



Research article

Influence of artificial drainage system design on the nitrogen attenuation potential of gley soils: Evidence from hydrochemical and isotope studies under field-scale conditions

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ABSTRACT

In North Atlantic Europe intensive dairy farms have a low nitrogen (N) use efficiency, with high N surpluses often negatively affecting water quality. Low feed input systems on heavy textured soils often need artificial drainage to utilise low cost grassland and remain profitable. Heavy textured soils have high but variable N attenuation potential, due to soil heterogeneity. Furthermore, drainage system design can influence the potential for N attenuation and subsequent N loadings in waters receiving drainage from such soils. The present study utilises end of pipe, open ditch and shallow groundwater sampling points across five sites in SW Ireland to compare and rank sites based on N surplus, water quality and “net denitrification”, and to develop a conceptual framework for the improved management of heavy textured dairy sites to inform water quality N sustainability. This includes both drainage design and “net denitrification” criterion, as developed within this study. N surplus ranged from 211 to 292 kg N/ha (mean of 252 kg N/sourha) with a common source of organic N across all locations. The predicted soil organic matter (SOM) N release potential from top-subsoil layers was high, ranging from 115 to >146 kg N/ha. Stable isotopes analyses showed spatial variation in the extent of specific N-biotransformation processes, according to drainage location and design. Across all sites, nitrate (NO₃-N) was converted to ammonium (NH₄⁺-N), which migrated offsite through open ditch and shallow groundwater pathways. Using the ensemble data the potential for soil N attenuation could be discriminated by 3 distinct groups reflecting the relative dominance of *in situ* N-biotransformation processes deduced from water composition: Group 1 (2 farms, ranked with high sustainability, NH₄⁺ < 0.23 mg N/l, δ¹⁵N-NO₃⁻ > 5‰ and δ¹⁸O-NO₃⁻ > 10‰), low NH₄⁺-N concentration coupled with a high denitrification potential; Group 2 (1 farm with moderate sustainability, NH₄⁺ < 0.23 mg N/l, δ¹⁵N-NO₃⁻ < 8‰ and δ¹⁸O-NO₃⁻ < 8‰), low NH₄⁺-N concentration with a high nitrification potential and a small component of complete denitrification; Group 3 (2 farms, ranked with low sustainability, NH₄⁺ > 0.23 mg N/l, 14‰ > δ¹⁵N-NO₃⁻ > 5‰ and 25‰ > δ¹⁸O-NO₃⁻ > -2‰), high NH₄⁺-N concentration due to low denitrification. The installation of a shallow drainage system (e.g. mole or gravel moles at 0.4 m depth) reduced the “net denitrification” ranking of a site, leading to water quality issues. From this detailed work an N sustainability tool for any site, which presents the relationship between drainage class, drainage design (if present), completeness of denitrification, rate of denitrification and NH₄-N attenuation was developed. This tool allows a comparison or ranking of sites in terms of their N sustainability. The tool can also be used pre-land drainage and presents the consequences of future artificial land drainage on water quality and gaseous emissions at a given site.

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1. Introduction

Global food demand is expected to increase by 100% by 2050 (Tilman et al., 2002; Godfray et al., 2010). The need for higher yields, in order to sustain a growing population, has fuelled fears that achievement of worldwide production targets will be at the expense of water and air quality targets (Mosier et al., 1998; Foster, 2000; Lesschen et al., 2011). The ambition for sustainable food production implies that increased productivity must be carefully managed to reduce negative externalities, such as impacts on soil and water quality, increased greenhouse gas emissions and reduction in habitat biodiversity (Schulte et al., 2014).

Agricultural landscapes are typically heterogeneous, in which soils have various important functions and capabilities supporting the *in situ* transformation of nutrients such as N. For example, soil texture can influence N attenuation and typically heavier textured gley soils have optimal conditions for N-biotransformation processes such as denitrification, which reduces NO_3^- -N to N_2O and N_2 (Saggar et al., 2013). Artificial land drainage, as a tool to manage water table levels and reduce the duration of soil saturation, plays an important role in improving crop yields and maintaining on-farm profitability but drainage system design can influence the potential for N attenuation and subsequent N loadings in waters receiving drainage discharge from such soils. In an 11 year study in Denmark, Erntsen et al. (2015) found varied N-fluxes from tile drains (depth: 1.1 m bgl, spacing: 10–20 m) installed in heavy textured clay tills, inferring natural attenuation or “net denitrification” gradient across sites due to site-specific hydrological settings (e.g. watertable elevation, length and intensity of the drainage) and crop cover.

Gley soils are either surface water gleys (fed by surface rainfall, where relatively impermeable horizons impede drainage causing periodic or permanent wetness), or groundwater gleys (wherein the substrata is seasonally or permanently wet and affected by free groundwater) (Thomasson, 1975). However, clay loam pseudo-gley soils are typically unprofitable due to annual grass yield deficits of 3–31% when subjected to continuous saturation (e.g. watertable of 0 m bgl) rather than at lower saturation (1.15 m bgl) (Mulqueen, 1985) and require the installation of artificial land drainage systems to increase the soil profile permeability as a management measure to improve their productivity. The fundamental aim of land drainage is to remove excess groundwater, thus lowering the water table and reducing the period of waterlogging (Armstrong and Garwood, 1991; Nijland et al., 2005). This provides suitable conditions for the cultivation, growth and harvesting of a crop. The design of land drainage entails the specification and installation of drains in the soil at such a depth and spacing to control the water table at a predetermined depth below ground level under a particular intensity of rainfall (Mulqueen, 1998). Various techniques have been developed to suit different soil types and conditions with associated drainage characteristics, with this end in mind. The type of drainage system installed could potentially alter the natural attenuation or “net denitrification” of a soil profile by modification of the soil water saturation and drainage characteristics (e.g. rate, permanence time, by-pass of the soil layers).

On dairy farms N originates from inorganic or organic fertilizer (e.g. cattle slurry and soiled water), with potential ammonium (NH_4^+ -N) and/or nitrate (NO_3^- -N) losses along surface or leached pathways. These two N-species are the main substrate for N-biotransformation processes (i.e. denitrification, nitrification, anaerobic ammonium oxidation (anammox) and dissimilatory nitrate reduction to ammonium (DNRA)), which can lead to the production of nitrous oxide (N_2O), a potent greenhouse gas, and di-nitrogen gas (N_2), effectively removing reactive N from biological cycling (Rütting et al., 2011; Burgin et al., 2013) (Fig. 1). Most studies

still consider NO_3^- -N the main species for N losses and focus attention only on denitrification when addressing sustainability targets and land use (e.g. Coyle et al., 2016). Soil type and physicochemical properties are generally the main factors which define the soil microbial community structure, with the first 20 cm of soil being the most important (and most investigated) in shaping the bacterial community of the underlying groundwater (Qin et al., 2014).

While it is well documented that land drainage can circumvent the N attenuation capacity of a soil, leading to nutrient losses (Skaggs et al., 1994; Billy et al., 2013), the effect of drainage system design on soil function, N-biotransformation processes and N-cycling “hotspots” is poorly understood. Poorly-drained soils amended with fertilizer can result in high N-losses, via increased N_2O emissions, due to favourable conditions for denitrification and a high NO_3^- -N content (Nash et al., 2012). Periods of extended saturation support denitrification by retaining the substrate for longer, favouring complete reduction to N_2 (Bergsma et al., 2002).

Combining chemical analysis of drainage water samples with stable isotope characterisation of N-species (e.g. NO_3^- -N and N_2O concentrations and isotopes and N_2 -excess) provides a convenient and effective approach to understand the complex interactions within the soil N-cycle of an agricultural system and the relationship with the drainage system.

