



**Quantifying the
nutrient flux within a
lowland karstic
catchment**

T. McCormack et al.

Quantifying the nutrient flux within a lowland karstic catchment

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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 nutrient flux occurring within the surface and groundwaters of a lowland karst catchment in western Ireland was investigated with the aid of alkalinity sampling and a hydrological model. Water samples were collected and tested from a variety of rivers, lakes (or turloughs), boreholes and springs at monthly intervals over a three year period. 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. Results indicated that at the system outlet to the sea, autogenic recharge had added approximately 35 % to the total flow and approximately 85 % to the total N-load. Within some turloughs, nutrient loads were found to reduce over the flooded period, even though the turloughs hydrological functioning (and the hydrological model) suggested this should not occur. As such, it was determined that nutrient loss processes were occurring within the system. Denitrification was deemed to be the main process reducing nitrogen concentrations within the turloughs whereas phosphorus loss is thought to occur mostly within the diffuse/epikarst zone.

1 Introduction

Global food production is predicted to increase by approximately 60 % by 2050 (Alexandros and Bruinsma, 2012), thereby increasing the contamination risks associated with agricultural runoff of raised nutrient concentrations in groundwater and surfacewaters. Nutrient contamination of groundwater has been reported across the world,

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 holes or estavelles, 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. Moreover, 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 risk failing to achieve the goals of the EU Water Framework Directive (2000/60/EC), whereby all water bodies should achieve at least “good” water status by 2015. As of 2012, approximately 30% of rivers, lakes, transitional and coastal waters within the Galway-Mayo region (the karstic region under study in this paper) have failed to meet this requirement (Environmental Protection Agency, 2012).

While a hydrochemical nature of permanent lakes in Ireland has been the subject of much research, relatively little work has been carried out into the nutrient flux within ephemeral lakes (turloughs) and their influence on their catchment (and vice versa). Hence, the objective of this research was to investigate the nutrient flux within a series

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of allogenicly fed turloughs (with the aid of alkalinity sampling and a hydraulic model) whilst also examining the nutrient flux within the overall catchment.

2 Area description and background

The Gort Lowlands is a 480 km² semi-karstic catchment located in Co. Galway in the west of Ireland. The eastern portion of the catchment is dominated by the Slieve Aughty Mountains and underlain by Devonian sandstone. The western portion of the catchment, however, 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.

The prevailing drainage direction in the catchment is east to west, with recharge from the non-carbonate Slieve Aughty Mountains flowing across the lowland karst towards a series of intertidal springs at Kinvara Bay. 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 Slieve Aughty Mountains and into the carboniferous lowlands: the Owenshree, the Ballycahalan and the Owendalulleagh (or Derrywee, which goes on to feed the Beagh River). These rivers supply chemically-aggressive acidic waters derived from the peaty non-carbonate catchments of the Slieve Aughty 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 ephemeral lakes known as turloughs.

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 estavella) in the springtime (Sheehy Skeffington et al.,

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to diffuse flow-through systems however water volumes tend to be larger with faster 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 Fig. 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.

The primary source of nutrients into the Gort Lowlands catchment is assumed to be agricultural. Nutrients enter the aquifer via allogenic point sources, such as the three rivers draining the Slieve Aughty Mountains, or by autogenic diffuse mechanisms within the lowlands. Each mechanism providing a hydrochemically distinct input. Allogenic recharge is characterised by relatively low alkalinity 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 intensity agriculture (mainly pasture for cattle) causes corresponding higher nutrient concentrations (particularly for N) within the diffuse groundwater.

The Gort Lowlands catchment has been hydrologically modelled successfully using Infoworks CS (Wallingford Software), 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, population, inflows etc. and represents the catchment as a complex network of pipes (conduits), tanks (turloughs) and subcatchments (diffuse/epikarst). The use of this model to predict turlough water levels and submarine groundwater discharge has been discussed previously by Gill et al. (2013) and McCormack et al. (2014). For this study, the model was adapted to simulate the movement of nutrients within the system.

3 Methodology

The overall strategy of this study was to characterise the nutrient behaviours of water as it moves across the catchment with particular emphasis on the sensitive turlough ecosystems. In addition, alkalinity sampling was carried out in an effort to understand the movement and source of water. The hydraulic model was used to predict how nutrients should behave conservatively in turloughs and then compared to the actual nutrient concentration results within the turloughs from the field-work sampling.

3.1 Hydrometry

Water levels in all turloughs 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.) were installed at the upper end of the catchment at Kilchreest, 70 m above ordinance datum (mAOD), and Francis Gap (250 mAOD). In addition, hourly rainfall and evapotranspiration data was received from synoptic weather stations run by the national weather service, Met Éireann.

River gauging stations were located on the three primary rivers draining off the Slieve Aughty Mountains, the Owenshree, Ballycahalan and Owendalulleagh, with an additional station located on the Beagh River 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 min timesteps. Rating curves were developed for each gauging station (see Fig. 3) using the mid-section velocity depth surveying method.

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 (NO_3), 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. 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 a turlough's alkalinity is its 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, the Owenshree River (ORL), which had a mean alkalinity of 148.1 mg L^{-1} CaCO_3 .

