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

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Abstract

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

1 INTRODUCTION

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

In non-carbonate aquifers, nitrogen (N) and phosphorus (P) are subject to separate transport dynamics. Nitrate (NO_3) is often found to be conservatively transported due to its high solubility and mobility characteristics while P is retained due to its affinity to particulate matter (Weiskel and Howes, 1992). In carbonate aquifers however, the existence of point recharge features, such as swallow or sink-holes, provide direct access points for N and P into the aquifer. This allows contaminants to bypass the protective soil cover associated with most diffuse recharge and enter the karst fracture/conduit network with little or no attenuation (Coxon, 2011). Within the conduit system, a contaminant can then be rapidly transmitted through an aquifer in ecologically significant quantities with very little attenuation or chemical breakdown.

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

While the hydrochemical processes in permanent lakes has been the subject of much research, relatively little work has been carried out into the nutrient flux within ephemeral lakes and their influence at a catchment scale. Ephemeral lakes, known as *turloughs* are a characteristic feature of the Irish karst landscape. Their flooding results from a combination of high rainfall and consequently high groundwater levels in topographic depressions in karst. Flooding typically occurs through underground conduits and springs in autumn forming a lake for several months in winter which then empties via swallow holes (or estavelles) in the springtime (Sheehy Skeffington et al., 2006). This flooding promotes a biodiverse habitat as species have to adapt to survive the oscillation between terrestrial to aquatic conditions. The turlough habitat is protected under the EU Water Framework Directive (2000/60/EC) and designated as a priority habitat under Annex 1 of the EU Habitats Directive (92/43/EEC). Numerous sites supporting ecological communities of national and international importance have been designated as Special Areas of Conservation (SAC) and afforded the highest level of protection available under EU conservational law.

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

2 AREA DESCRIPTION AND BACKGROUND

The Gort Lowlands is a 480 km^2 catchment located in County Galway in the west of Ireland. The eastern portion of the catchment is dominated by the Slieve Aughty Mountains and underlain by Devonian Old Red Sandstone (Figure 1). The western portion of the catchment is mostly flat and underlain by pure carboniferous limestone. Similar to the majority of karstic regions found within Ireland, the catchment is primarily lowland (rarely rising above 30 m) and as such, the region is subject to considerable interaction between ground and surface waters.

As demonstrated by previous tracer studies (Drew, 2003), the prevailing drainage direction in the catchment is east to west, with recharge from the non-carbonate Slieve Aughty Mountains (hereafter referred to as just ‘mountains’) flowing across the lowland karst towards a major intertidal spring at Kinvara Bay (known as Kinvara West). This significant contribution of allogenic recharge into the karst aquifer imparts the catchment with a distinctive hydrochemical flux as well as unique hydrological and ecological characteristics.

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

In the Gort Lowlands (Figure 1), turloughs form a key component of the hydrological regime, offering a zone of temporary storage for water surcharging out of the active conduit network. Numerous turloughs are present within the Gort Lowlands but five turloughs in particular (Blackrock, Coy, Coole, Garryland and Caherglassaun) are known to be highly influential upon the active conduit network (Gill et al., 2013b). The chemically-aggressive allogenic recharge entering the Lowlands has contributed to the development of a complex conduit network with relatively high flow rates. The five turloughs within the network are all relatively eutrophic and deep in comparison to other turloughs around Ireland and are underlain by non-alluvial mineral soil types (of relatively low $CaCO_3$ concentration) compared to the organic and marly soil types generally associated with turloughs of longer periods of inundation (Kimberley et al., 2012).

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

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

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

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

3 METHODOLOGY

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

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

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

3.1 Hydrometry

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

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

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

3.2 Hydrochemistry

Monthly sampling was carried out at turloughs, rivers, springs and two upland sites (F and PE) between March 2010 and March 2013, in addition to groundwater samples from boreholes and wells within the carboniferous aquifer surrounding the turlough network (Figure 3). Water samples were tested within 24 hours of collection. Samples were tested for alkalinity based on Standard Methods (APHA, 1999) and Total Nitrogen (TN), nitrate (NO_3-N), nitrite (NO_2) and ammonium (NH_4) were analysed using a Merck Spectroquant Nova 60 spectrophotometer and associated reagent kits. Quality control (QC) was carried out using Merck Combicheck standards for each batch of monthly samples.

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

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

3.3 Modelling

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

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

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

where: M_J = Mass of dissolved pollutant in node J (kg)
Q_i = Flow into node J from link i ($m^3\,s^{-1}$)
C_i = Concentration in the flow into node J from link i ($kg\,m^{-3}$)
M_{sJ} = Additional mass entering node J from external sources (kg)

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

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

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

where: C = Concentration ($kg\,m^{-3}$)
u = Flow velocity ($m\,s^{-1}$)
t = Time (s)
x = The spatial co-ordinate (m).