The analysis of these N species (concentrations) in soil pore water and gas can indicate system outputs, e.g. total biological N_2 production and dissolved N_2O , but cannot distinguish between production processes, which could include (anammox, DNRA, nitrification and denitrification) (Jahangir et al., 2012a, 2012b and 2013). Therefore these complementary analytical techniques must be used simultaneously to gain a full understanding of N-biotransformation in soils. Stable isotope analysis (e.g. quantification of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) has been widely used to deduce sources, biotransformation processes and rates of turnover for NO_3^- -N in soil

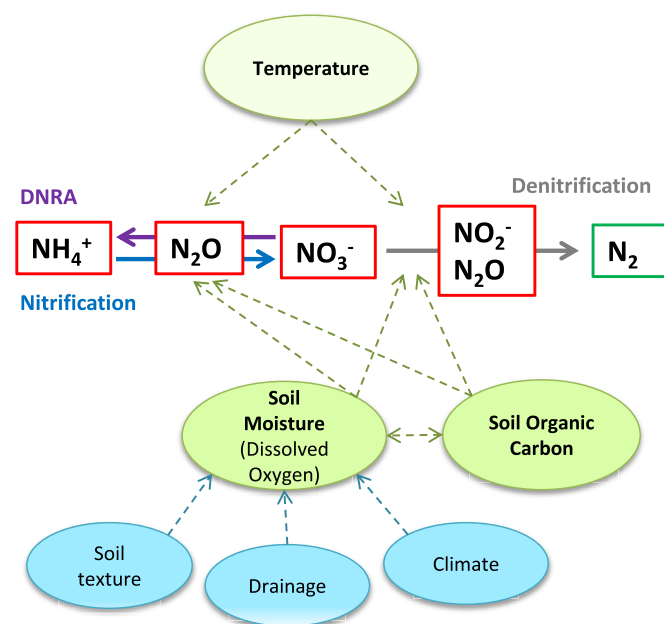


Fig. 1. Key parameters affecting N attenuation and speciation in soil and groundwater. Red boxes represent all species that might be lost causing the deterioration of water quality; Green box represent a favourable outcome; green circles represent proximal factors affecting these processes; Blue circles represent distal factors (from Coyle et al., 2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

environments (Smith and Kellman, 2011; Pastén-Zapata et al., 2014; Snider et al., 2015; Wells et al., 2016). However, N-biotransformation processes which do not originate with NO_3^- -N (nitrifier-denitrification and anammox) can be overlooked even though they produce N_2O and N_2 .

Further studies are needed to understand the relationship between the design of artificial land drainage systems and the N-attenuation potential of host gley soils. This must encompass the characterisation of the hydraulic connectivity of an agricultural system, its hydrochemistry, gas and isotopic signature in order to identify which factors control the spatial distribution of N biotransformation potential across agricultural landscapes, and the N release to the drainage waters and environment (Baggs and Philippot, 2010; Bednorz et al., 2016). Therefore, the objectives of the present study utilising end of pipe, open ditch and shallow groundwater sampling points across five sites in the southwest of Ireland were to: a) compare and rank sites based on N surplus, water quality and “net denitrification”, and b) develop a conceptual framework for the management of heavy textured dairy sites, which includes the results of the present site and the literature, to inform water quality N sustainability.

2. Materials and methods

2.1. Study sites

Five permanent grassland sites were selected in SW Ireland as part of the Teagasc Heavy Soils Programme (HSP): Kishkeam (KM), Doonbeg (DG), Castleisland (CD), Athea (AA) and Rossmore (RE). Before drainage installation, each site was soil mapped at 1:25,000 scale and divided into surface and groundwater gleys. At each site a site assessment including excavation of soil profiles and examination of the soil profile was conducted. Then various soil horizons were sampled and a drainage design was constructed, including drain spacing, depth of installations, materials to be used. A bespoke artificial drainage system was installed in a paddock at each site, comprising either a shallow drainage design or a groundwater drainage design (Tuohy et al., 2016). To compare sites in terms of soil and drainage design specification consult Table 1. The layout and location of the sites are presented in Fig. 1, replication within plots is achieved by the presence of multiple sampling points (end-of pipes).

Individual meteorological stations (Campbell Scientific Ltd., Loughborough, U.K.) were installed at all locations to estimate and compare a water balance for each site. Average daily rainfall (mm), wind speed and hours of sunshine were used in the hybrid soil moisture deficit (SMD) grassland model of Schulte et al. (2005) to estimate a daily effective drainage (ED, mm) value (Table 1).

Farm N balances (2015) were calculated following the methodology of Treacy et al. (2008), which utilises stocking rate, N inputs (chemical and organic fertilisers), concentrate feed (volume and composition) and milk production (volume and composition).

Milking was conducted at 07:30 h each morning and 15:30 h each evening. Milk yield per cow (kg) was recorded at each milking. Milk composition (fat, protein and lactose concentrations) for each cow was measured twice forth-nightly on a successive morning and evening milking using a Milkoscan 203 (Foss Electric DK-3400, Hillerød, Denmark) following normal quality controls protocols. Solids corrected milk yield was calculated using the equation of Tyrell and Reid (1965). The N value in concentrates fed, and in milk produced is an average across the farm while the N (fertilizer plus slurry) is in one paddock only (the drained paddock).

Estimated N release was calculated from soil organic matter (SOM) for each soil horizon of every farm (Brookside Laboratories

Inc. OH, USA) (Pastor and Binkley, 1998). This is a computed estimate of the N that may be released annually through OM decomposition. The calculation is based on the loss on ignition method at 360 °C (Schulte and Hopkins, 1996).

2.2. Water samples

Monthly water samples were taken from shallow groundwater piezometers, end-of-pipe, and open ditch locations (Fig. 1) from August 2015 to August 2016. Additional fieldwork was conducted between October and November 2015. The end-of-pipe samples give a “net” representation of water provenance, source, N-transformation processes over their entire length and zone of contribution. The zone of contribution of each paddock was calculated by multiplying the length of the piped drainage system for the spacing of the system. This equated approximately to 1.4, 1.7, 2.4, 1.7 and 1.1 ha for KM, AA, CD, RE and DG, respectively. In addition, due to the high number of drainage sections installed and presence of open ditches, these paddocks can be considered isolated from horizontal water flow from adjacent paddocks. The drainage water is therefore representative of the superficial layers only of the paddocks studied.

Open ditch water samples represent water from the drained paddock and other areas of the farm. Shallow piezometers were installed to different depths (see Table 1) at various locations (Fig. 2) to measure continuous water table depth (electronic dipper, Van Walt Ltd., Surrey, UK). Shallow groundwater samples (Fig. 2) were collected using low-flow micro-purging of the piezometers, following standard protocols (CL:AIRE, 2008). A peristaltic pump (Model 410, Solinst Canada Ltd.) fitted with Teflon outlet tubing (Ø 0.6 cm) was used to collect these water samples. End-of-pipe and open ditch water samples were collected in duplicate (50 ml, HDPE screw top bottles). One replicate was filtered in the field through 0.45 µm cellulose acetate filters (total recoverable vs. dissolved analytes) (Sartorius Stedim Biotech GmbH, Germany). A Multi-parameter Probe (In Situ Inc., USA) was used to measure pH, temperature (T), electrical conductivity (EC), turbidity (Turb.), dissolved oxygen (DO) and redox potential (Eh) of each water sample.

Water quality maximum admissible concentrations (MAC) provided within the EU WFD were used as baseline threshold values to identify N impacts. It should be noted that some of these MACs are for surface water or drinking water and therefore are not necessary applicable to land drainage discharges. However, this approach provides a consistent basis to compare water quality data for the different samples, given the emphasis on deducing potential impacts to receiving waters. For N species MAC were for NO_3^- -N (surface drinking water): 11.3 mg NO_3^- -N/l MAC (OJEC, 2006; EU, 2014); NO_2^- -N: 0.15 mg NO_2^- -N/l (EU, 2014), NH_4^+ -N: 0.23 mg NH_4^+ -N/l (EU, 2014). MAC for other chemical parameters were 12 mg/l for potassium (K^+), 2.2 mg/l for dissolved reactive phosphorus (P) and 250 mg/l for chloride (Cl^-) (all surface water standards, EC, 1998; EU, 2014). Additional thresholds have been further highlighted to assess the degree of contamination of groundwater (and therefore are drinking water standards) and are indicative of early signs of contamination. These concentration limits are: 4 mg/l for K^+ , 25 mg/l for Cl^- , 0.4 mg/l for potassium and sodium ratio (K/Na), 0.1 mg/l for P and 5.65 mg NO_3^- -N/l for NO_3^- -N (organic contamination limit) (Daly, 2000; OECD, 2001).

