



Investigating “net” provenance, N source, transformation and fate within hydrologically isolated grassland plots

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ABSTRACT

Agricultural landscapes contain many different soil types with heterogeneous nitrogen (N) attenuation capacity. Typically, a zone of contribution (ZOC) surrounding a borehole is used to interpret subsurface hydro-biogeochemical functional capacity. This presents a “net” interpretation of source and attenuation within these calculated areas. Herein, we use the concept of ZOC commonly used for borehole screen intervals but for an end-of-pipe location within four hydrologically isolated plots. Water samples from end-of-pipe and piezometer locations are examined for nitrogen (N), biogeochemical, dissolved gas and isotopic viewpoints to elucidate multi-layered “net” water provenance, N source, transformations and fate. Results showed a nitrate (NO_3^- -N) plume migrating in shallow groundwater (between 0.39 and 8.07 mg N/L), with low concentrations in the shallow artificial drainage system (below 3.22 mg N/L). Water provenance data showed distinct signatures of: precipitation and deep groundwater at 3–4 m below ground level (bgl) and water entering, migrating and discharging at the end of pipe location. The latter signature was caused by enrichment of $\delta^{18}\text{O}$ - H_2O during migration. This means there was disconnectivity on site with no interaction between water migrating through the drainage pipe at 1 m and deeper groundwater migrating at 3–4 m depth. The analysis of NO_3^- -N concentration and its isotopic signature ($\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^-) identified further connections between screen interval depths and an up-gradient organic point source with elevated NO_3^- -N migrating at this depth and different transformation processes occurring at different depths. Temporally NO_3^- -N concentrations at this depth have decreased over time. Fenton et al. documented an average of 7.5 (± 4.5) mg N/L whereas Ibrahim et al. documented an average of 6.8 (± 3.7) mg N/L at this depth. The point source was removed in 2006 and NO_3^- -N concentration in the present study have further reduced to an average of 3.9 (± 2.8) mg N/L. End-of-pipe data at 1 m bgl highlighted connectivity with the overlying plot and showed different water attenuation functionality than the deeper system. End-of-pipe locations clustered together along the denitrification line. This highlighted a consistency of signals across the four plots in terms of what occurs in the soil profile above the drain installation depth of 1 m. At 3–4 m bgl however, samples varied spatially showing inconsistency between the end-of-pipe locations and plots indicating the occurrence of different processes.

A fuller characterisation of dairy farm N sustainability can be deemed using the “net” provenance, N source, N transformation and fate methodology presented. Future work should investigate how drainage design (shallow and groundwater) affects N transformation and the “net” concept developed herein should be rolled out to rank dairy farms in terms of their N attenuation capacity.

1. Introduction

Agricultural landscapes contain many different soil types with varied drainage classes. This spatial arrangement of soils presents a soil-scape of varying soil functional capacity. All soils perform a set of

functions (i.e. water purification, carbon sequestration, nutrient cycling, food production, fibre and fuel, habitat for biodiversity). However, they differ in terms of rate (Schulte et al., 2014). One such function is water attenuation, the ability to naturally reduce water contamination, which in terms of N changes across drainage classes

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(Coyle et al., 2016). Poorly drained soils present highest capacity while free draining soils present the lowest capacity. Nitrate lost from agricultural systems migrates and transforms along many different subsurface pathways. Once NO_3^- -N leaches to a drainage system it migrates laterally and the transformation potential becomes reduced. This pathway has been well characterised in terms of NO_3^- -N concentration and flow, which of course enables flux calculations (Skaggs et al., 1994; Kladienko et al., 2004; Tiemeyer et al., 2008; Zhao et al., 2016). Attenuation over time using flux is a tool used to infer natural attenuation (Fenton et al., 2009) but gives no insights into water origin, source of N or indeed what transformation processes are involved. Others have investigated different aspects such as spatial and temporal changes in N speciation (Ibrahim et al., 2013) and indirect emissions (Weymann et al., 2008).

On pasture, artificial drainage systems are installed in imperfect or poorly drained plots, potentially altering the inherent natural attenuation or water purification function in the immediate area of the drain installation (around the pipe, mole, gravel mole, gravel pack) thereby altering transformations within the ZOC drained by this system. As used within flux calculations a single sampling point, i.e. an end-of-pipe (EOP) location, can be therefore used to examine the functional capacity of this larger area. This concept has been already explored in groundwater systems using boreholes and associated ZOCs. Typically, subsurface hydro-biogeochemical functional areas (Gonzalez-Inca et al., 2015) are difficult to delineate, with studies such as Jahangir et al. (2012a, 2012b) or Rivas et al. (2017) relying on borehole networks to identify various factors that can be used to characterise the transformational potential of these subsurface environments. For example, Fenton et al. (2009) used similar techniques (boreholes and associated ZOCs) and identified a strong correlation between NO_3^- -N concentration in shallow groundwater, distance from a known point source and subsoil saturated hydraulic conductivity (k_s). This allows prediction of natural attenuation areas but gives no further insights into origin, N source or attenuation.