4 RESULTS

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

4.1 Alkalinity

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

4.1.1 Surface-water

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

Blackrock and Coy turloughs had mean alkalinities of 138.4 and 150.3 mg l^{-1} $CaCO_3$ respectively. These concentrations reflect the alkalinity of their primary source of water, SA1, which had a mean alkalinity of 148.1 mg l^{-1} $CaCO_3$. The alkalinities of Coole, Garryland and Caherglassaun turloughs were slightly lower (114.4, 134.6 and 121.3 mg l^{-1} $CaCO_3$) reflecting the lower concentration contributions of SA2 (68.2 mg l^{-1} $CaCO_3$) and SA3 (38.8 mg l^{-1} $CaCO_3$) rivers. However, these turloughs have noticeably higher concentrations than would be expected from a weighted mean alkalinity based on the percentage flow contribution from the three rivers (71 mg l^{-1} $CaCO_3$). Their increased alkalinity, relative to what would be expected from the river inputs, can be attributed to three factors. Firstly, these turloughs receive a minor influx of water from the more alkaline Cloonteen River catchment to the south of the Gort Lowlands (see Figure 1), most significantly at Garryland turlough. Secondly, as SA2 and SA3 rivers enter the limestone system under-saturated in dissolved $CaCO_3$ their water is chemically aggressive and has a high dissolution potential. This is likely to cause considerable solution of the limestone bedrock as they flow towards Coole. Thirdly, as the river/conduit water moves through the catchment towards the lower three turloughs, it is being diluted by the addition of high-alkalinity recharge from the diffuse groundwater.

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

The trend of increasing alkalinity over the flooding season as seen in the surcharge tank systems is unusual for turloughs. Typical autogenically recharged turloughs tend to have much higher alkalinity levels, due to the $CaCO_3$ rich waters that feed them, which does not increase over time (as they are saturated) but tends to decrease (as observed by (Cunha Pereira, 2011)). Such losses in $CaCO_3$ from turloughs have been attributed to the influx of water (saturated with CO_2) which comes into contact with the air and gradually loses its CO_2 to the atmosphere, primarily from physiochemical processes but also possibly biogenic processes (Coxon, 1994).

4.1.2 Groundwater

Groundwater alkalinity measured across the catchment generally varied between 300 and 400 mg l^{-1} $CaCO_3$ but overall was found to be quite consistent (standard deviation ≤40 mg l^{-1}) with a mean value of 365.1 mg l^{-1} $CaCO_3$. The broad agreement and lack of variation between most groundwater samples indicates the presence of a large diffuse/epikarst type aquifer with low transmissivity which surrounds the active conduit network (McCormack et al., 2014).

4.2 Nutrients

The results of the NO_3, TN, total TDP and TP sample analysis are shown in Table 1. NO_2 and NH_4 were initially measured but were often near-to or below detection limits and as such, their measurement was ceased.

4.2.1 Surface-water: Rivers

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 concentrations ranged between 0 and 0.12 mg l^{-1} with a mean value of 0.026 mg l^{-1}. Nutrient concentrations in the rivers showed a high degree of variation, although a seasonal trend was apparent with N and P highest in summer whereas lowest concentrations were in the winter for N and the spring for P. Contrasting source/transport dynamics between N and P are apparent in the river nutrient concentrations. Mean values of TN for each river were quite similar, ranging between 0.87 and 1.12 mg l^{-1} whereas for TP, the rivers showed a wide range of mean values between 0.011 and 0.032 mg l^{-1} (Table 1).

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

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

4.2.2 Surface-water: Turloughs

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

The lower mean nutrient concentrations in Coole, Garryland and Caherglassaun turloughs tended to reflect the concentrations of the rivers feeding them. For example, mean concentrations of TN and TP in Coole turlough were within ±1% of their primary source of water, the SA3 River. Nutrient concentrations in Caherglassaun show similar values to Coole indicating a direct relationship between these turloughs. However, Garryland turlough displays lower nutrient concentrations, most likely due to the influx of water from the southern Cloonteen catchment as discussed previously. Figure 7 shows the time-series of nutrient concentration data and turlough volume data across the 2011/2012 season. For purposes of clarity, and as the flooding patterns in the five turloughs are quite similar, only the average volume of the five turloughs is shown (as a percentage of maximum volume) rather than the five individual time-series (for individual flooding patterns, see Figure 4). While the nutrient concentrations in these plots are shown to be quite variable, a trend can be seen whereby nutrient concentrations appear to decrease over the flooded period (between December and February/March). This pattern is seen clearly seen for TN, NO_3 and TDP. However, a high TP concentration in Blackrock during January 2012 does not conform to the trend, the reason for which is unclear. One hypothesis is that the sample was influenced by point source contamination from an abattoir on the south eastern edge of Blackrock Turlough. Nutrients are seen to increase (significantly in the case of TN) after the main flood volumes have receded but with a small quantity of water still remaining. These spikes could be due to the increased sensitivity of the turloughs to their river inputs during such dry periods.