All water samples were analysed for NO_2^- -N, NH_4^+ -N, Total Oxidised Nitrogen (TON) and Cl^- using an Aquakem 600 Discrete Analyser (Aquakem 600A, 01621 Vantaa, Finland). Method detection limits (MDL) were 0.006 mg/l, 0.05 mg/l, 0.25 mg/l and 0.8 mg/l, respectively. Concentrations of NO_3^- -N were calculated by subtraction of NO_2^- -N from TON (NO_3^- -N + NO_2^- -N). Total Nitrogen (TN) was determined by alkaline persulfate oxidation (Askew and Smith,

Table 1Site parameters pertaining to drainage system and soil profile (based on data from [Tuohy et al., 2016](#)).

Site	Soil	Horizon Depth: Type (Texture)	Weather data, Water <i>in situ</i> parameter, Drainage design and sampling depths.
KM - 1.59 ha, Co. Cork, 52° 12', 09° 08'	Humic SW Gley	0–32 cm: AO (silty clay loam), 33–70 cm: Btg (silt loam), 71–97 cm: Cg (loam), 98–125 cm: Cr (loam), 126–190 cm: R (shale)	<ul style="list-style-type: none"> - Average annual rainfall 1629 mm, Av. AE: 0.6 mm/day, Av. ED: 3.9 mm/day, Av. SMD: -8.2 mm, T: 8.5 °C - WT: 0.6 m bgl, pH: 6.8, Eh: 726 mV, DO: 8.9 mg/l, T: 11.0 °C (Av. for site Oct–Nov 2015) - Drainage system: Subsoiling (0.6 m bgl, 1.5 m spacing), In-field pipes (1.1 m bgl, 15 m spacing) - End of pipe samples equate with 0–1.1 m bgl; Groundwater water samples equate with 1.9 m bgl depth of the soil profile; Open ditch samples equate to 1.5 m bgl
AA - 2 ha, Co. Limerick, 52° 27', 09° 19'	Humic SW Gley/Shale	0–40 cm: Ap/O (clay loam), 41–62 cm: Btg (silty clay), 63–140 cm: Cg1 (silty clay loam), 140–170 cm: Cg2 (silty clay loam)	<ul style="list-style-type: none"> - Average annual rainfall 1444 mm, Av. AE: 1.1 mm/day, Av. ED: 2.9 mm/day, Av. SMD: -7.1 mm, T: 9.1 °C - WT: 0.1 m bgl, pH: 6.7, Eh: 433 mV, DO: 9.7 mg/l, T: 11.5 °C (Av. for site Oct–Nov 2015) - Drainage system: Gravel moles (0.45 m bgl, 1.5 m spacing), In-field (0.9 m bgl, 20 m spacing) - End of pipe samples equate with 0–0.9 m bgl; Groundwater water samples equate with 1.8 m bgl depth of the soil profile; Open ditch samples equate to 1.5 m bgl
CD -1.31 ha, Co. Kerry, 52° 13', 09° 28'	Typical SW Gley	0–36 cm: Ap (silty clay loam), 37–100 cm: BCtg (silty clay loam), 101–190 cm: Cr (loam)	<ul style="list-style-type: none"> - Average annual rainfall 1148 mm, Av. AE: 1.1 mm/day, Av. ED: 1.8 mm/day, Av. SMD: -8.2 mm, T: 10.0 °C (missing values: 12–14/04/15, 04–07/05/15) - WT: 0.8 m bgl, pH: 7.2, Eh: 582 mV, DO: 9.4 mg/l, T: 11.6 °C (Av. for site Oct–Nov 2015) - Drainage system: subsoiling at (0.5 m bgl with 1.5 m spacing), then gravel moles at (0.45 m bgl with 1.5 m spacing), In-field pipes (0.9 m bgl, 20 m spacing) - End of pipe samples equate with 0–0.9 m bgl; Groundwater water samples equate with 1.8 m bgl depth of the soil profile; Open ditch samples equate to 1.2 m bgl
RE -2.56 ha, Co. Tipperary, 52° 36', 08° 01'	Paddock 1: Typical SW Gley Paddock 2: GW Gley	Paddock 1: 0–28 cm: Apg (loam), 29–50 cm: Eg (sandy loam), 51–90 cm: C (sandy clay loam), 91–140 cm: Cr (typical old red sandstone) Paddock 2: 0–30 cm: Apg (loam), 31–53 cm: Eg (sandy loam), 54–70 cm: Btg (sandy clay loam), 70–100 cm: C1 (Sandy clay loam) 100–140 cm: C2 (Sandy loam)	<ul style="list-style-type: none"> - Average annual rainfall 852 mm, Av. AE: 1.1 mm/day, Av. ED: 1.7 mm/day, Av. SMD: -1.8 mm, T: 9.9 °C (missing values: 10/12/14–04/02/15, 20–21/11/15). - WT: 1.2 m bgl, pH: 7.2, Eh: 319 mV, DO: 8.7 mg/l, T: 11.3 °C - Drainage system: In-field pipes (1.6 m bgl, 15 m spacing in paddock 1, 30 m spacing in paddock 2) - End of pipe samples equate with 0–1.6 m bgl of the soil profile; Groundwater water samples equate with 2.0 m bgl depth of the soil profile; Open ditch samples equate to 0.6 m bgl
DG - 2.09 ha, Co. Clare, 52° 44', 09° 30'	Humic Stagnic GW Gley	0–26 cm: Apg (silty clay loam), 27–48 cm: Btg (clay loam), 49–75 cm: Cg1 (silt loam), 76–140 cm: Cg2 (clay loam)	<ul style="list-style-type: none"> - Average annual rainfall 1144 mm, Av. AE: 1.2 mm/day, Av. ED: 2.0 mm/day, Av. SMD: -4.1 mm, T: 9.8 °C (Weather station not on the farm, 25 km away, similar climate). - WT: 0.2 m bgl, pH: 7.2, Eh: 308 mV, DO: 7.7 mg/l, T: 10.5 °C (Av. for site Oct–Nov 2015) - Drainage system: naked moles (0.60 m bgl, 1.5 m spacing) In-field (0.9 m bgl with 10 and 15 m spacing) - End of pipe samples equate with 0–0.9 m bgl; Groundwater water samples equate with 1.8 m bgl depth of the soil profile; Open ditch samples equate to 1.2 m bgl

2005). Dissolved Ca^{2+} , Cu^{2+} , Fe^{2+} , K^{+} , Mg^{2+} , Mn^{2+} , Na^{+} and Zn^{+} were quantified by inductively coupled plasma spectrophotometer ICP-OES (Varian, CA, USA) following manufacturer's procedures ([Szikla, 2001](#)), with (MDL: 1 µg/l, 1 µg/l, 1 µg/l, 185 µg/l, 2 µg/l, 0.4 µg/l, 17 µg/l and 1 µg/l, respectively). Dissolved SO_4^{2-} was determined turbidimetrically using the method of [Askew and Smith \(2005\)](#) with an MDL of 0.25 mg/l. Dissolved organic carbon (DOC) and TOC was measured as Non-Purgeable Organic Carbon using through a Total Organic Carbon Analyser (Shimadzu Corporation, Japan) (MDL 0.06 mg/l). Quality control (QC) samples were analysed with each run in the following order; start, after every 10 samples and at the end. All QC samples are made from stock solutions certified to ISO 17025 or traceable to NIST certified reference material. Quality control values were set at approximately 30% of the calibration range for each analyte, e.g. TON, range 10 mg/l, routine QC 3 mg/l. Results were rejected if QC values were outside $\pm 10\%$, and all samples, back to the previous correct QC, reanalysed. Sample results over range were diluted automatically or ran on a higher range calibration.

