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Exploring the relationship between groundwater geochemical factors and denitrification potentials on a dairy farm in south east Ireland.

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ABSTRACT

Nitrate (NO_3^-) loss from agriculture to shallow groundwater and transferral to sensitive aquatic ecosystems is of global concern. Denitrifying bioreactor technology, where a solid carbon (C) reactive media intercepts contaminated groundwater, has been successfully used to convert NO_3^- to di-nitrogen (N_2) gas. One of the challenges of groundwater remediation research is how to track denitrification potential spatially and temporally within reactive media and subsoil. First, using $\delta^{15}N/\delta^{18}O$ isotopes, eight wells were divided into indicative transformational processes of ‘nitrification’ or ‘denitrification’ wells. Then, using N_2/argon (Ar) ratios these wells were divided into ‘low denitrification potential’ or high denitrification potential’ categories. Secondly, using falling head tests, the saturated hydraulic conductivity (K_{sat}) in each well was estimated, creating two groups of ‘slow’ (0.06 m day^{-1}) and ‘fast’ (0.13 m day^{-1}) wells, respectively. Thirdly, two ‘low denitrification potential’ wells (one fast and one slow) with high NO_3^- concentration were amended with woodchip to enhance denitrification. Water samples were retrieved from all wells using a low flow syringe to avoid de-gassing and analysed for N_2/Ar ratio using Membrane Inlet Mass Spectrometry. Results showed that there was good agreement between isotope and chemical (N_2/Ar ratio and dissolved organic C (DOC)) and physio-chemical (dissolved oxygen, temperature, conductivity and pH) parameters. To explain the spatial and temporal distribution of NO_3^- and other parameters on site, the development of predictive models using the available datasets for this field site was examined for NO_3^-, Cl^-, N_2/Ar and DOC. Initial statistical analysis was directed towards the testing of the effect of woodchip amendment. The analysis was formulated as a repeated measures analysis of the factorial structure for treatment and time. Nitrate concentrations were related to K_{sat} and water level ($p<0.0001$ and $p=0.02$ respectively), but did not respond to woodchip addition ($p=0.09$). This non-destructive technique allows elucidation of denitrification potential over time and could be used in denitrifying bioreactor technology to assess denitrification hotspots in reactive media, while developing a NO_3^- spatial and temporal predictive model for bioreactor site specific conditions.

Keywords: bioreactor; denitrification; isotope; MIMS; nitrate; groundwater; Water Framework Directive.

1. Introduction

Excess reactive nitrogen (N), such as nitrate (NO_3^-) and ammonia (NH_3), which contribute to eutrophication of aquatic/terrestrial ecosystems and the potent greenhouse gas, nitrous oxide (N_2O), are of global concern (Stark and Richards, 2008). The loss of N from agricultural land to a waterbody is a serious concern in river basin management in many countries (Kurz et al., 2005).

Subsoil denitrifying bioreactors are used to remediate shallow groundwater NO_3^- pollution from point sources, and comprise organic carbon (C) media placed in the flow path of NO_3^- contaminated groundwater. The C in the media acts as an energy source to support denitrification and the conversion of NO_3^- into di-nitrogen (N_2) and N_2O gases (Carmichael, 1994), or through a dissimilatory nitrate reduction to ammonium (NH_4) (DNRA) pathway. The application of such reactive media has been applied in permeable reactive barriers (denitrification walls) (Schipper et al., 2004, 2005; Robertson and Merkley, 2009), drain pipe installations (Jaynes et al., 2004), soil reactive layers, effluent beds and wetlands (van Driel et al., 2006; Robertson and Schiff, 2008; Robertson and Merkley, 2009; Hien et al., 2010).

A knowledge gap in denitrifying bioreactor research is the methodological constraints that prevent the direct measurement of denitrification within a bioreactor, the identification of 'denitrification hotspots', and denitrification potential changes over time. To overcome such limitations, studies have calculated NO_3^- removal rates in laboratory experiments with reactive media of different ages (Robertson, 2010), or by quantifying the performance of bioreactors over time (Schipper and Vojvodic-Vukovic, 2001). As monitoring of NO_3^- removal in bioreactors is performed using narrow diameter wells, a methodology to determine denitrification potential that uses this existing well network may be beneficial.

Whereas natural abundance stable isotopic techniques identify possible NO_3^- sources and transformational processes in a monitoring well, N_2/argon (Ar) ratios point to denitrification potential in the same well. As NO_3^- sources have distinct nitrogen (δ

^{15}N) and oxygen ($\delta^{18}O$) isotopic compositions, N sources, such as chemical fertilizer, manure, and atmospheric deposition (Kendall, 1998); and processes such as denitrification (Aravena and Robertson, 1998; Fukada et al., 2004) and nitrification (Kendall, 1998) can be ascertained in a groundwater monitoring well. Groffman et al. (2006) reviewed methodologies to determine the spatial and temporal extent of denitrification potential and suggested that direct N_2 and N_2/Ar measurements in aquatic and marine systems using Membrane Inlet Mass Spectroscopy (Kana et al., 1998) should be investigated further. The novelty of this high through-put technique is that it requires a small sample of groundwater (< 10 ml); it eliminates a manned degassing step, and has an error of < 0.5% for N_2 and Ar concentrations across a wide range of temperature equilibriums.