4.2.3 Groundwater

The primary land use in the catchment is agriculture and as such, there are significant additional sources of N and P. Mean groundwater concentrations across the catchment were recorded as 2.30 mg l^{-1} and 0.031 mg l^{-1} for TN and TP respectively (Table 1) with overall mean N concentrations being almost double those of surface water bodies while the overall mean P concentrations of the turloughs and groundwater were shown to be similar. The results obtained from boreholes within the Gort Lowlands showed a wide range of recorded results for N (0.2-10.4 mg l^{-1} TN) with a standard deviation of 0.92 mg l^{-1} TN, although the mean concentrations at each borehole across the catchment are within a similar range (between 1.2 and 3.3 mg l^{-1}). P showed a greater range of measured results (0-0.58 mg l^{-1} TP) with a standard deviation of 0.027 mg l^{-1} TP, but more significantly, the mean concentrations at each borehole showed large differences (between 0.005 and 0.072 mg l^{-1} TP). These results indicate that N was able to reach the groundwater relatively easily due to the high mobility and solubility of NO_3, and more or less equalised across the catchment. P, on the other hand, being much less mobile would only be likely to enter the groundwater in areas of extreme vulnerability (i.e. through shallow and/or permeable subsoils). Thus, while the sources of P could be equally as widespread, its ability to reach the groundwater is highly variable. However, once in the conduit system, P is known to be transported conservatively with negligible attenuation (Mellander et al., 2013;Kilroy and Coxon, 2005).

4.2.4 Kinvara Springs

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

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

4.3 Nutrient Modelling

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

4.3.1 Nutrient Retention

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

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

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

4.3.2 Diffuse Contribution

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

5 DISCUSSION

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

5.1 Alkalinity

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

5.2 Nitrogen

The typical pattern of N in the turloughs is peak concentrations occurring in early-winter (coinciding with peaks or near-peaks in water levels) followed by a reduction in concentrations (and load) throughout the spring and summer. This pattern is also reported in numerous permanent water bodies in Ireland such as Lough Bunny (Pybus et al., 2003) and Lough Carra (King and Champ, 2000) as well as in Scotland (Petry et al., 2002) and Wales (Reynolds et al., 1992). The trend is usually explained by reduced effective rainfall and increased plant and microbial N-uptake in the catchments during the growing season (late spring to early autumn) and the reverse process occurring in the late autumn and winter (Cunha Pereira, 2011;Kaste et al., 2003). This pattern would thus be expected of Blackrock and Coole turloughs (as they should reflect the N of the water feeding them), and indeed the results generally supported this. Interestingly however, the trend can also be seen in Coy, Garryland and Caherglassaun turloughs. This suggests that N is being lost from these turloughs by alternative processes.

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

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

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

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

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

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

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

When this same calculation is carried out over the same period for Garryland turlough, the Reddy and DeLaune (2008) removal rate prediction is between 356-597 kg N but only 151 kg is removed from Garryland. This lesser removal rate in Garryland may be related to the fact that the turlough is occasionally linked with the southern Cloonteen catchment as well as Coole turlough depending on water levels which would discourage the stable conditions required for denitrification. This is similar to Coy, which over this particular period appears to show no denitrification at all. Again this may be linked to instability at certain water levels as Coy is known to have an elevated swallow hole which acts as an overflow at high water levels. As river flow through turloughs, Blackrock and Coole were not considered for calculation as they are known to be unstable over flooded periods. Thus Caherglassaun, which is the deepest and last turlough in the network, and consequently the most stable, is predictably found to be the most likely site for denitrification to occur within the system.

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

5.3 Phosphorus

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

In terms of temporal variation, the turloughs appear to be similarly influenced by loss mechanisms for P as for N (Figure 7). Unlike N, the P cycle in lakes has no gaseous loss mechanism, thus any P added to the surcharge tank turloughs should remain within the system until drainage, but not necessarily the water column (Reddy and DeLaune, 2008). One of the predominant mechanisms by which P is transformed / removed from lake systems is sedimentation and subsequent accumulation and soil deposition. If P has been sorbed onto particulate matter, it can settle and accumulate at the base of the turlough, thus reducing the total P (TP) concentration of the water column, i.e. the flux of particulate matter is generally from the water column to soil. This was confirmed by Keane (2010) who found that turlough soils do not re-release significant P amounts back into the water column. Also, turloughs with mineral soils (such as the Gort Lowlands turloughs) are more likely to accumulate P than turloughs with organic soils (Waldren, 2015). As the P is retained in the soil, it can transfer from available P pools into much larger immobile P pools and thus keep accumulating in the soil, a well-documented phenomenon in ordinary agricultural soils. The sedimentation process would result in a reduction of both TP and TDP species, as can be seen occurring in the turloughs. Indeed, this process was somewhat evidenced by Kimberley and Waldren (2012) who found elevated P concentrations in soil samples taken from the more saturated lower zones of turloughs. Thus, the pattern of reducing P within the turloughs could be partially due to adsorption of P from a dissolved form to a particulate form and subsequent sedimentation out of the water column into the soil. However, further research is required into the minerology of turlough soils and the relative importance of different P removal mechanisms (adsorption, precipitation) under the prevailing hydrochemical conditions in this karst area covered by glacially derived calcareous limestone till