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



The alkalinities of Coole, Garryland and Caherglassaun turloughs were slightly lower (114.4, 134.6 and 121.3 mg L⁻¹ CaCO₃) reflecting the lower concentration contributions of the Ballycahalan (68.2 mg L⁻¹ CaCO₃) and Owendalulleegh (38.8 mg L⁻¹ CaCO₃) 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 CaCO₃). 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 catchment to the south of the Gort Lowlands (see Fig. 1) resulting in higher concentrations, most significantly at Garryland turlough (similar to the findings of the Gort Flood Studies, Southern Water Global, 1998). Secondly, as the Ballycahalan (BRL) and Owendalulleegh (DRL) Rivers enter the limestone system under-saturated in dissolved CaCO₃ 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.

By comparing the hydrochemical behaviours of the turloughs to that of the rivers feeding them, an insight into their varying hydrological functioning can be gained. Coy, Garryland and Caherglassaun operate as surcharge tank turloughs fed via a single estavelle (with a degree of isolation from the main karst flows through the system). 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 Fig. 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 as shown in Fig. 4. 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 CaCO₃ 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 CaCO₃ from turloughs have been attributed to the influx of water (saturated with CO₂) which comes into contact with the air and gradually loses its CO₂ 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 mgL⁻¹ CaCO₃ but overall was found to be quite consistent (standard deviation of below 40 mgL⁻¹ for most boreholes) with a mean value of 365.1 mgL⁻¹ CaCO₃. 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.

4.2 Nutrients

The results of the nitrate (NO₃), total nitrogen, (TN), total dissolved phosphorus (TDP) and total phosphorus (TP) sample analysis are shown in Table 1. Nitrite (NO₂) and ammonium (NH₄) were also tested for at times but were often near-to or below detection limits and as such, their measurement was ceased.

4.2.1 Surface-water: rivers

Values for N in all rivers ranged between 0 and 3.9 mgL⁻¹ with a mean of 1.01 mgL⁻¹, whilst P concentrations ranged between 0 and 120.8 µgL⁻¹ with a mean value of

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



26 μgL^{-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 (similar to the findings of Drew and Daly, 1993) 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 mgL^{-1} whereas for TP, the rivers showed a wide range of mean values between 11.2 and 32.3 μgL^{-1} (Table 1).

The lack of variation between all sampling locations for N, and the lack of variation between upper and lower river sampling locations for both N and P indicates that there is a minor but constant addition of nutrients to the rivers as they travel down through their catchments. This might suggest that overall agriculture and forestry practices on the Slieve Aughty Mountains catchment add very little nutrients into the rivers or that the net attenuation processes leave only low levels of nutrients in the surface water. Figures 5 and 6 show examples of nutrient variation for the Owenshree River (upper and lower sampling locations). The peak in P in July 2012 (Fig. 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 calculated by combining the measured nutrient concentration data with the observed flow data. TN loading for the Owenshree, Ballycahalan, Owendalulleagh and Beagh rivers was found to be 118, 122 and, 281, 348 kg day^{-1} respectively while TP loading was found to be 3.1, 3.5, 7.9 and 9.8 kg day^{-1} respectively.

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.2.2 Surface-water: turloughs

Mean TN and TP concentrations for the turloughs were 1.12 and 33.7 $\mu\text{g L}^{-1}$ with highest concentrations recorded of 4.3 mg L^{-1} TN and 115 $\mu\text{g L}^{-1}$ TP. It should be noted that the mean TP concentration lies just below 35 $\mu\text{g L}^{-1}$, the OECD threshold for TP in eutrophic lakes (OECD, 1982). Generally, the upper two turloughs (Blackrock and Coy) showed higher nutrient concentrations than the lower three turloughs. The upper turloughs also showed mean concentrations greater than those of the Owenshree River feeding them (except NO_3 in Coy) which suggest that the turloughs act as sources rather than sinks of nutrients. This increase in mean nutrient concentration is particularly evident for TP with Blackrock and Coy turloughs displaying mean TP concentrations exceeding those found in the Owenshree River by 75 and 65 % respectively which can be attributed to three main factors. Firstly, both turloughs are actively grazed during the summer months. This would lead to increased nutrient concentrations at the onset of flooding due to the release of soluble P from manure deposition. Secondly, nutrient concentrations within Blackrock are likely being enhanced by the presence of an abattoir on its south eastern edge. Thirdly, the elevated nutrient concentrations (particularly N) could indicate additional flows coming in from the nutrient enriched diffuse sources (groundwater N concentrations found to be double surface water N concentrations). 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.

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 Owendalulleagh (DRL). Nutrient concentrations in Caherglassaun

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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.

Nutrient loads in the turloughs were calculated by combining the turlough volume data with the nutrient concentration data, as shown across the 2011/2012 season in Fig. 7. The general variability of nutrients within the turloughs is evident, although, in a number of cases, a pattern can be seen whereby the nutrient load within the turlough starts to drop before the turlough water level begins to drop. This pattern might be expected in flow-through turloughs but the pattern is also seen in Coy (for P), Garryland (N) and Caherglassaun (N) turloughs which are known to operate as surcharge tanks. The comparison between the expected behaviour and the observed behaviour is discussed further in Sect. 4.3.1.

