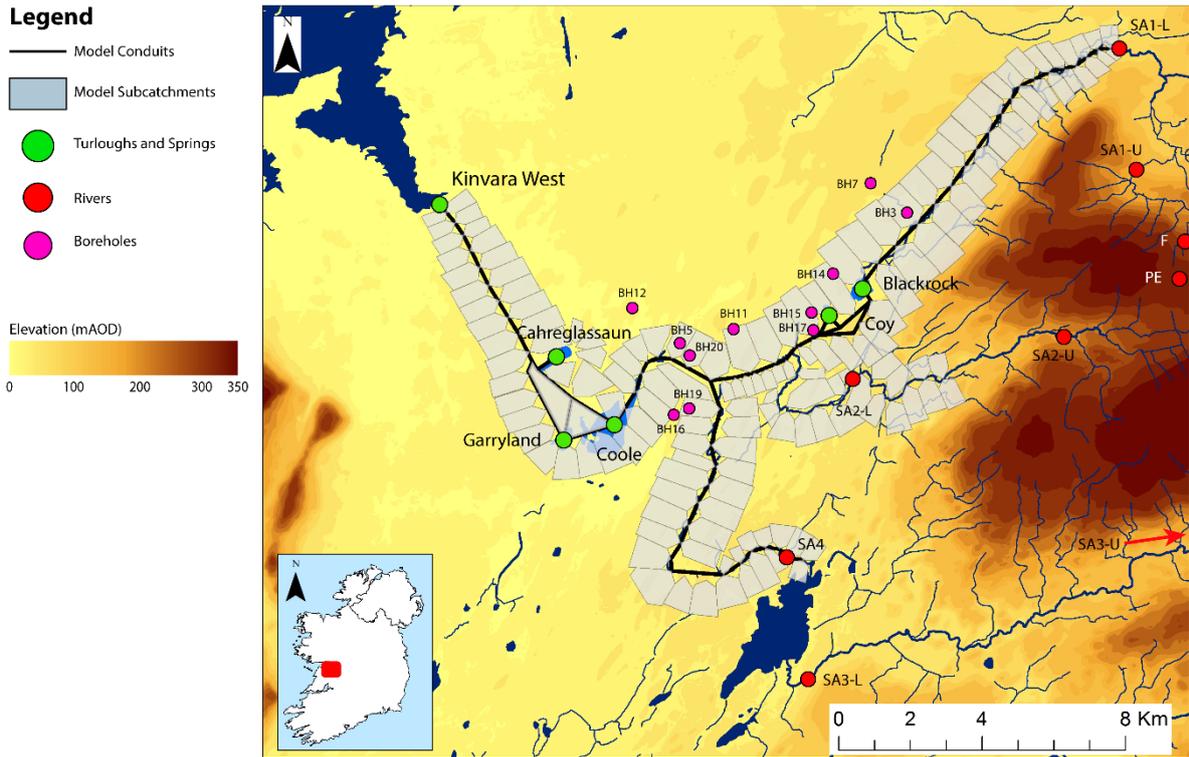
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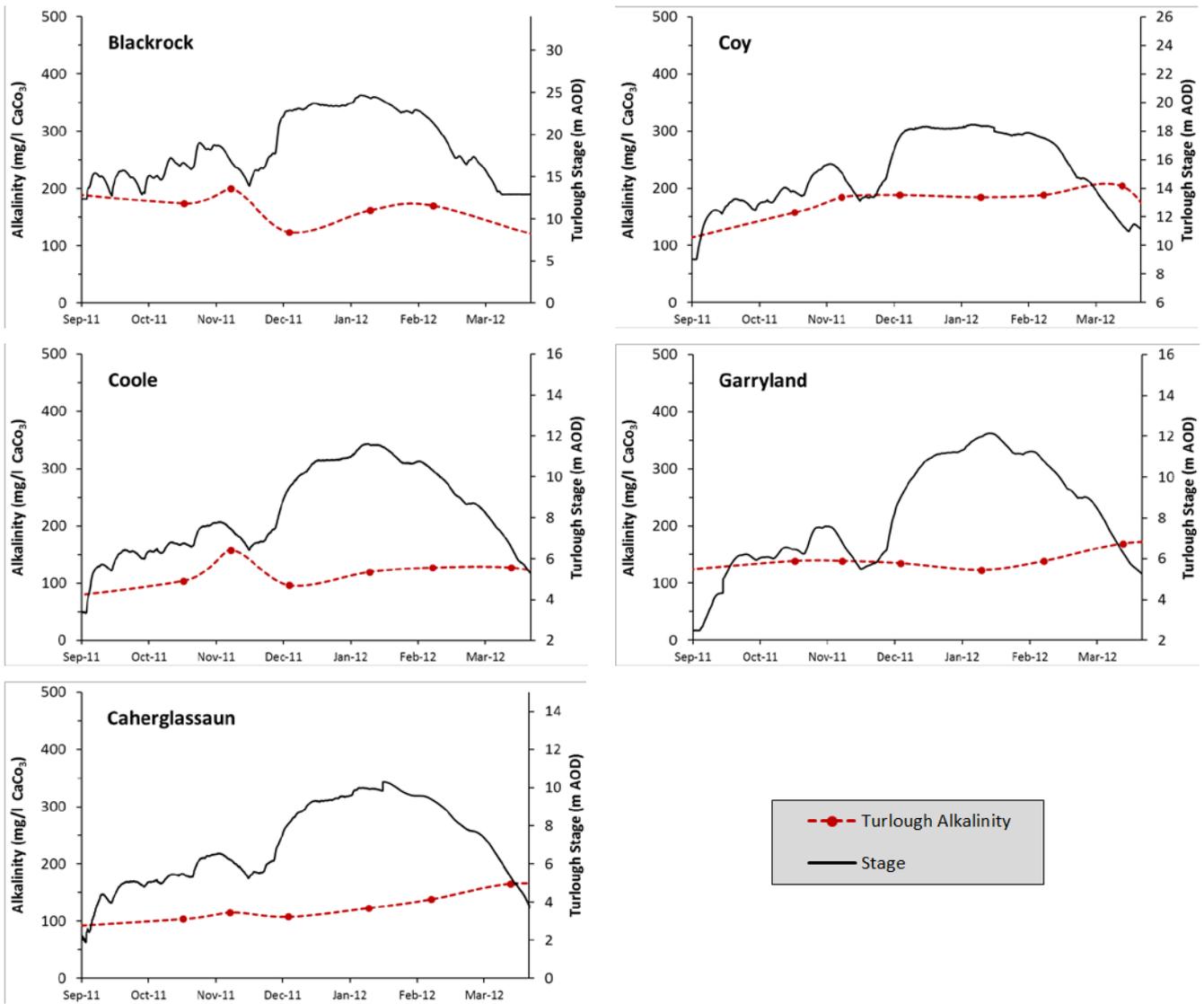
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Figure 1: Geology of study area displaying turloughs, raingauges, Kinvara, river gauging stations, the direction of underground conduit flow and the Kinvara springs catchment.