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

6 CONCLUSIONS

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

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

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

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Table 1: Ranges and mean values for alkalinity Nitrate (NO_3), Total Nitrogen (TN), Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP) for turloughs, groundwater, selected rivers and Kinvara (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}NO3-N)**		**TP (mg l^{-1})**		**TDP (mg l^{-1})**	
	range	*mean*	*range*	*mean*	*range*	*mean*	*range*	*mean*	*range*	*mean*
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**

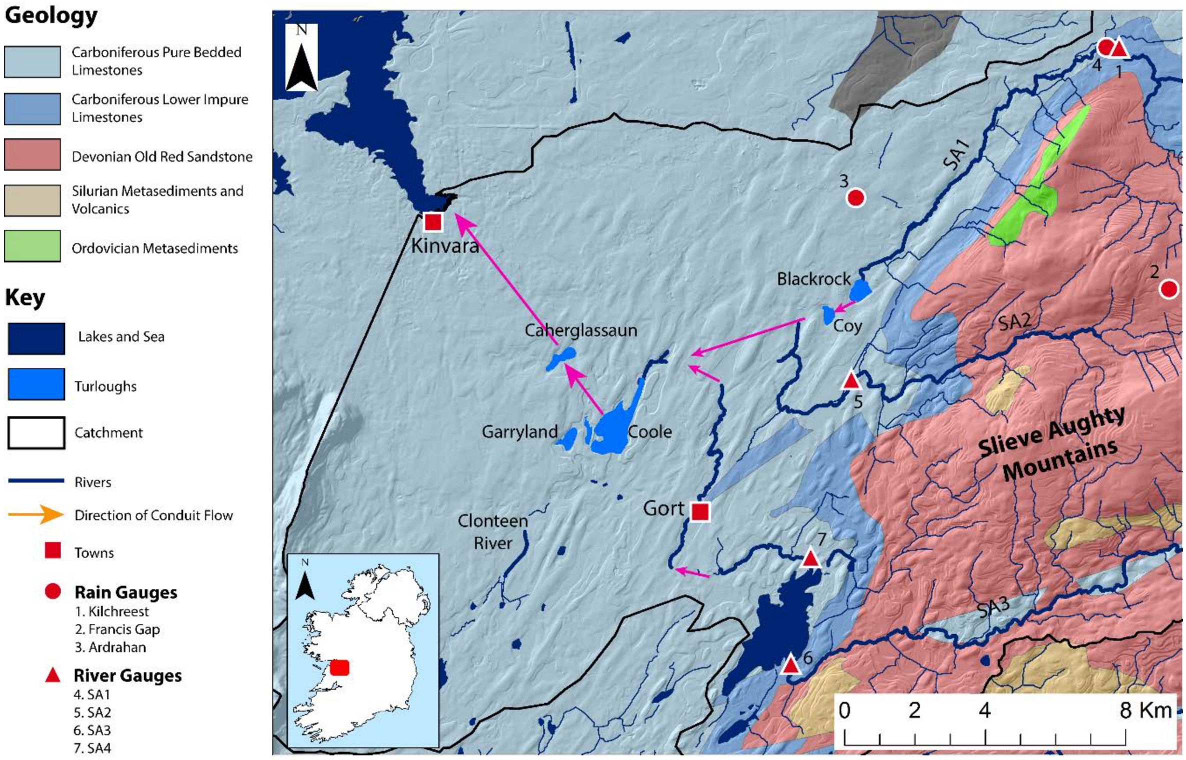

Figure 1: Geology of study area displaying turloughs, raingauges, Kinvara, river gauging stations, the direction of underground conduit flow and the Kinvara springs catchment.

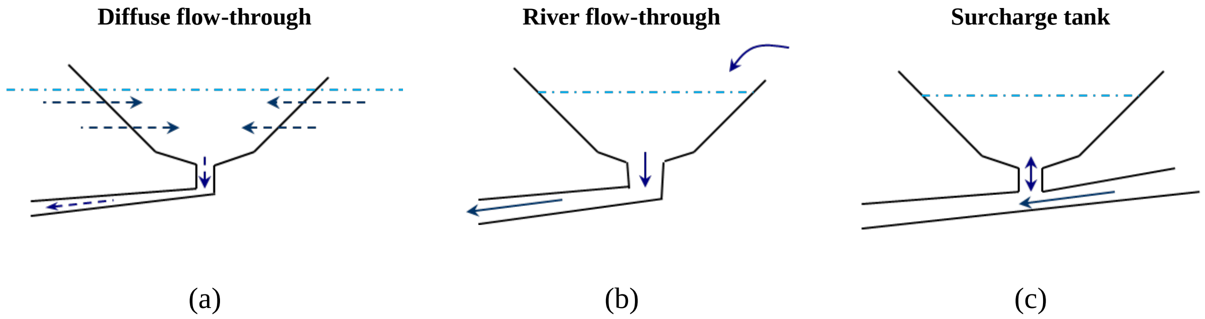

Figure 2: Conceptualisation of diffuse flow-through, river flow-through and surcharge tank turlough systems (modified from (Gill et al., 2013a)).