4.2.3 Groundwater

The results obtained from boreholes within the Gort Lowlands N showed a wide range of recorded results for N ($0.2\text{--}10.4\text{ mgL}^{-1}$ TN), although the mean concentrations at each borehole across the catchment are within a similar range (between 1.2 and 3.3 mgL^{-1}). P showed a greater range of measured results ($0\text{--}582\text{ }\mu\text{gL}^{-1}$ TP) but more significantly, the mean concentrations at each borehole showed large differences (between 5.1 and $72\text{ }\mu\text{gL}^{-1}$ TP). These results indicate that N was able to reach the groundwater relatively easily and due to its mobility, more or less equalised across the catchment. P, on the other hand, being much less mobile, would only enter the groundwater in areas of extreme vulnerability (i.e. through shallow and/or permeable subsoils); however, once in the conduit system, P is known to be transported conservatively with negligible attenuation (Mellander et al., 2013; Kilroy and Coxon, 2005).

Mean groundwater concentrations across the catchment were recorded as 2.30 mgL^{-1} and $31.28\text{ }\mu\text{gL}^{-1}$ 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.

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.2.4 Kinvara Springs

The TN concentration for Kinvara West (KW) is measured as 1.05 mgL^{-1} compared to the mean TN at Kinvara East (KE) of 1.99 mgL^{-1} . The N concentrations at KW reflected the mean concentrations of the turloughs (1.12 mgL^{-1} TN) while the higher mean concentration of KE indicated the greater proportion of diffuse flow (with its higher TN) emerging at this spring. Little difference was observed for P between KW and KE with concentrations of 22.9 and $24.2 \text{ } \mu\text{gL}^{-1}$ respectively (TP). P concentrations at the springs were among the lowest mean concentrations found within the catchment 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 (see Fig. 10) were calculated by combining the mean daily outflow from KW (using the results from the hydraulic model simulations which also account for temporal tidal effects) with the appropriate nutrient concentration data. The average daily TN load was calculated as 914 kg day^{-1} with a measured range of $250\text{--}2150 \text{ kg day}^{-1}$. The average daily TP load was 20 kg day^{-1} with a measured range of $9.1\text{--}28.4 \text{ kg day}^{-1}$.

4.3 Nutrient modelling

The hydraulic model was used to simulate a mass balance of the nutrients 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. The contribution of nutrients from the diffuse portion of the catchment was also estimated by combining groundwater nutrient concentrations with diffuse discharge as estimated by the model using subcatchments.

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.3.1 Nutrient retention

In many catchment types, conservative-only limitation of the modelling software would serve as a drawback to pollutant modelling. However 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. Figures 9 and 10 show examples from simulations predicting how nutrients/contaminants would behave after entering river flow-through and a surcharge tank turloughs. In these simulations, a nutrient plume was injected into the Owenshree River at the onset of flooding. Blackrock turlough (Fig. 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 indicates a constant flux of water through the turlough whether it is flooding or emptying. Due to this peak-recession pattern, the nutrient mass within the turlough (Fig. 9b) can be seen to drop slightly before the water volume does. The simulated response of Coy, the surcharge tank type turlough, in Fig. 10 however, is distinctly different to that of Blackrock. Once the contaminant has entered the water body, the concentration remains relatively constant (the slight recession of concentration seen in Fig. 10a is due to the presence of a second swallow hole which only influences the turlough at a depth above 10 m).

While these simulations are based on a hypothetical nutrient plume and cannot be compared directly to the observed behaviour within the turloughs, they offer a useful conceptual distinction between how flow-through and surcharge tank turloughs should behave. Looking at the observed results in Fig. 7, the flow-through/surcharge tank patterns are not as prevalent as might be anticipated. However, in a number of cases, the pattern expected of flow-through turloughs was found to occur with reductions in the nutrient mass commencing before the water volume starts to recede. Hence, this

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



suggests that some non-conservative nutrient removal/transformation processes must be occurring within these turloughs.

4.3.2 Diffuse Contribution

The hydraulic model calculates conduit flow using a series of interconnected pipes and calculates diffuse type flow (which subsequently feeds conduit flow) using a network of subcatchments which are linked to the conduit network via permeable pipes (Gill et al., 2013). As such, it is possible to separate the contribution of autogenic conduit flow from allogenic diffuse flow at each turlough. For a particular turlough, its diffuse contribution was calculated by comparing the flow (and nutrient content) of its main feeding conduit with the contribution from all subcatchments upstream of that turlough. Overall, the contribution of modelled diffuse flow to the turloughs was found to add approximately 35% to the conduit flow. By combining mean groundwater concentrations with the estimated diffuse flow from each subcatchment it was possible to determine a mean loading rate for each subcatchment. Overall, the diffuse influx was found to add approximately 60% of additional N load to the turloughs, rising to approximately 85% at Kinvara. For P, the influx was lower, adding approximately 30–40% (although results for P are less reliable due to its heterogeneity within the groundwater).

5 Discussion

5.1 Hydrochemical/nutrient behaviour across the catchment

The majority of water feeding the karst network originates from precipitation falling on the Slieve Aughty Mountains. As this water runs off the mountains via the three main rivers down towards the lowlands, it starts to pick up alkalinity through dissolution but experiences relatively little nutrient enhancement. This lack of nutrient enhancement indicates only minor input from agricultural/forestry practices in the Slieve Aughty Mountains.