Duplicate water samples for dissolved gas analyses were taken at the same locations as nutrient samples. For excess N_2 estimation

samples were taken in 12 ml exetainers (LabcoWycomb Ltd., UK) after overflow of 10 ml. Exetainers were sealed without headspace using double septum (butyl rubber and teflon) stoppers. The exetainers were transported in water-filled containers at groundwater temperature (12 °C) and stored at 4 °C submerged inverted in water to prevent gas diffusion across the septa. N_2 quantification was carried out within one week using a high precision membrane inlet mass spectrometer (MIMS) (Pfeiffer Vacuum TMQMS 200 quadrupole mass spectrometer) set at the groundwater temperature of the time of sample collection ([Kana et al., 1994](#)) (MDL: < 0.03% (N_2/Ar), QCS: standard tap water was air-equilibrated at known temperature close to that of the samples). MIMS was calibrated before the initial reading and after every 10 samples to correct analytical drift. Deionised water previously equilibrated with air in a condition of constant temperature and pressure was used as standard ([Kana et al., 1994](#)). Gaseous N_2 concentrations were calculated as per [Weymann et al. \(2008\)](#).

For the detection of dissolved N_2O , carbon dioxide (CO_2) and methane (CH_4) duplicate groundwater samples were collected in 160 ml serum bottles after an overflow of 150 ml. Bottles were capped without headspace with butyl rubber septa and aluminium

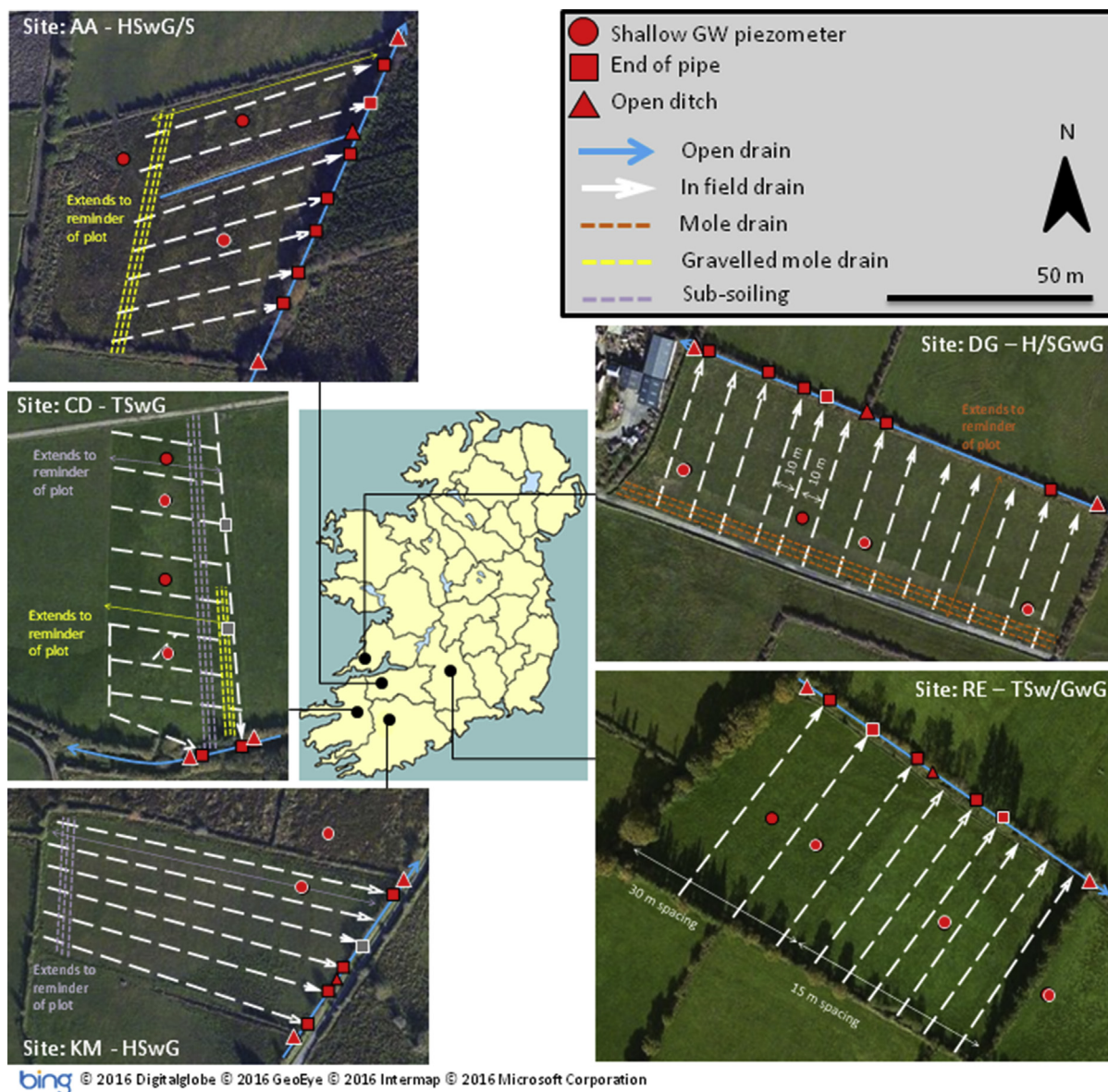


Fig. 2. Site locations, drainage design layouts (details are in Table 1) and sampling positions at end of pipe, open ditch and shallow groundwater (GW) piezometer locations. Symbols with a white outline indicate location in common between monthly sampling (Table S1) and Oct–Nov 2015 sampling (Table 3). Grey symbols with a white outline indicate location of monthly sampling but not for Oct–Nov 2015.

crimp caps (Wheaton, USA) and stored as above. Samples were degassed by simultaneous water extraction and addition of high purity helium (He:water 1:3; v/v) (BOC, Linde Group, Germany), creating a 40 ml headspace (Lemon, 1981). Samples were agitated at 400 rpm (Gyrotory shaker G-10, New Brunswick Scientific, USA) for 5 min before being left to stand for 30 min. The gas in the headspace was then transferred into evacuated 12 ml exetainers. Extra 12 ml exetainers, two replicates for each sample, were conserved and used for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ composition of dissolved- N_2O . N_2O , CO_2 and CH_4 were quantified by auto-sampler gas chromatography (CP-3800, Varian Inc. USA) (MDL for N_2O , CH_4 and CO_2 was 0.02, 0.74 and 62 ppm respectively, QCS used were ARGO International standards at different and known N_2O , CH_4 and CO_2 concentrations) and final concentrations were calculated using Henry's Law for the ambient groundwater temperature.

The indirect N_2O -N emission factor for groundwater (N_2O -N EF_{5g}) was calculated from the relationship between dissolved- N_2O and N inputs, as per Weymann et al. (2008), using the equation:

$$\text{EF}_{5g}(1) = (\text{N}_2\text{O-N}) / (\text{dissolved-}\text{N}_2\text{O} + \text{Excess } \text{N}_2 + \text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N} + \text{NO}_2^-\text{-N} + \text{DON}).$$
 The alternative equation: $\text{EF}_{5g}(2)$ ($\text{EF}_{5g}(2) = (\text{N}_2\text{O-N}) / (\text{NO}_3^-\text{-N})$) used by the intergovernmental panel on climate change (IPCC, 2006), was also used, although it assumes no processing of $\text{NO}_3^-\text{-N}$ and N_2O -N throughout the system (Weymann et al., 2008; Jahangir et al., 2013).