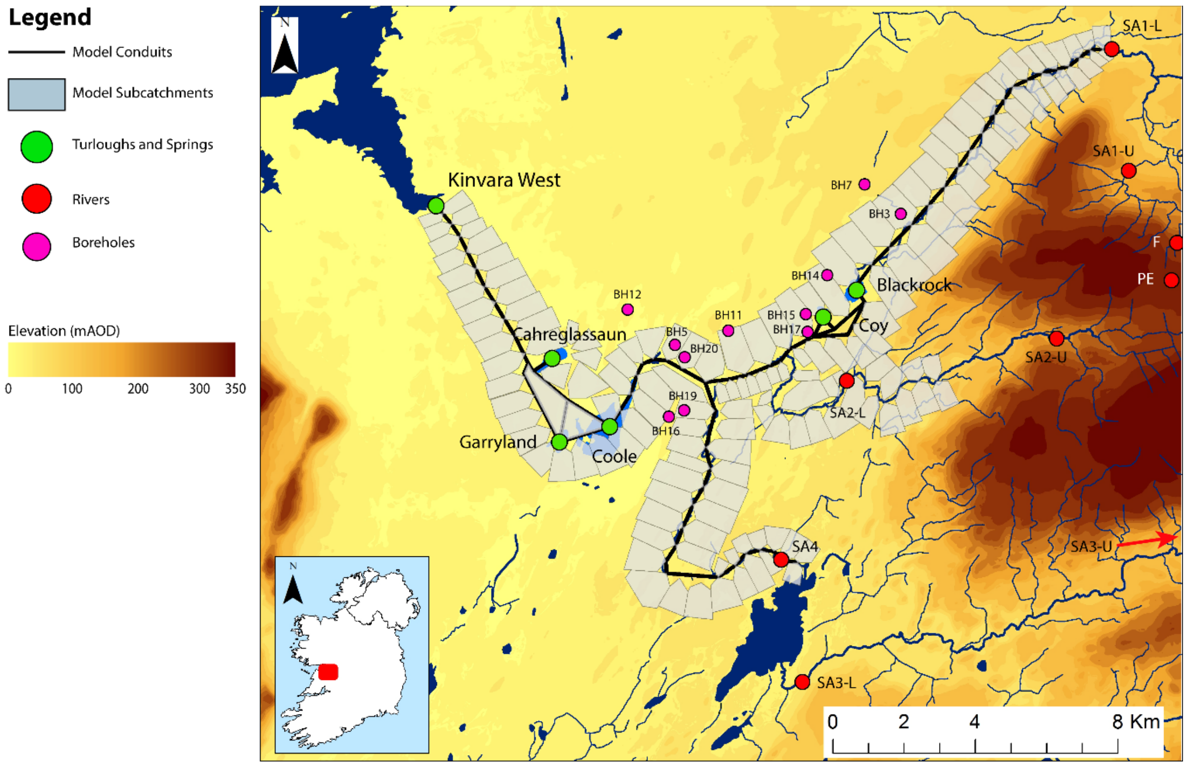

Figure 3: Pipe network model schematic and sampling locations of turloughs, rivers and boreholes. Note: The additional 'U' and 'L' labels on the river names refer to upper and lower sampling locations.