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In the lowlands, the groundwater of the non-active diffuse portions of the limestone bedrock inevitably showed high levels of alkalinity with an average concentration of $365.1 \text{ mgL}^{-1} \text{ CaCO}_3$. The primary land use in these lowlands is agriculture and as such, there are significant additional sources of N and P which is reflected by the N concentration of groundwater having a mean value (2.3 mgL^{-1}) of double that found in the active conduit/turlough network (1.12 mgL^{-1}). N was also well distributed across the catchment due to the high mobility and solubility of NO_3 . Although the sources of P would be equally as widespread, its ability to reach the groundwater is highly variable due to its poor mobility. As a result, concentrations of P in groundwater were highly erratic across the catchment. Water quality modelling estimated that the diffuse contribution of nutrient loads in the turloughs was approximately 60 % for N and 30–40 % for P.

In the conduit/turlough network, the water at the top of the system in Blackrock turlough had an alkalinity that matched its feeding river but the measured nutrient concentrations in the turlough exceeded those measured in the river, particularly for P. This suggests an internal source of nutrients such as from grazing animals or the nearby abattoir and that the turlough acts a source of nutrients to the downstream karst system. As the water moves through the karst network from Blackrock through Coole towards Kinvara, the nutrients should be transported fairly conservatively in the turbulent flow conditions of the active conduits. N appeared to retain its concentration throughout while concentrations of P seem to drop en-route.

At Coole, the alkalinity and nutrient concentrations of the water reflected that of the combined flow from the three main rivers (with alkalinity suggesting some contribution from diffuse sources). Although Garryland turlough lies beside Coole and is known to be intimately hydraulically connected (particularly at high water levels), it shows evidence of influx from the Cloonteen catchment to the south. The influx of this high alkalinity, low nutrient water results in Garryland having the lowest nutrient concentrations of the five turloughs. Caherglassaun turlough however displayed nutrient concentrations very similar to Coole indicating the presence of a direct linkage, as opposed to

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Garryland which lies slightly off the main conduit line. As water moves onwards from Caherglassaun towards the Kinvara West Spring at the coast, nutrient concentrations dropped slightly (5 % drop in TN, 13 % drop in TP). This reduced concentration is likely due to the contribution of water from separate systems regions such as the Burren or the Cloonteen which tracing studies have proven to join the main conduit system at some point between Caherglassaun and Kinvara (Southern Water Global, 1998).

An alternative method of analysing nutrient dynamics throughout the catchment is to consider the changes between input (rivers) and output (KW) nutrient loads. The mean daily TN load entering the system through the rivers is approximately 590 kg day^{-1} while the mean daily load exiting the system is estimated as 800 kg day^{-1} , as calculated with the aid of the hydraulic model. This indicates that even though the concentrations remain similar, there is a net gain of TN as water moves through the system. This net gain of N at Kinvara amounts to a 36 % increase from that of the rivers. Considering that the overall diffuse input of N at Kinvara was estimated at approximately 85 % (Sect. 4.3.2), this suggests that the contribution of high-N diffuse water to the system is offset by losses, most likely within the turloughs (discussed in Sect. 5.2.2).

Unlike TN, TP shows only a slight reduction in daily loading rate between the rivers (16.5 kg day^{-1}) and Kinvara (17.6 kg day^{-1}) which indicates very little net gain of P as water moves through the system. Again, the model indicates a much greater increase in loading (approximately 30–40 %, Sect. 4.3.2) which suggests some losses of P within the karst system.

5.2 Hydrochemical/nutrient behaviour within turloughs

Hydrologically, turloughs sit within a spectrum of different types ranging from diffuse flow-through dominated to conduit dominated, although the majority of turloughs in Ireland have little or no allogenic recharge but are fed by local diffuse catchments and so fall into the diffuse flow-through category. The turloughs of the Gort Lowlands, however, predominantly fall under the conduit dominated category. These turloughs are known to operate as river flow-through systems (Blackrock and Coole), or surcharge systems

(Coy, Garryland and Caherglassaun), all of which are heavily controlled by conduit type hydraulics. Conceptually, 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).

5.2.1 Alkalinity

In terms of alkalinity, the turloughs behaved somewhat as would be expected from the conceptual model. 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 (as would be expected of a surcharge tank). The most noticeable trend, particularly for the surcharge tank turloughs, was the increase in alkalinity across the flooding season. As mentioned in Sect. 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.

5.2.2 Nitrogen

The typical pattern of N in turloughs is peak concentrations occurring in mid-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 was seen for the most part. Interestingly however, the

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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). In the turloughs under study (and most turloughs in general), 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 ($> 10 \text{ mg L}^{-1}$) (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 $57 \text{ mg N m}^{-2} \text{ day}^{-1}$. Looking at the example of Caherglassaun over the 2011–2012 flooding season, that would suggest a removal of 755–1266 kg N via denitrification

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



between sampling points A and B (one month apart) highlighted in Fig. 11. The actual amount of N removed can be calculated as follows:

- N load at point A is 3121 kg ($1.1 \text{ mg L}^{-1} \times 2837295 \text{ m}^3$). 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 2463.7 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). As such, it can be suggested that denitrification is a plausible cause of N removal from the turloughs during flooded periods.