2.3. Stable isotope analysis

For isotopic measurements of NO_3^- , water samples (40 ml) were collected at the same locations as other parameters, filtered in the field through 0.2 μm polyethersulfone filters (Sartorius Stedim Biotech GmbH, Germany), and stored at -20°C in 50 ml polyethylene screw cap tubes. Gas exetainers (12 ml) from the previous section were additionally used for measurement of dissolved- N_2O isotopic abundances. Isotopic compositions ($^{15}/^{14}\text{N}$ and $^{18}/^{16}\text{O}$) of NO_3^- -N were determined using the denitrifier method at the UC Davis Stable Isotope Facility, Davis, California (McIlvin and Casciotti,

2011).

Isotope values for both NO_3^- -N and dissolved- N_2O were determined by using a Thermo Finnigan Gas Bench + PreCon trace gas concentration system interfaced to a Thermo Scientific Delta V Plus isotope-ratio mass spectrometer (Bremen, Germany). The calibration standards used were the nitrates USGS 32, USGS 34, and USGS 35 while additional laboratory reference materials are included in each batch to monitor and correct for instrumental drift and linearity. Limit of quantitation for ^{15}N and ^{18}O of N_2O from NO_3^- are 2–1500 μM NO_3^- in water. For ^{15}N and ^{18}O of N_2O , a calibration was carried out by thermally decomposing N_2O to convert N_2O to N_2 and O_2 . The resulting N_2 was calibrated against the Oztech N_2 standard, and the O_2 was calibrated against an Oztech O_2 standard ($\delta^{18}\text{O}$ vs. VSMOW = 27.48). Limit of Quantitation for N_2O are approx. 150 pmol. Isotopes values were reported in $\delta\text{‰}$ relative to international standards (AIR for N and VSMOW (Vienna Standard Mean Ocean Water) for O).

2.4. Statistics

Different methods (*t*-test, one way ANOVA and Tukey's HSD test (IBM SPSS Statistics version 24)) were used to determine if relationships existed between nutrient and gaseous data and other measured variables to identify significant differences amongst the main variables controlling processes and attenuation rates.

3. Results

3.1. Farm N balances

The five farms had similar stocking rates and grazing periods. The N-inputs ranged from 261 kg N/ha at AA to 341 kg N/ha at DG with an average of 307 kg N/ha (Table 2). Milk outputs ranged from 46 kg N/ha (CD) to 69 kg N/ha (DG). Mean excess N was 252 kg N/ha; CD had high excess (292 kg N/ha) together with KM and DG (both 272 kg N/ha), while AA and RE had lower outputs (both 211 kg N/ha). The highest potential for N that can be released by SOM decomposition from superficial layers was found in AA and KM, respectively an estimated N release of >146 kg N/ha and 144 kg N/ha. Lowest values were found at DG (120 kg N/ha) (Table 2).

3.2. Water quality

Longer term NO_3^- -N, NO_2^- -N and NH_4^+ -N across sites and sampling locations is presented in Table S1. Both spatial and temporal NO_3^- -N and NO_2^- -N concentrations were all consistently below MAC (Table S1). Ammonium-N concentrations appear to be elevated and exceeded MAC across sites but not in all sampling locations (see

Table S1 for number of sample events and % breaches).

Data for the more intensive sampling period in October 2015 is presented in Table 3 (see also Fig. S1). KM had a concentration of 0.05 ± 0.05 mg NH_4^+ -N/l NH_4^+ -N, with a 0.14 ± 0.03 mg NH_4^+ -N/l NH_4^+ -N value in groundwater, AA had a concentrations of 0.31 ± 0.12 mg NH_4^+ -N/l over the threshold in groundwater, CD had average concentrations above MAC (0.43 ± 0.46 mg NH_4^+ -N/l), with EOP (0.86 ± 0.39 mg NH_4^+ -N/l) and GW (0.28 ± 0.31 mg NH_4^+ -N/l) locations exceeding MAC, RE had low average concentrations (0.09 ± 0.15 mg NH_4^+ -N/l) but elevated groundwater concentrations (0.22 ± 0.21 mg NH_4^+ -N/l) and DG had low average concentrations (0.07 ± 0.06 mg NH_4^+ -N/l) with groundwater concentrations of 0.15 ± 0.04 mg NH_4^+ -N/l.

Dissolved organic carbon showed high inter-farm variability. The highest concentration was found at DG (22.35 mg C/l), with lowest at KM and RE (5.91 and 4.73 mg C/l). AA had an intermediate average concentration, i.e. 14.22 mg C/l, similar too CD at 15.00 mg C/l (Table S2; Fig. S2).

The K^+ concentration ranged from 0.51 to 25.23 mg/l. AA had the highest K^+ concentration (14.65 mg/l), with all end-of-pipe and one piezometer locations above MAC. AA, together with one piezometer at DG (19.77 mg/l), was the only other paddocks with a K^+ concentration above MAC. DG, CD and KM showed organic contamination in most locations (farm averages for K^+ were 6.76, 6.89, 4.79 mg/l, respectively), while K^+ was only detected in two piezometers at RE (2.74 mg/l) (Fig. S3). Cl^- values ranged from 12.92 to 68.01 mg/l, with DG (53.10 mg/l) and AA (48.78 mg/l) having the highest farm averages. Most piezometer locations were above those concentrations, indicating some organic contamination. RE (19.18 mg/l) and KM (20.72 mg/l) had the lowest concentrations, with only a few locations indicating contamination, while CD (35.69 mg/l) had intermediate values (Fig. S3). AA had the highest K/Na ratio (0.74), indicating organic waste influences. RE had a high concentration in piezometers (0.99 and 0.77), while end-of-pipe and open ditch locations remained unpolluted. CD (0.44) and KM (0.43) indicated contamination of open ditches, whereas DG (0.22) only exceeded the threshold in one piezometer and end-of-pipe sample location (Fig. S3).

3.3. Dissolved gasses

Dissolved N_2O concentrations ranged from 0.106 mg N/l to 0.001 mg N/l. The highest values were at CD (av. 0.026 mg N/l) and lowest at DG (av. 0.002 mg N/l) (Table 4). The N_2O concentration was generally higher in end-of-pipe locations than in groundwater or in open ditches. CD had the greatest variation in dissolved N_2O values, with highest concentrations in a piezometer location characterised by low NH_4^+ -N. RE had high N_2O values within end-of-pipe locations. (Table 4, Fig. S4).

Table 2

N annual balance and management for the five Paddocks in 2015. N input included fertilizer (chemical and organic) and concentrates; N output corresponds to milk; N surplus was calculated subtracting N outputs from N inputs. N release for other soil layers represent the average (\pm standard deviation) calculated for the soil layers underlying the top layer.

Site	Stocking rate (LU/ha)	Grazing period (days)	Management	N input	N output	N surplus	Estimated N release	
							Top soil	Other soil layers
(kg N/ha)								
KM	2.38	251	Synthetic fertilizer (monthly)	329	57	272	144	54 (±13)
AA	2.46	254	Synthetic fertilizer (monthly), cattle slurry (Feb., Apr., Oct.)	261	50	211	>146	68 (±34)
CD	2.59	229	Synthetic fertilizer (monthly), cattle slurry (Feb., Apr., Oct.)	338	46	292	131	52 (±5)
RE	2.56	251	Synthetic fertilizer (monthly), cattle slurry (Mar., May, Sep.) and parlour washings (Oct.)	264	53	211	115	25 (±10)
DG	2.37	249	Synthetic fertilizer (monthly), urea (Jul.) and parlour washings (Sep.)	341	69	272	120	52 (±18)

Table 3
Average values for NO_3^- -N and NH_4^+ -N within the five paddocks in October 2015 (NO_2^- -N was below 0.04 mg NO_2^- -N/l at all locations); open ditches (OD), end of pipes (EOP) and shallow groundwater piezometers (GW) at the five sites.