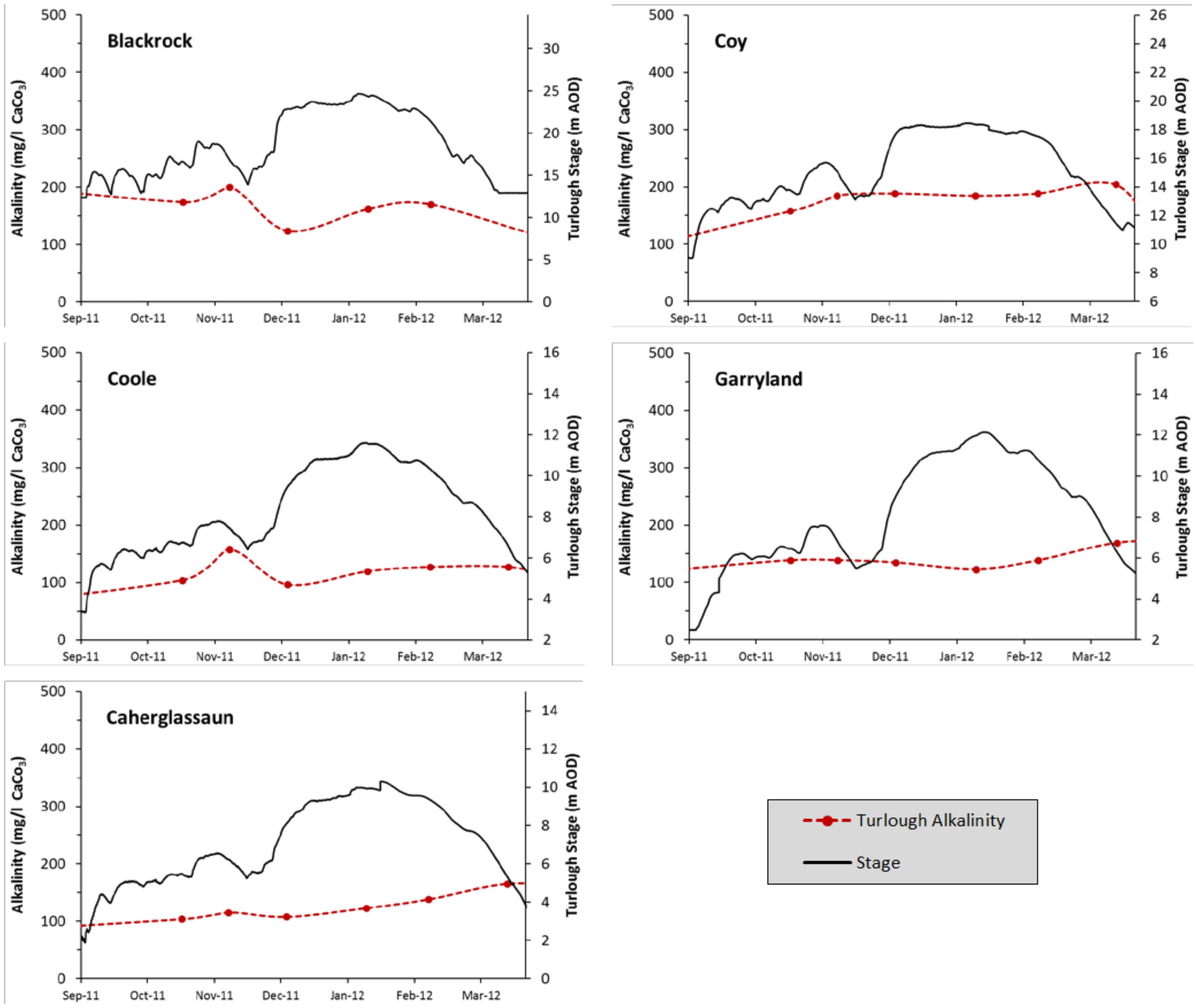

Figure 4: Turlough stage and alkalinity results for Blackrock, Coy, Coole, Garryland and Caherglassaun turloughs over the 2012/2013 flooding season.

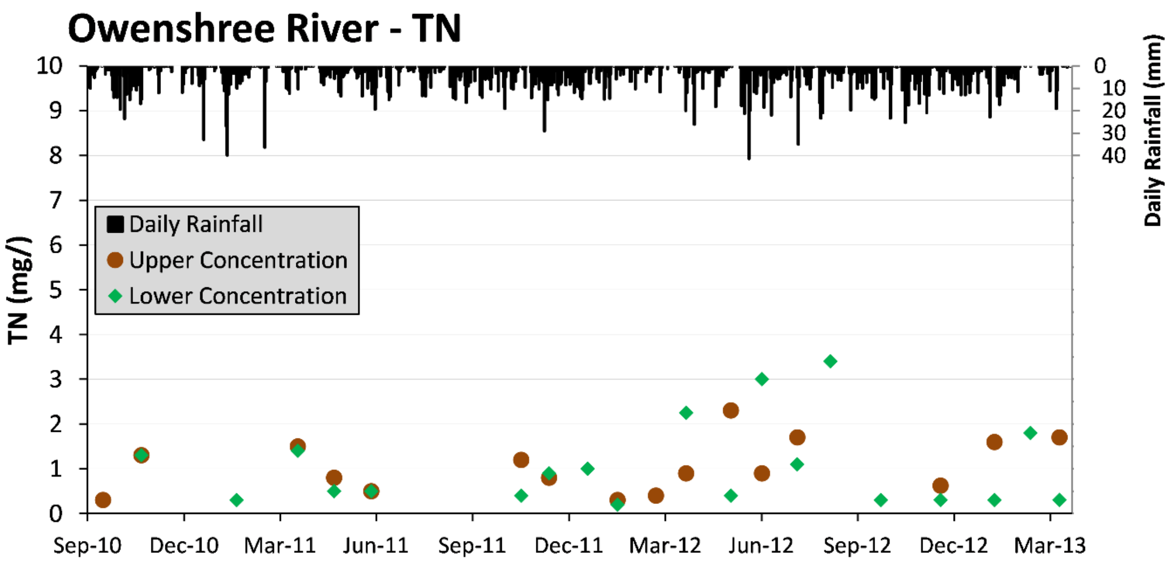

Figure 5: Daily Rainfall and TN concentrations at the upper (U) and lower (L) sampling locations on the SA1 River.