Daily N loading from the rivers has been calculated as $590 \text{ kg N day}^{-1}$. Thus, the monthly N loading was approximately 17700 kg N, compared to the monthly N loss from Caherglassaun of 986 kg N. These values suggest that, during flooded periods, 4.8% of the N brought into the catchment from the rivers can be lost from Caherglassaun turlough alone. As such, the turloughs can be considered as considerable 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.

5.2.3 Phosphorus

The major source of P to the turloughs is via river inputs. For the lower three turloughs, 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 (Owenshree River) 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). The cause of this elevated P is likely due to the presence of an abattoir located

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

next to Blackrock or due to grazing during dry periods on both turloughs. Indeed grazing has been shown to have a positive correlation with P concentrations in turlough soil (Kimberley et al., 2012) which suggests that at the beginning of a flooded period the turloughs experience a burst in soluble forms of P which can be released upon inundation. In terms of temporal variation, the turloughs appear less influenced by loss mechanisms for P than for N (Fig. 7), although Coy turlough did display some P losses over the flooded period. 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. In turloughs however, the relatively short residence times probably limit the impact of sedimentation. Also, the occurrence of “internal loading” (whereby P is adsorbed onto sediment during eutrophic periods only to be re-released back into the water column later on when concentrations are reduced) might hinder any reduction in P concentrations over the flooded period.

Finally, in carbonate aquifers, P is known to be lost from water due to the formation of calcium phosphate compounds (von Wandruszka, 2006; Cable et al., 2002). This process is unlikely to affect water within the turloughs, although it could be an active process within the diffuse portion of the catchment. As such, this process may limit that amount of P entering the conduit system from the diffuse portion of the catchment (i.e. the model subcatchments), which could explain the apparent loss of P by the time the water reaches the main outfall spring at Kinvara (Sect. 5.1) while very little loss of P was evidenced within the turloughs (i.e. P loss from autogenic recharge occurs within the groundwater before it reaches the turloughs).

6 Conclusions

The alkalinity and 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 the alkalinity results. The allogenic-ly 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 somewhat as would be expected, the surcharge tank turloughs showed evidence of N losses (i.e. non-conservative behaviour) occurring over the course of the flooded season, which was attributed to be most likely due to the process of denitrification. As a result of the loss of N within the turloughs, the gain in nutrient loading observed at Kinvara West (due to the influx of N-rich diffuse groundwater) was found to be lower than expected (an increase of 36 % rather than 85 % as predicted by the model). For P, net losses were also evident at Kinvara, but not as obvious within the turloughs, suggesting perhaps that the main P sink within the catchment is the carbonate aquifer itself – due to the formation of calcium phosphate compounds.

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



As the eventual outfall of the Gort Lowlands network, Kinvara/Galway Bay, is a protected area under the EU Habitats Directive, and many of the turloughs which occupy the catchment are protected under both the EU Habitats and Water Framework Directives (as GWDTes), their conservation status is of great significance. As such, nutrient flux within these systems is an important process to understand and quantify. The process is especially important in the context of the likely future pressures which the catchment faces. Food Harvest 2020 is 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 will encourage nutrients to bypass the protective soil cover and enter the karst aquifer via point source features.

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Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Petry, J., Soulsby, C., Malcolm, I. A., and Youngson, A. F.: Hydrological controls on nutrient concentrations and fluxes in agricultural catchments, *Sci. Total Environ.*, 294, 95–110, doi:10.1016/S0048-9697(02)00058-X, 2002.

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HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

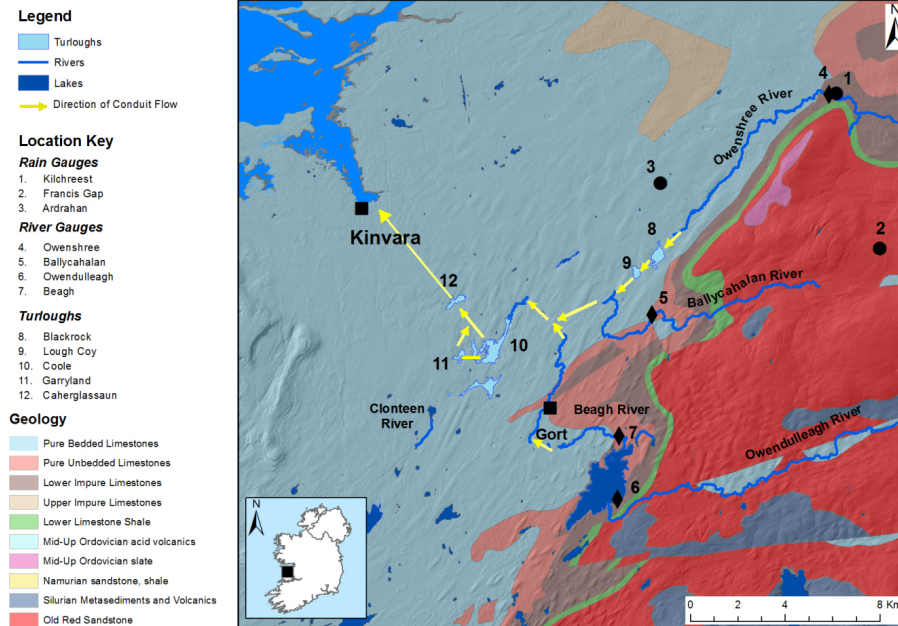


Figure 1. Geology of study area displaying turloughs, raingauges, Kinvara, river gauging stations and the direction of underground conduit flow.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