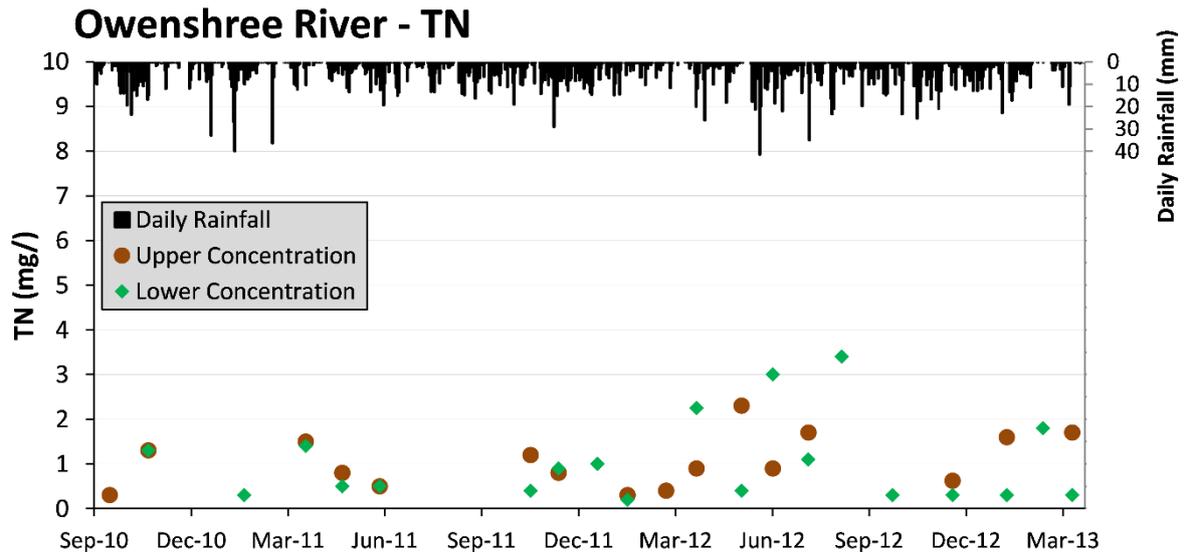


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Figure 3: Pipe network model schematic and sampling locations of turloughs, rivers and boreholes. Note: The additional ‘U’ and ‘L’ labels on the river names refer to upper and lower sampling locations.



836 **Figure 4: Turlough stage and alkalinity results for Blackrock, Coy, Coole, Garryland and Caherglassaun**
 837 **turloughs over the 2012/2013 flooding season.**