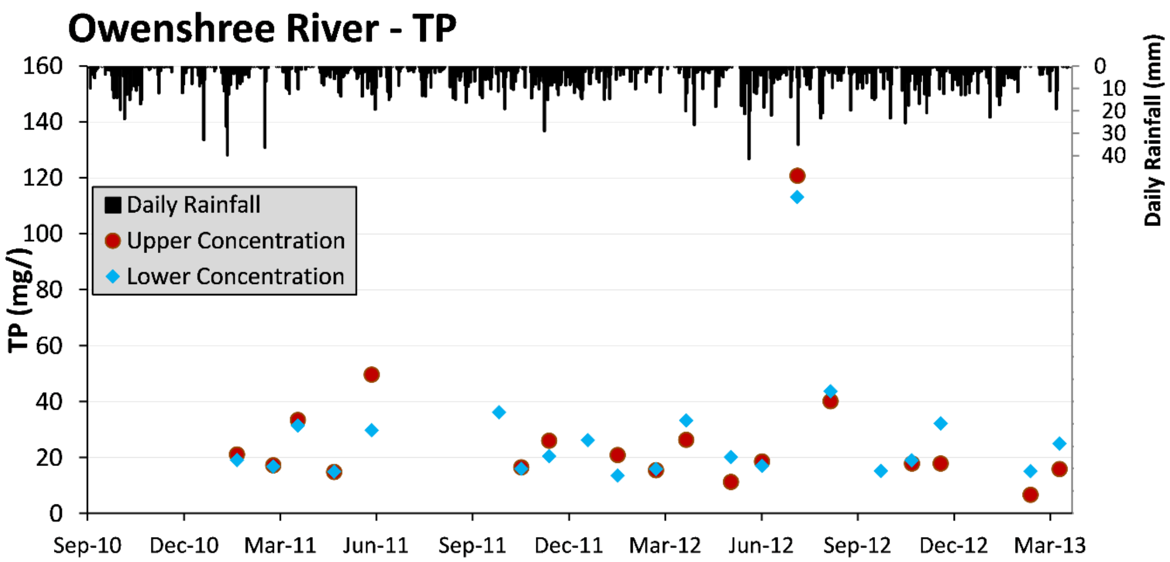

Figure 6: Daily Rainfall and TP concentrations at the upper (U) and lower (L) sampling locations on the SA1 River.

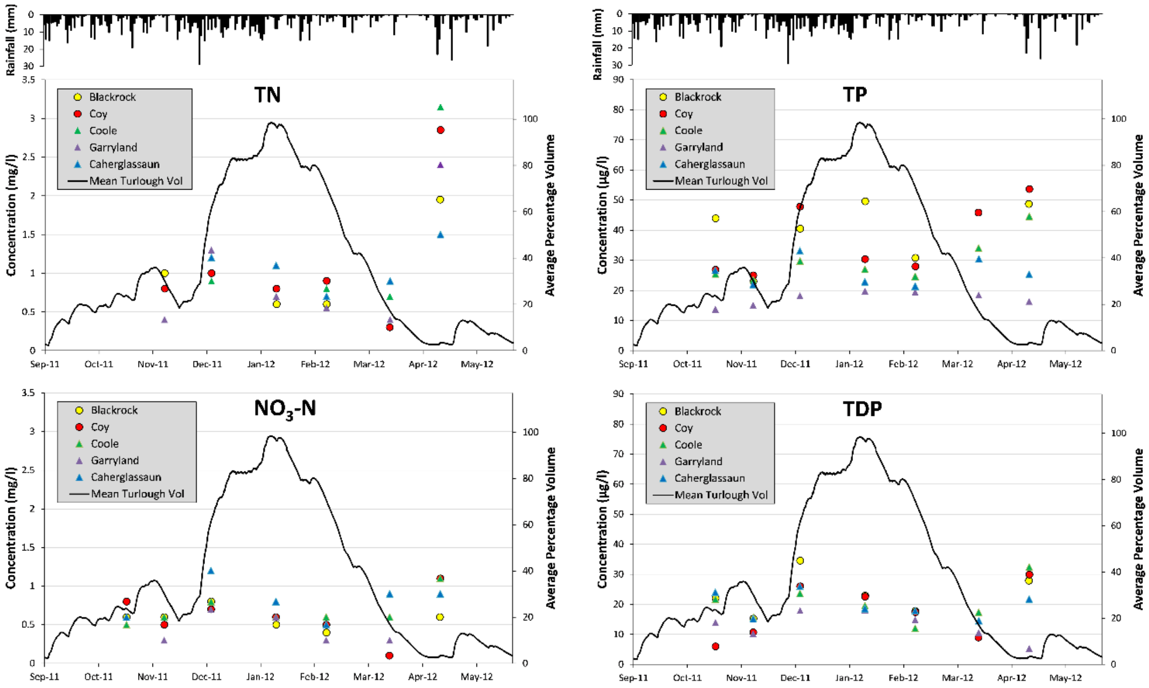

Figure 7: Concentrations of TN, NO_3-N, TP and TDP in Blackrock, Coy, Coole, Garryland and Caherglassaun Turloughs plotted together with average percentage volume of the five turloughs (i.e. volume as a percentage of the max volume over the period shown).