Site	NO_3^- -N (mg NO_3^- -N/l)				NH_4^+ -N (mg NH_4^+ -N/l)			
	Site	OD	EOP	GW	Site	OD	EOP	GW
KM	0.80 ± 0.90	0.76 ± 0.43	1.19 ± 1.24	0.10 ± 0.03	0.05 ± 0.05	0.03 ± 0.01	0.01 ± 0.01	0.14 ± 0.03
AA	0.47 ± 0.37	0.42 ± 0.56	0.66 ± 0.28	0.08 ± 0.07	0.17 ± 0.18	0.08 ± 0.04	0.13 ± 0.20	0.31 ± 0.12
CD	1.78 ± 1.29	0.60 ± 0.00	2.92 ± 1.46	1.43 ± 0.36	0.43 ± 0.46	0.02 ± 0.01	0.86 ± 0.39	0.28 ± 0.31
RE	0.76 ± 0.80	1.97 ± 0.02	0.35 ± 0.40	0.38 ± 0.42	0.09 ± 0.15	0.02 ± 0.02	0.02 ± 0.02	0.22 ± 0.21
DG	0.22 ± 0.13	0.23 ± 0.14	0.30 ± 0.11	0.09 ± 0.05	0.07 ± 0.06	0.03 ± 0.02	0.04 ± 0.02	0.15 ± 0.04

Table 4
Mean values for excess- N_2 and dissolved- N_2O for whole farm, open ditches (OD), end of pipes (EOP) and shallow groundwater piezometers (GW) at the five sites.

Site	Excess- N_2 (mg N/l)				Dissolved- N_2O ($\mu\text{g N/l}$)			
	Site	OD	EOP	GW	Site	EOP	FD	GW
KM	0.34 ± N/A	N/A	N/A	0.34 ± N/A	6.67 ± 6.83	1.95 ± 0.40	11.27 ± 7.24	2.48 ± N/A
AA	0.42 ± 0.25	0.13 ± N/A	N/A	0.56 ± 0.05	3.30 ± 1.50	2.01 ± 0.27	4.44 ± 0.68	1.94 ± 1.48
CD	0.17 ± N/A	N/A	N/A	0.17 ± N/A	25.95 ± 43.21	2.28 ± 0.18	9.42 ± 6.31	0.11 ± N/A
RE	0.19 ± 0.12	N/A	0.19 ± 0.12	N/A	6.31 ± 4.68	1.74 ± 0.18	9.06 ± 3.65	N/A
DG	0.35 ± 0.26	0.44 ± 0.24	0.13 ± 0.041	0.61 ± 0.21	1.99 ± 0.65	2.17 ± 0.84	2.17 ± 0.64	1.46 ± 0.21

In most of the farms, excess- N_2 was below background levels. Therefore the values ranged from below background levels to 0.859 (DG) mg N/l. On sites where excess- N_2 was above background level this range was from 0.053 (RE) to 0.859 (DG) mg N/l. The highest excess- N_2 was found in DG, and lowest in RE (0.05 mg/l) (Table 4, Fig. S4). Due to the presence of excess N_2 values below background levels limited data were available for the EF5g(1) calculation. EF5g(1) ranged between 0.0010 (AA) to 0.0288 (CD) (IPCC set default value: 0.0025). When looking at the EF5g(2) (data not shown) emission values were from 0.0008 to 0.0980, with 87% of locations above the IPCC set default value; every field site had averages above limits, with the highest concentration at RE (0.0296) and lowest at KM (0.0115) (data not shown). Dissolved CO_2 values were between 2.3 (KM) and 108.3 mg C/l (RE). Higher dissolved CO_2 concentrations were found in groundwater and in-field pipes, rather than in open drains (Table S2, Fig. S5). Values for CH_4 varied between 1.45 and 38.00 $\mu\text{g C/l}$, except for two extreme values in AA

groundwater (58 and 650 $\mu\text{g C/l}$) (Table S2, Fig. S5).

3.4. Stable isotopes

The NO_3^- -N isotopic values ranged from 25.5 to -4.8‰ for $\delta^{15}\text{N}$ - NO_3^- (av. 10.1 ‰) and from 23.3 to -1.7‰ for $\delta^{18}\text{O}$ - NO_3^- (av. 5.7 ‰). Different farms showed specific and significantly different $\delta^{15}\text{N}$ - NO_3^- enrichment ($p < 0.005$), with KM (av. 20.0 ‰ $\delta^{15}\text{N}$ - NO_3^- and 8.1 ‰ $\delta^{18}\text{O}$ - NO_3^-) and RE (av. 12.5 ‰ $\delta^{15}\text{N}$ - NO_3^- and 7.9 ‰ $\delta^{18}\text{O}$ - NO_3^-) showing the highest enrichment, whereas DG had the least enriched values (av. 4.7 ‰ and 4.2 ‰ for $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- respectively). CD and AA showed similar $\delta^{15}\text{N}$ - NO_3^- enrichment (av. 8.4 ‰ and 8.3 ‰ respectively) ($p > 0.05$). However CD showed lower $\delta^{18}\text{O}$ - NO_3^- values (av. 2.2 ‰) than AA (6.5 ‰) (Fig. 3).

The $\delta^{18}\text{O}$ - NO_3^- was higher in piezometer (10.0 ‰) than end-of-pipe (3.2 ‰ ; $p < 0.005$) and open ditch (5.2 ‰ ; $p < 0.05$) locations. End-of-pipe locations at RE had a higher $\delta^{15}\text{N}$ - NO_3^- (15.9 ‰) than open ditches and piezometers (10.1 and 9.1 ‰ respectively). The highest values of $\delta^{18}\text{O}$ - NO_3^- were in a piezometer (14.5 ‰) and the end-of-pipe location (15.5 ‰). These locations also had highest the NH_4^+ -N and NO_3^- -N concentrations at time of sampling. Two AA piezometers had the highest $\delta^{18}\text{O}$ - NO_3^- values (23.3 and 20.5 ‰). At DG piezometers showed high variability, with alternatively low $\delta^{15}\text{N}$ - NO_3^- or high $\delta^{18}\text{O}$ - NO_3^- values. The two DG piezometer locations had the lowest $\delta^{15}\text{N}$ - NO_3^- values (-4.8 and -1.1‰) (Fig. 3). The $\delta^{15}\text{N}$ - N_2O values ranged from 4.3 to -20.3‰ while $\delta^{18}\text{O}$ - N_2O was 68.2 to 27.2 ‰ . No difference was evident in $\delta^{15}\text{N}$ - N_2O values between the farms (Fig. 4).

4. Discussion

4.1. Farm N balances

A high input of N on these farms is necessary to sustain milk production. However, inputs on these paddocks farm are well above the average (223–228 kg N/ha) for Irish intensive farms (Treacy et al., 2008; Mihailescu et al., 2014). These paddocks have low efficiency with respect to N utilisation (between 14 and 20%) (averages for dairy farms: 20% (Treacy et al., 2008), 28% (Mihailescu et al., 2014)) and high N-surplus (between 211 and 292 kg N/ha) (average for Irish farms (227 kg N/ha (Treacy et al., 2008), 175 kg N/ha (Mihailescu et al., 2014))). In addition, soil from these field sites

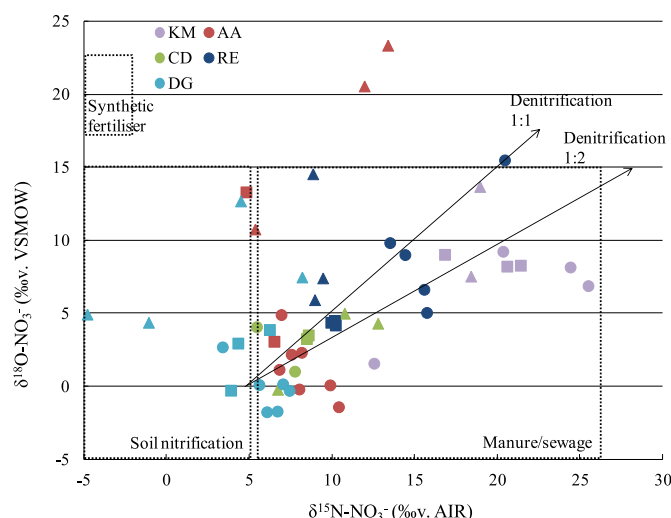


Fig. 3. $\delta^{18}\text{O}$ - NO_3^- versus $\delta^{15}\text{N}$ - NO_3^- values for the sites, also showing 1:1 and 1:2 denitrification slope and $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ ranges for N-sources (after Kendall, 1998). Open ditch (OD): squares, end of pipe (EOP): circles and shallow groundwater piezometers (GW): triangles.