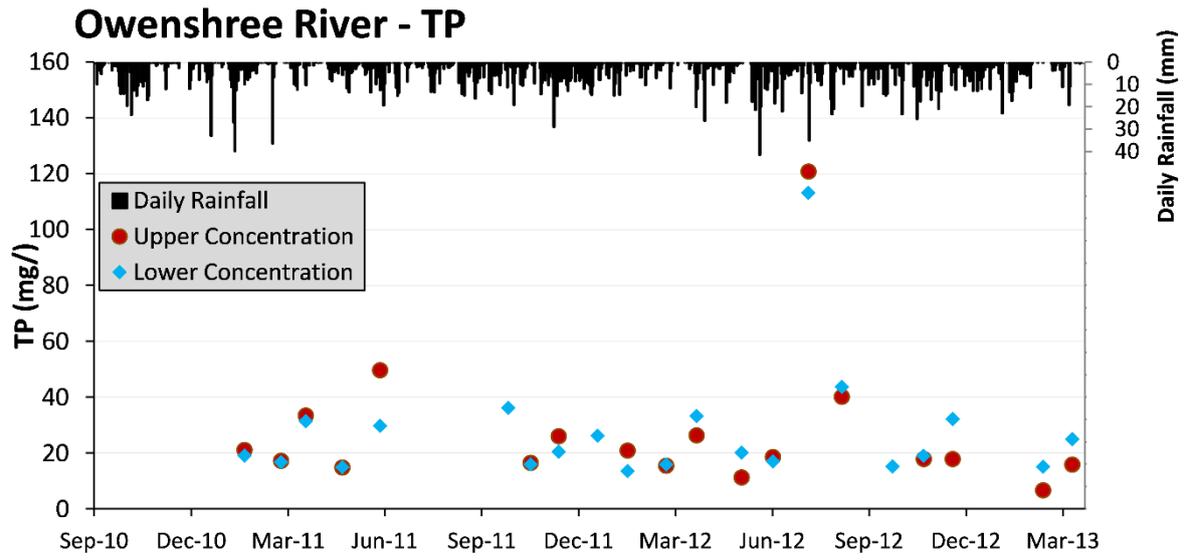


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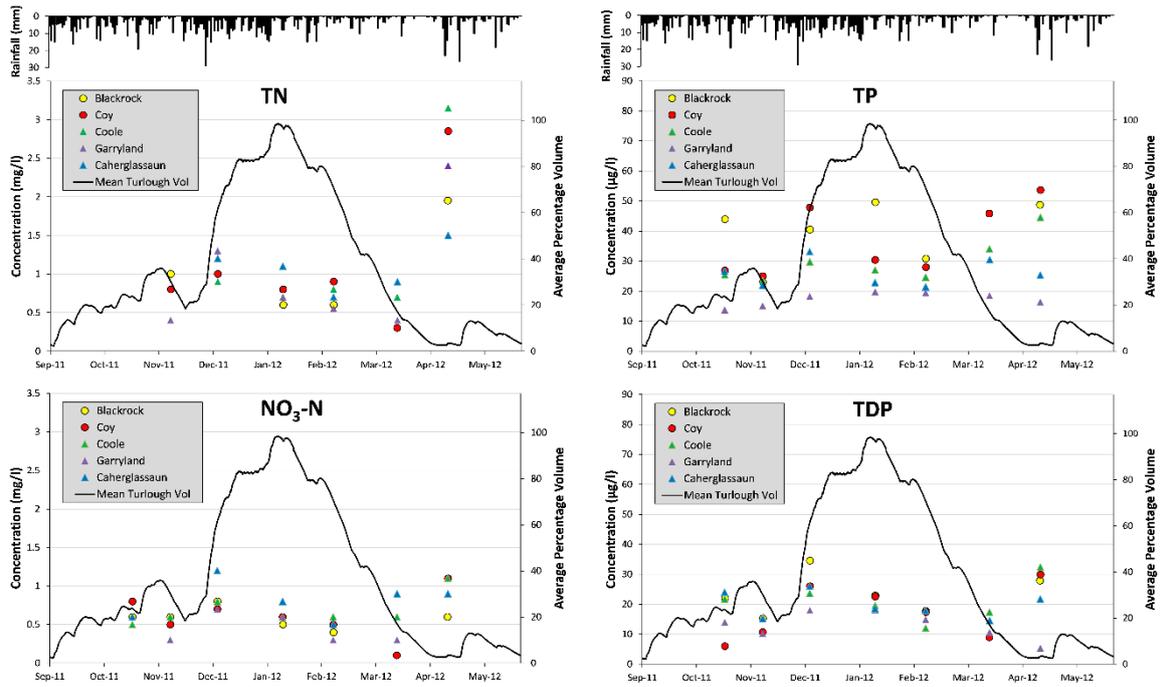
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Figure 5: Daily Rainfall and TN concentrations at the upper (U) and lower (L) sampling locations on the SA1 River.

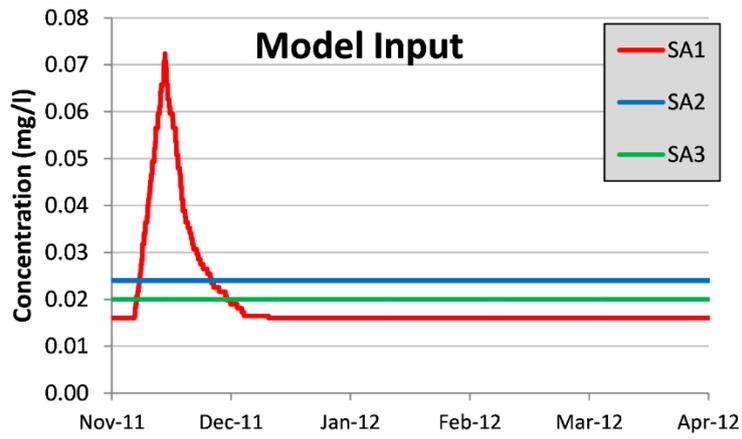


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Figure 6: Daily Rainfall and TP concentrations at the upper (U) and lower (L) sampling locations on the SA1 River.