An artificial drainage system, if characterised correctly in terms of position, depth of installation and lateral extent and connectivity with a set of multi-techniques (physiochemical, dissolved gases and isotopic analyses), could provide such insights and give more characterisation power above that of flux alone. Kellman (2005) investigated EOP water samples under controlled conditions to investigate $\delta^{15}\text{N}$ - NO_3^- signature differences between inorganic and organic inputs. Whereas the signature data was distinct to a particular known source it was demonstrated that isotopic fractionation did not alter source signatures. On another isolated site (the same as the present study), Ibrahim et al. (2013) investigated N speciation in runoff, artificial land drainage installed at 1 m depth and shallow groundwater at 3–4 m depth. Tracing N losses across rainfall events that study showed that N losses were higher in runoff and groundwater with lowest losses discharging from the subsurface drains. This pointed to a multi-layered system in terms of source connectivity and the present study investigates this further. Dissolved organic nitrogen (DON) dominated losses but dissolved inorganic N was more abundant in subsurface drains. Both studies did not characterise the provenance/origin of the water within the system or the transformational processes that resulted in particularly high or low N concentrations.

Natural isotopic techniques (δD - H_2O , $\delta^{18}\text{O}$ - H_2O , $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^-) can be used for the identification of water provenance, processes such as nitrification and denitrification and sources. This procedure can be carried out at a single moment, whereas N concentrations need to be taken over time. When combined with other methods these natural isotopic techniques, e.g. dissolved gas in water samples and biogeochemical parameters, could give greater insight into N source and transformational processes at a given site (Baily et al., 2011; Jahangir et al., 2012a; Pastén-Zapata et al., 2014; Wells et al., 2016). To our knowledge, the use of a combination of multiple techniques, e.g. physiochemical, dissolved gases and isotopic analyses, has

never been attempted under hydrologically isolated field conditions. Such controlled conditions enable a more defined interpretation of results and therefore present an opportunity to examine a) single EOP water samples as “net” provenance, source and transformation indicators for a large ZOC and b) single shallow groundwater samples from screen intervals as “net” provenance, source and transformation indicators for an associated ZOC Knowledge pertaining to on site, EOP and shallow groundwater NO_3^- -N flux has already been established in various publication (Fenton et al., 2009; Ibrahim et al., 2013). Therefore, the objectives of the present study using historic and additional fieldwork were to utilise EOP and piezometer “Net” approaches across four isolated grassland plots in the South East of Ireland to 1) characterise N migration through the multi-layered site using dissolved gases, N species and biogeochemical parameters and 2) to characterise isotopic signatures of H_2O and NO_3^- -N to elucidate the “net” provenance of water, source of N and the transformational processes and the interaction of fate of N on this multi-layered site.

2. Materials and methods

2.1. Site description

The site is located on the beef farm at the Teagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford, SE Ireland ($52^\circ 17' 36''\text{N}$, $6^\circ 31' 6''\text{W}$) (Fig. 1a). It has a cool maritime climate with mean annual precipitation of 1002 mm and annual temperature 9.6°C (Ibrahim et al., 2013). The isolated plots (~ 4.2 ha in total, 2% slope) were installed in 2005 and contain six plots separated by 4 m deep open ditches that intersect shallow groundwater. To understand the overburden (soil and subsoil) lateral variations and thicknesses, an electromagnetic (EM) conductivity and resistivity survey was conducted on site in September 2009 (APEX Geoservices Ltd., IE) (Fig. 1b). For the EM survey, values ranged from 15 to 38 mS/m and were interpreted as > 26 mainly silt clay, $20 - 26$ mainly gravelly clay and < 20 represent silty-clayey gravel lenses within the gravelly clay. This means that in Fig. 1b plots 1–2 are dominated by > 20 (green, yellow red, heavier in terms of soil texture) with some < 20 (blue, lighter in texture and better drainage) whereas plots 3–4 are dominated by < 20 (blue) with some > 20 (green). From a NO_3^- -N distribution perspective this interpretation matches that of Fenton et al. (2009) where higher NO_3^- -N concentration migrates in blue areas of Fig. 1b, which have a high k_s and a lower water attenuation capacity (i.e. natural ability of the soil to bioremediate contaminants, in this case NO_3^- -N, depending upon hydrologic and biological factors). Plots 1 and 2 are grouped as poorly drained whereas plots 4 and 5 are grouped as imperfectly drained.

In terms of geology, the Cullenstown Formation is present on site except in the south-west where rocks of the Shelmalier Formation are indicated. The Cullenstown Formation is described as grey-green metagreywacke and slate and ranges from 6.5 m to 16.5 m depth. The Geological Survey of Ireland subsoils map (GSI, 2018) indicates till derived from metamorphic rocks. A narrow strip of alluvium is indicated along the western boundary of the survey area and also along the stream valley to the south. The Geological Survey of Ireland vulnerability map for the area indicates that the groundwater vulnerability rating of the site is “High”. The bedrock is listed as a locally important aquifer.

All plots had three installed piezometers at top, middle and bottom locations drilled to 4 m depth with a 1 m screen section (sample depth 3–4 m) at the bottom of each installation (plot 2 only middle and bottom due to damage at the top position) (Fig. 1). A herring bone drainage design (primary drain with side laterals 10 m spacing, with a single end of pipe discharge point, which can be sampled) installed at 1 m depth in each plot intercepted infiltrating water but also drained shallow groundwater when the water table raised above the position of the drains. An important aspect of the present study is to use isotopes to elucidate the origin of EOP water when it is sampled and to find out if it

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