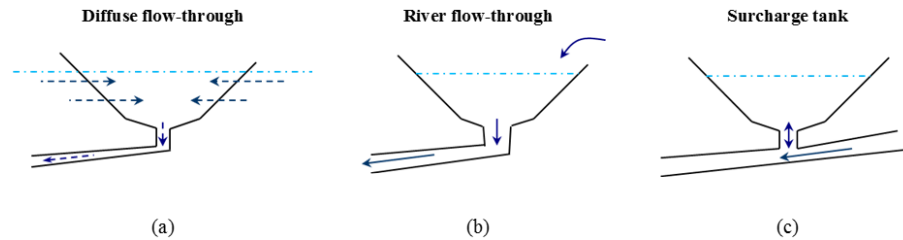


Figure 2. Conceptualisation of diffuse flow-through, river flow-through and surcharge tank tur-lough systems (modified from Gill et al., 2013).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

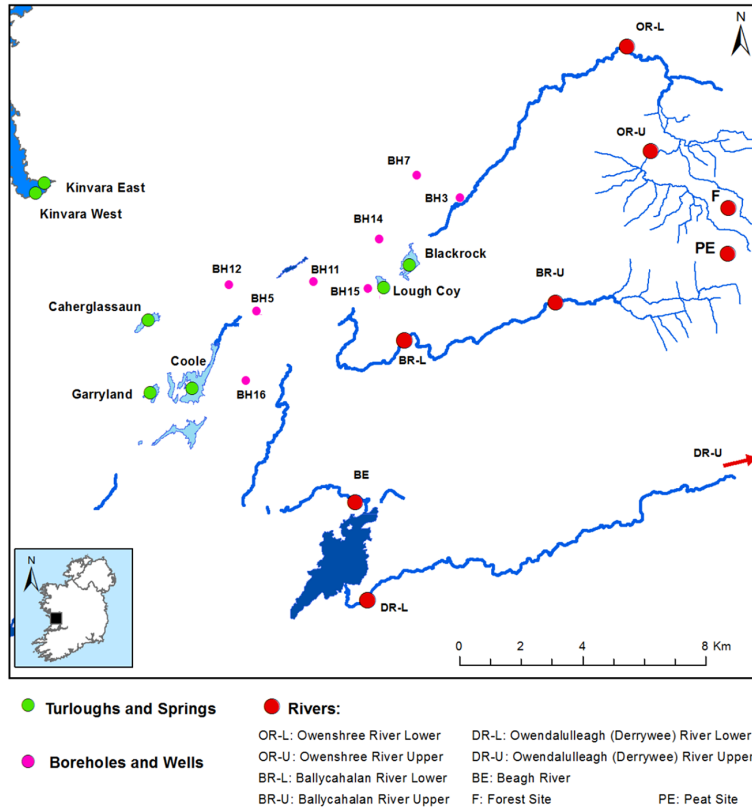


Figure 3. Sampling locations of turloughs, rivers and boreholes.

[Title Page](#)

[Abstract](#) | [Introduction](#)

[Conclusions](#) | [References](#)

[Tables](#) | [Figures](#)

[◀](#) | [▶](#)

[◀](#) | [▶](#)

[Back](#) | [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



HESSD

12, 93–134, 2015

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

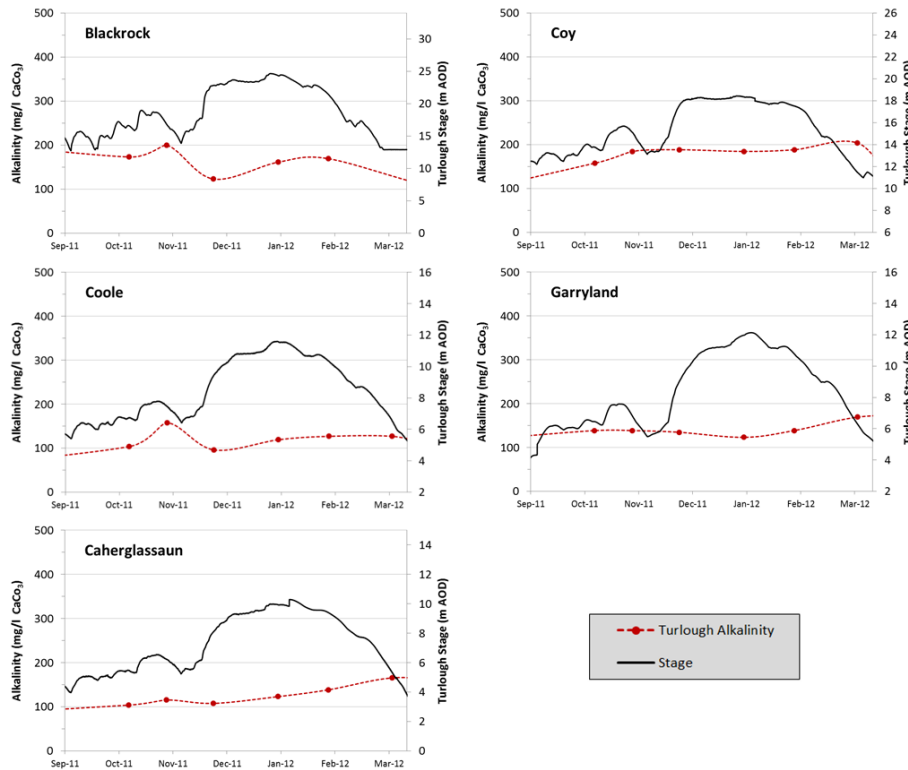


Figure 4. Turlough stage and alkalinity results for Blackrock, Coy, Coole, Garryland and Caherglassaun turloughs over the 2012/2013 flooding season.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