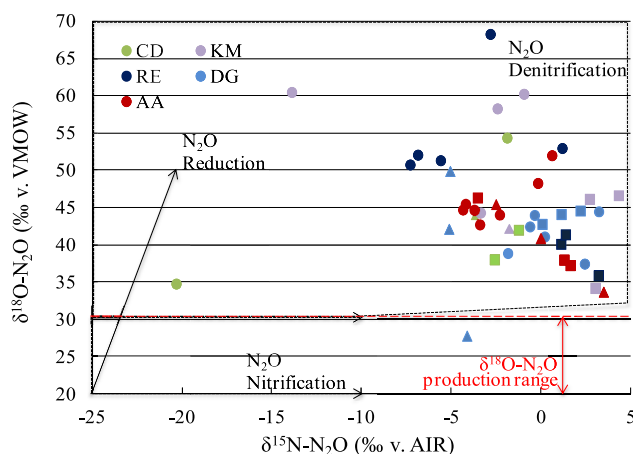


Fig. 4. $\delta^{18}\text{O}-\text{N}_2\text{O}$ versus $\delta^{15}\text{N}-\text{N}_2\text{O}$ values for the farms, also showing 2.5:1 N_2O reduction slope and source boxed as identified by Li et al. (2014). Red line represents the limit for N_2O production calculated for the sites. Open ditch (OD): squares, end-of-pipe (EOP); circles and shallow groundwater piezometers (GW). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

has a high estimated N release potential, suggesting high N storage by SOM, with high leached losses expected as decomposition occurs (Table 2). Nitrogen is more likely to accumulate and be retained by SOM in soil when it is not lost through denitrification or leaching (Jarvis et al., 1996). Hence, the N balances for these farms indicate a high potential for N-losses. However, the high N inputs and low N efficiency indicates that simple improvement related to nutrient use efficiency could decrease environmental impact without significantly affecting yields (Mihailescu et al., 2014).

4.2. Water quality

Ammonium is the pollutant of concern across the sites. Low NO_3^- -N concentrations occurred in shallow groundwater and end-of-pipe locations, indicating a high NO_3^- -N attenuation potential in the upper 1 m of the soil profile, but with pollution swapping also evident (see Stevens and Quinton, 2009). The high saturation, poor aeration and low permeability of soil profiles on the farms increase the potential for denitrification (Hanson et al., 1994). In addition, weather data showed, from the biogeochemical standpoint, that the systems could promote high rates of anaerobic N reduction processes (e.g. denitrification, DNRA) (Giles et al., 2012; Cardenas et al., 2017) (Table 1).

Incomplete denitrification is likely due to excess fertilizer, which leads to high N_2O emissions. However, Burchill et al. (2014) studied groundwater gleys with deep groundwater drainage designs and showed that a high water-filled pore space still remained in topsoil layers, creating conditions for complete denitrification and a corresponding increased release of N_2 rather than N_2O .

The high C content of these soils also creates conditions for pollution swapping, leading to an increased amount of N being transformed back to NH_4^+ -N by DNRA, as this process is thought to dominate under low O_2 , high C conditions (Rütting et al., 2011). Highly anaerobic conditions could also increase NH_4^+ -N concentrations, by inhibiting nitrification (aerobic conversion of NH_4^+ -N to NO_3^- -N) (Redding et al., 2016). However, at some sites with high saturation content, the installation of artificial drainage systems could encourage nitrification and NH_4^+ -N attenuation, due to greater DO infiltration to deeper levels. This could also have caused an increase in NO_3^- -N losses, with lower levels of complete denitrification.

At AA, where waterlogged areas persist, the high concentration of NH_4^+ -N is attributed to the suppression of nitrification (Redding et al., 2016). CD has a general contamination problem, with NH_4^+ -N values above MAC, whereas at RE only the groundwater sampling location within the wider spaced i.e. 30 m shows NH_4^+ -N contamination. The elevated NH_4^+ -N concentration at these locations is persistent and does not originate from farm management or application of organic or inorganic fertilizer. The 30 m treatment was installed on a groundwater gley site (some higher permeability at depth), whereas the 15 m treatment was installed on the adjoining surface-water gley (limited permeability through the profile). However, a groundwater-type drainage system was installed across the entire site with no disruption techniques deployed on the surface water gley section. This is interesting as a shallow drainage system in the surface water gley site would create conditions for increased N losses. However, the tighter spacing achieved drainage-production goals by controlling the water table and preventing water quality issues.

Tighter spacing of pipes, rather than connecting an 80 mm pipe at 1 m with a disruption technique (e.g. mole or gravel moles) should be explored as a water quality sustainability measure. The purpose of shallow drainage designs is to increase infiltration in the first metre of impermeable soil profiles (Tuohy et al., 2015; Filipovic et al., 2014), but this soil disruption will decrease the N attenuation potential of this soil layer.

The dissolved gas surveys show that there is no significant difference between contaminated and uncontaminated locations at the AA and DG sites, while CD has the highest dissolved- N_2O values in groundwater characterised by a low NH_4^+ -N concentration. Jahangir et al. (2012a) examined GHGs emissions on farms with low and high permeability characteristics. Results from comparable sites to the present study (same soil drainage class) had mean values for groundwater dissolved N_2O of 0.024 and 0.011 mg N/l. The present study found lower averages for dissolved N_2O , from 0.002 to 0.006 mg N/l. Herein, CD had the highest average of 0.022 mg N/l. A lower N_2O value in groundwater could be caused by decreased denitrification, nitrification, and/or a higher enhanced reduction of N_2O to N_2 however this result alone is not sufficient to discriminate which process is responsible (Jurado et al., 2017) (Table 4, Fig. S4). Reduction of N_2O to N_2 is favoured under the low NO_3^- -N and high saturation conditions at the five study sites here.

Excess- N_2 is below background levels in most of the farm, possibly implying *in situ* degassing of water and N_2 formation below solubility (Weymann et al., 2008; Well et al., 2012). However, no indications of degassing due to sampling errors were found (decreasing Ar concentration within a group). Excess- N_2 values (farm av. between 0.171 and 0.346 mg/l) are higher than those previously reported for the low permeability farms (2.28 and 2.33 mg/l) in Jahangir et al. (2012a). With a higher number of piezometer locations having excess- N_2 , DG had a higher level of N_2 production, potentially due to complete denitrification or other N_2 production process, i.e. anammox (Table 4, Fig. S4). The CO_2 in shallow groundwater ranged from 2.3 to 108.3 mg C/l, compared with 19–45 mg C/l in Jahangir et al. (2012b). The present sites have a CH_4 concentration mostly between 1.4 and 57 μg C/l, which are generally in the range of those (1.7–1001 μg C/l) found by Jahangir et al. (2012b) (Table S2, Fig. S5).