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 845 **Figure 7: Concentrations of TN, NO₃-N, TP and TDP in Blackrock, Coy, Coole, Garryland and**
 846 **Caherglassaun Turloughs plotted together with average percentage volume of the five turloughs (i.e.**
 847 **volume as a percentage of the max volume over the period shown).**
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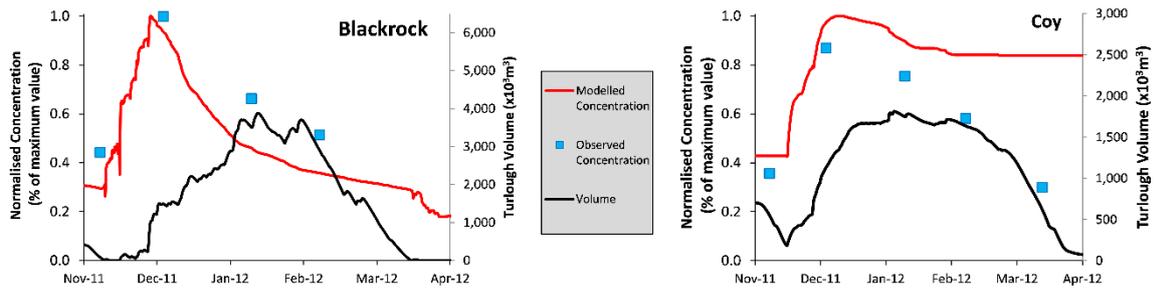
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Figure 8: Model input signal to simulate a pulse of TDP occurring in SA1. SA2 and SA3 are inputted as constant signals based on mean observed TDP concentrations.

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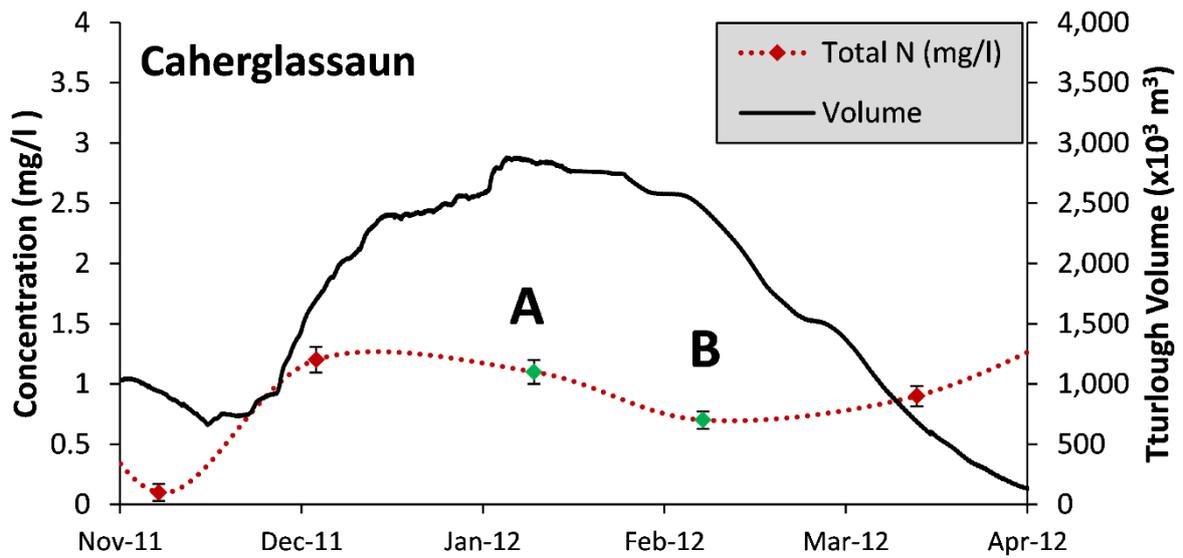


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Figure 9: Observed (blue points) and simulated (red line) normalised results of a nutrient plume in a flow-through system (Blackrock) and a surcharge tank system (Coy)

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Figure 10: Denitrification example, Caherglassaun. Denitrification occurring between points A and B.

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Standard deviation of duplicate samples shown by error bars.

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