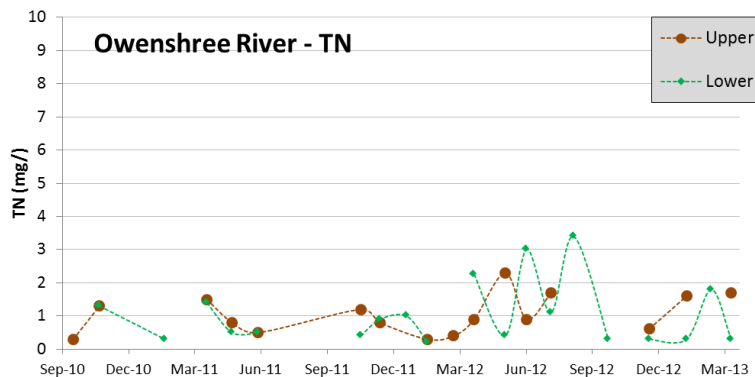


Figure 5. TN concentrations at the upper and lower sampling locations on the Owenshree River.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

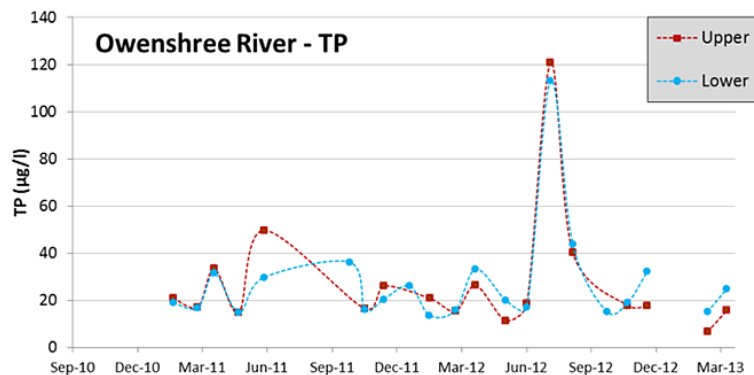


Figure 6. TP concentrations at the upper and lower sampling locations on the Owenshree River.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

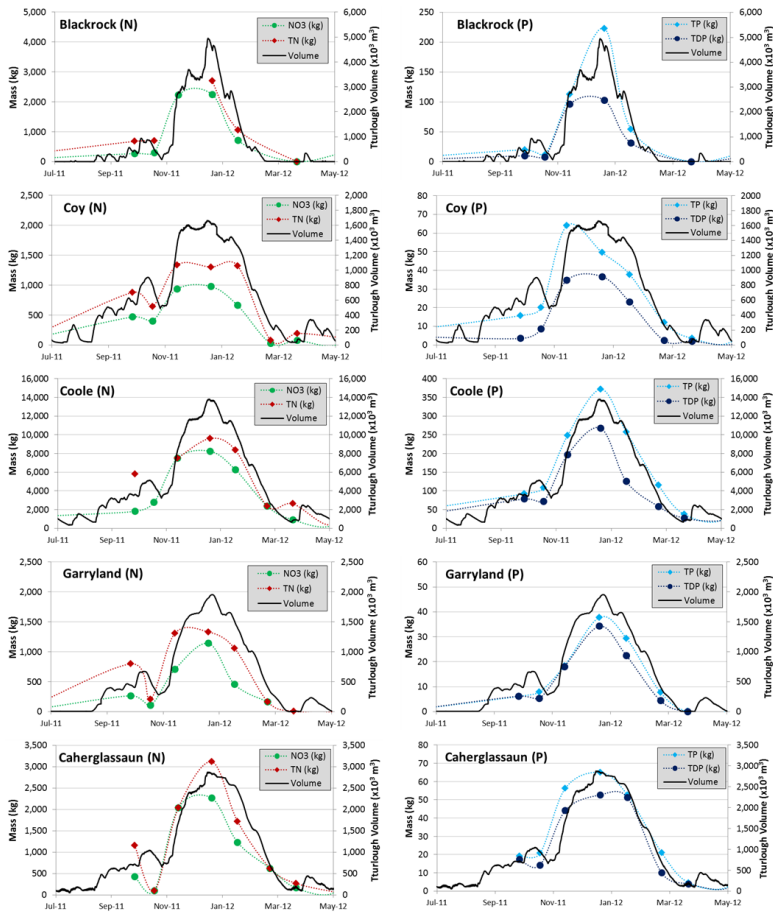


Figure 7. Time-series plots of Total Nitrogen (TN), Nitrate (NO_3), Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP) loads for Blackrock, Coy, Coole, Garryland and Caherglassaun turloughs.