4.3. Isotopes

The NO_3^- -N isotope values in most locations are within the range attributed to organic fertilisers (Kendall, 1998; Xue et al., 2009), and more recently recognised as characteristic of a “mixed source”, represented by NO_3^- -N leached from pasture soils (Wells et al., 2014). Two samples had a $\delta^{18}\text{O}-\text{NO}_3^-$ signature within the range of

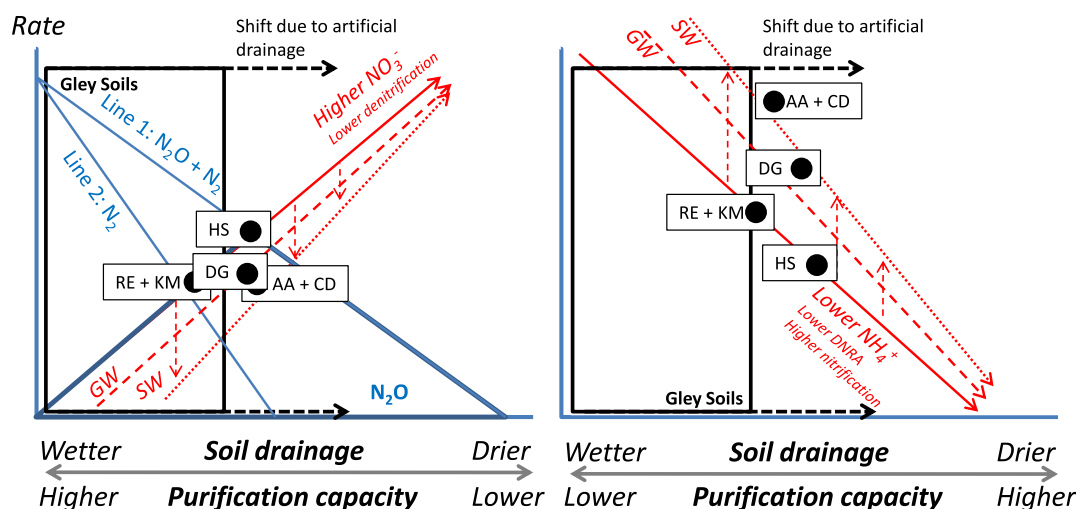


Fig. 5. **Left.** Conceptual diagram showing $\text{NO}_3\text{-N}$ water purification capacity represented by denitrification in relation to soil drainage. Red line shows $\text{NO}_3\text{-N}$ loss; dotted red line shows $\text{NO}_3\text{-N}$ loss in water from artificial drainage systems (GW: groundwater design; SW: surface water design) enhanced by soil bypass; line 1 indicates the first step of denitrification where $\text{NO}_3\text{-N}$ is converted to N_2O (Incomplete denitrification); line 2 represents the second step of denitrification where N_2O is converted to N_2 (Complete denitrification); HS indicates the low permeability sites from Jahangir et al. (2012a). **Right.** Conceptual diagram showing $\text{NH}_4\text{-N}$ water purification capacity represented by nitrification in relation to soil drainage. Red line shows $\text{NH}_4\text{-N}$ loss; dotted red line shows $\text{NH}_4\text{-N}$ loss in water from artificial drainage systems (GW: groundwater design; SW: surface water design) enhanced by soil bypass (from Coyle et al., 2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

synthetic fertilizer (Fig. 3). Overall, the isotope data plotted along a $\delta^{18}\text{O}\text{-NO}_3\text{:}\delta^{15}\text{N}\text{-NO}_3$ ratio between 1:1 and 1:2, suggesting that variable degrees of denitrification affect the $\text{NO}_3\text{-N}$ pool across the sampled locations (Kendall, 1998; Wells et al., 2014) (Fig. 3). A shift from this denitrification line can arise from a variation in the degree of nitrification relative to denitrification, which creates $\text{NO}_3\text{-N}$ with relatively low $\delta^{15}\text{N}$ but consistent $\delta^{18}\text{O}$ values (Granger and Wankel, 2016).

Different field sites have different isotopic signatures and dispositions along the denitrification line (Fig. 3). KM and RE have $\text{NO}_3\text{-N}$ derived from organic sources, with the highest enrichment values due to denitrification. In contrast, DG has the least isotopically enriched values, with locations mainly characterised by a nitrification signal. The higher enrichment at KM with respect to RE, may indicate a higher net denitrification at KM and therefore an enrichment in both $\delta^{18}\text{O}\text{-NO}_3$ and $\delta^{15}\text{N}\text{-NO}_3$, with a shift upwards along the denitrification line (Wells et al., 2016). However, it could also result from variability (e.g. a slightly different “starting point” of the $\text{NO}_3\text{-N}$ signature between the two farms) due to a different history of mixing processes which modify the isotopic composition. Most locations in AA lie near the intercept of the denitrification line, indicating a homogenous organic source and negligible net denitrification. However, two AA piezometers have $\delta^{18}\text{O}\text{-NO}_3$ values high enough to be attributed to synthetic fertilizer, while a third piezometer and section of the open drainage shows a predominance of nitrification processes, with a shift towards lower $\delta^{15}\text{N}\text{-NO}_3$ values from the denitrification line. CD is similar to AA, with a homogeneous organic $\text{NO}_3\text{-N}$ and low/absent net denitrification.

The N_2O isotope data fall within the range of values for freshwaters (Snider et al., 2015) and further confirm the importance of denitrification across the farms. Farm N_2O signatures can be attributed to reduction (Li et al., 2014), indicating that denitrification occurs on every farm, but to different extents.

4.4. Ranking the N attenuation potential of the sites

As Fig. 5 includes both nitrate and ammonium attenuation it goes beyond the present conceptual diagram of Coyle et al. (2016).

After collating all datasets from the present study, three groups emerge. As can be seen from Fig. 5 there is a spread in the location of these sites within both figures. Groups emerge as follows: 1) (KM and RE) Low $\text{NH}_4\text{-N}$ concentration and high denitrification potential, 2) (DG) Low $\text{NH}_4\text{-N}$ concentration and high nitrification potential, 3) (AA and CD) High $\text{NH}_4\text{-N}$ concentration and low denitrification potential. This means that the highest ranked sites in terms of N attenuation were those in Group 1 i.e. KM and RE. From Fig. 5 (left) it can be seen that this group has a higher complete denitrification capacity and from Fig. 5 (right) such sites have a higher attenuation of $\text{NH}_4\text{-N}$. The lowest ranking sites in terms of N sustainability are those in Group 3. The conceptual diagram clearly shows that shallow disruption techniques (e.g. moles and gravel moles) installed within the top 1 m of the soil profile negatively affect the N attenuation potential of the soil profile. Deeper groundwater systems do not negatively affect the N attenuation potential of the soil profile.

Other studies should utilise Fig. 5 and include data on drainage class, drainage design (if present), completeness of denitrification, rate of denitrification and $\text{NH}_4\text{-N}$ attenuation. For example, Jahangir et al. (2012a, HS) results have been added to Fig. 5. These results were from a moderately drained site without land drainage. Plotted results from that study exhibit another type of signal with less complete denitrification and greater N_2O losses and some $\text{NH}_4\text{-N}$ losses. The conceptual diagrams can be used as a tool to highlight the consequences of draining the HS site (both cases can be considered i.e. GW or SW). If drainage was installed on the HS site the tool shows that the levels of N_2O are likely to increase with higher associated $\text{NH}_4\text{-N}$ losses. The conceptual diagram can therefore be used to rank any site in terms of N sustainability and in addition be used as a management tool to inform likely outcomes with respect to installation of land drainage (GW versus SW) on any site.

5. Conclusions

Five gley soils were artificially drained and water from end-of-pipe, shallow groundwater and open ditch locations sampled for dissolved gas (N_2O), hydrochemical species and stable isotopes

(NO₃ and N₂O). Both soil N surpluses and (organic) source were consistent across the sites, but the soil N attenuation potential differed across sites. Deep groundwater drainage systems maintain their soil N attenuation potential but installation of shallow drainage systems can cause a negative shift, resulting in loss of this function, pollution swapping and increased water quality impacts from nutrient loadings in drainage. From this detailed work an N sustainability tool for any site, which presents the relationship between drainage class, drainage design (if present), completeness of denitrification, rate of denitrification and NH₄-N attenuation was developed. This tool allows a comparison or ranking of sites in terms of their N sustainability. The tool can also be used pre-land drainage and presents the consequences of future artificial land drainage on water quality and gaseous emissions at a given site.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jenvman.2017.11.069>.

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