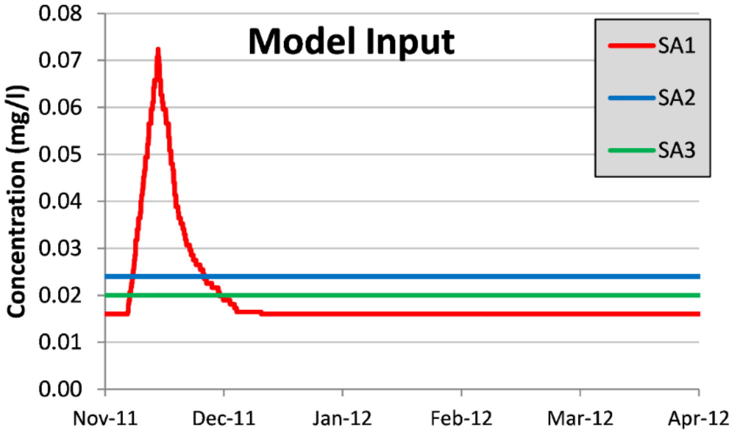

Figure 8: Model input signal to simulate a pulse of TDP occurring in SA1. SA2 and SA3 are inputted as constant signals based on mean observed TDP concentrations.

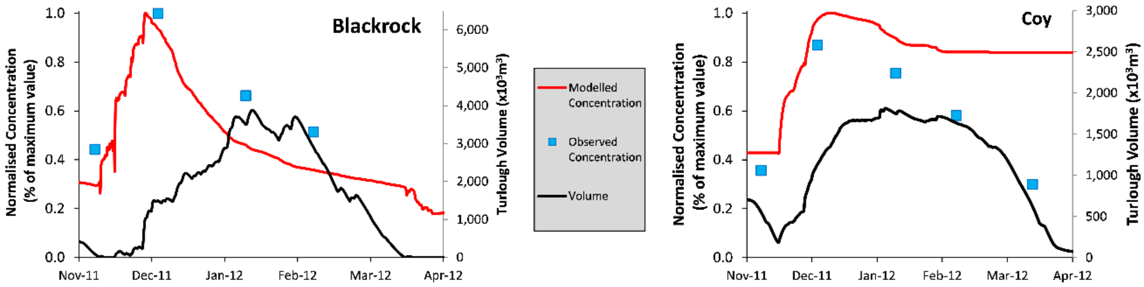

Figure 9: Observed (blue points) and simulated (red line) normalised results of a nutrient plume in a flow-through system (Blackrock) and a surcharge tank system (Coy)

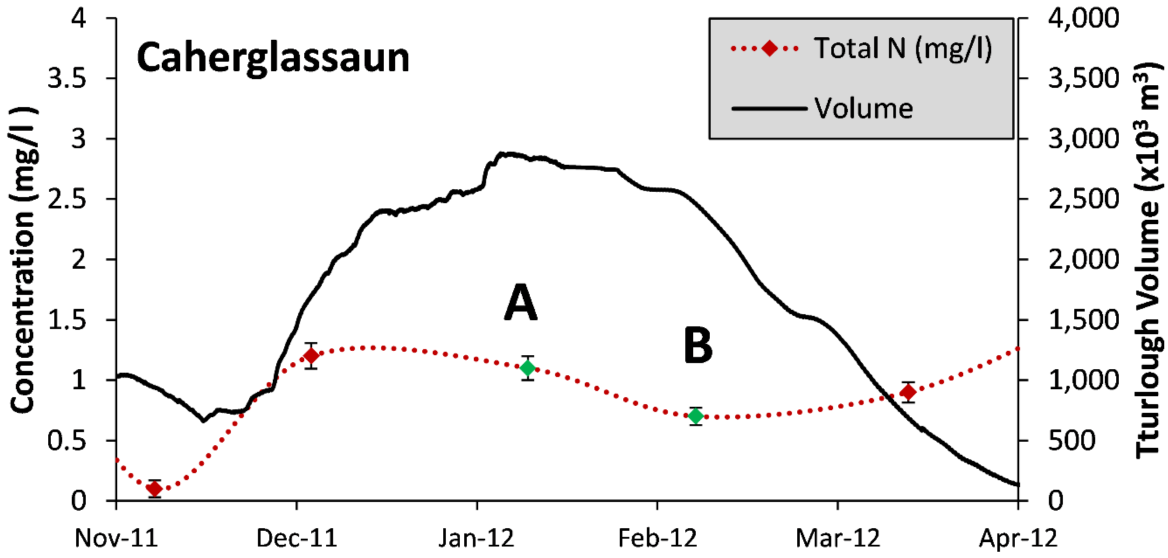

Figure 10: Denitrification example, Caherglassaun. Denitrification occurring between points A and B. Standard deviation of duplicate samples shown by error bars.