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

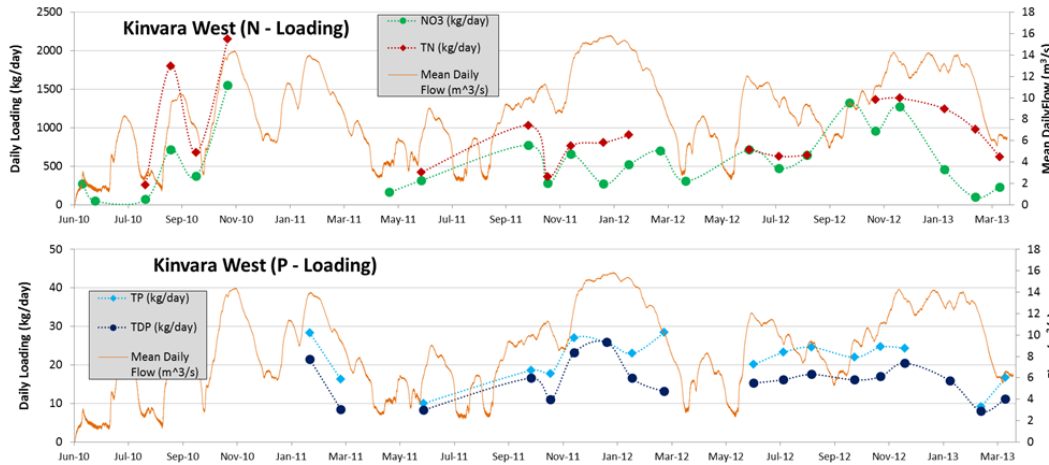


Figure 8. Daily Nutrient Loads exiting the system at KW (based on modelled outflow).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

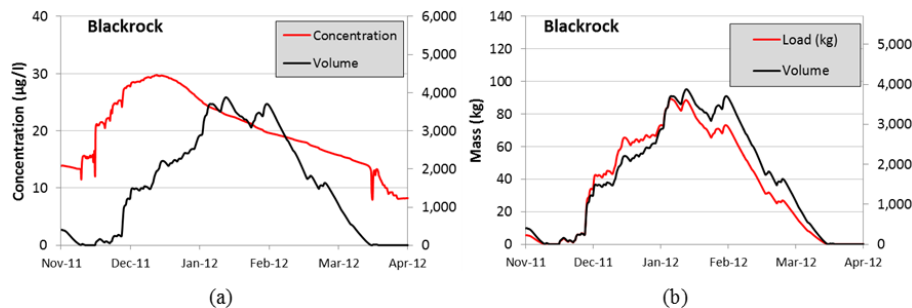


Figure 9. Simulation plots of a nutrient plume in a flow-through system (Blakcrook). Subplot (a) – Concentration, Subplot (b) – Load.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

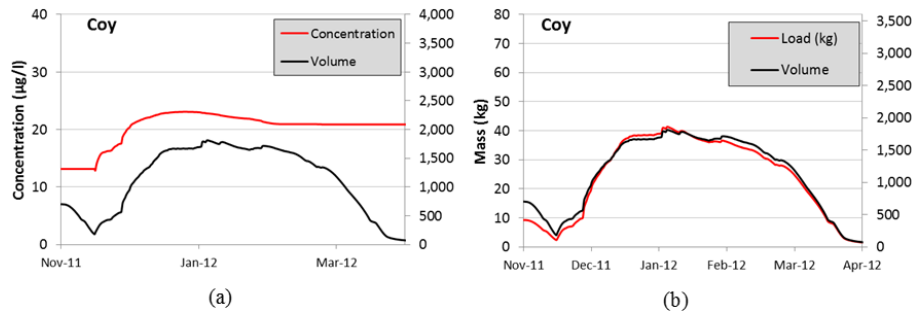


Figure 10. Simulation plots of a nutrient plume in a surcharge tank system (Coy). Subplot (a) – Concentration, Subplot (b) – Load.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Quantifying the nutrient flux within a lowland karstic catchment

T. McCormack et al.

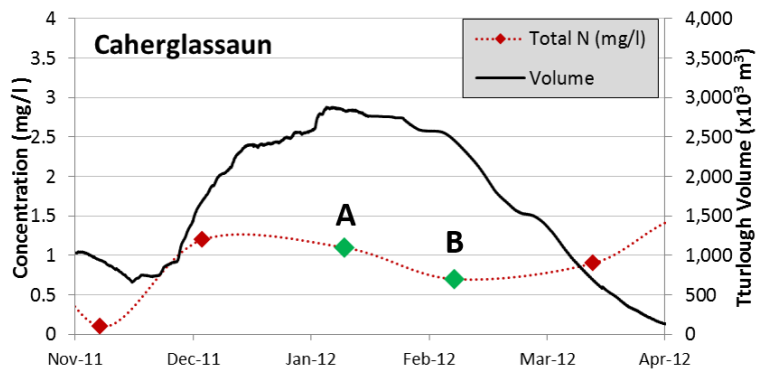


Figure 11. Denitrification example, Caherglassaun. Denitrification occurring between points A and B.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)