The objectives of the current study, based on a dairy farm with shallow groundwater NO_3^- in south east Ireland, were to:

1. Identify different NO_3^- sources and transformational processes within a monitoring network using natural abundance
2. Identify high/low denitrification potential wells using N_2/Ar ratios
3. Investigate N_2/Ar ratios over time in: low/high denitrification wells and C enhanced low denitrification wells with different saturated hydraulic conductivies, K_{sat}.
4. Determine factors of importance in the development of predictive spatial and temporal distribution models for groundwater geochemical factors (nitrate and chloride) and denitrification potentials (N_2/Ar, dissolved organic C (DOC), total organic C (TOC)) using K_{sat} and other variables.

2. Methods

2.1 Study site description

The 20 ha study site was situated on a dairy farm 60.8 ha in size, located at Johnstown Castle, Wexford, south east Ireland (latitude 52º 12 N, longitude 6º 30 W) (Fig 1). This location has a temperate maritime climate, with rainfall ranging from 1000 to 1400 mm and a mean annual temperature of 9.6 ºC. The site comprises mature, medium permeability till overburden (K_{sat}, 5 x 10^{-8} m s^{-1} to 5 x 10^{-4} m s^{-1}), which is heterogeneous and morainic in nature. Vertical unsaturated travel times (months to years) on site varies for each well based on unsaturated zone thickness, effective rainfall (600 mm) and effective porosity (η_e) (from 5 to 30%) (Fenton et al., 2010). The soil is underlain by an unproductive, low conductivity pre-Cambrian greywacke, schist and massive schistose quartzites that have been subjected to low-grade metamorphism. Depth to bedrock on site is approximately 12 m. The study site consists of eight wells (25 mm LDPE casing; Van Walt Ltd, Surrey, U.K.) installed to shallow groundwater (mean drilling depth was 6.3 m), using rotary drilling (60 mm in diameter) – using a Giddings soil excavation rig to several metres below water strike.

2.2 Isotopic signatures

Using a subset of isotopic results from Baily et al. (submitted), the occurrence of denitrification in April (spring), August (summer) and December (autumn) of 2008 in the studied wells was determined. Baily et al. (submitted) showed that the spatial pattern of NO_3^- in shallow groundwater differs, but, as the mild and moist climate present on this site allows biological processes to continue all year round, the temporal pattern is relatively constant. The temporal nature of the site allowed the current study to be carried out at any time of the year. A summary of results from the Baily et al. (submitted) study is presented in Table 1.

2.3 K_{sat}, watertable height and effective rainfall

The K_{sat} of each well was calculated using the Bouwer and Rice slug injection test method (Bouwer and Rice, 1976). A mini electronic diver (Van Walt, U.K.), set at a 0.5 s resolution, collected drawdown data. The linear part of the response curve was tested, after which the influence of the filter pack had dissipated. Whereas isotopic results identified the shallow groundwater NO_3 source and differentiated wells into 'nitrification' and 'denitrification' transformational categories, K_{sat} divided such wells further into high and low permeability within medium permeability tills. Wells were dipped for watertable depth each day to ensure the screened intervals of the wells were saturated at all times. Daily meteorological data was collected from the Johnstown Castle Weather Station, which is located on the farm. To estimate daily effective rainfall, temperature, total rainfall, wind speed, solar radiation and humidity were inputted into a hybrid model designed for grassland in Ireland (Schulte et al., 2005). This was to investigate recharge to shallow groundwater during the experiment and to elucidate the effects of dilution on NO_3^- concentration. The major mechanism of NO_3^- remediation is dilution and denitrification. If denitrification is dominant, isotope composition is heavier in times of high recharge.

2.4. Water samples

Use of peristaltic or low flow pumps can be limiting in bioreactor studies due to the inner diameter of wells. Such equipment can cause degassing of water samples and make them unsuitable for use in groundwater investigations. To overcome de-gassing, in each well, gas impermeable tubing, with an inner diameter 5 mm, was installed to the centre of the screen interval. At surface level, a three-way stop cock and 50 ml syringe were attached. To elucidate potential denitrification in the screened interval of each well based on dissolved N_2 and the N_2/Ar ratio (Kana et al., 1998; An et al., 2001), three water samples at selected sample dates were taken (24th -25th and 27th-28th August, 1st, 4th, 10th, 17th, 24th, 30th September, 8th, 16th, 28th October, 5th November, 2009). Water samples were transferred from the syringe to a 12 ml Exetainer® (Labco Ltd, U.K.) filled from the base of each container, overfilled, and then sealed to avoid any air entrapment with a butyl rubber septum. Samples were then placed upside down under water (below the average groundwater temperature of 12ºC) in an ice box, transported to the laboratory, and kept in a cold room at 4°C prior to analysis. Dissolved N_2, O_2 and Ar were analyzed using a Membrane Inlet Mass Spectrometry (MIMS) at the temperature measured (11°C) during groundwater sampling (Kana et al. 1998).

Calculation of excess N_2 was after Weymann et al. (2008), using 15ºC water bath temperature, pressure 755 mm HG, based on elevation of site above sea level and a headspace temperature of 15º. In addition, Reaction Progress (RP), representing the extent of NO_3^- elimination, was calculated after Böhlke et al. (2002) by dividing the denitrification product, N_2 (considering N_2O production was negligible as reported by Khalil and Richards (2010)), by the initial concentration of NO_3^- and excess N_2.

Nutrient concentrations of water samples were determined using a Thermo Konelab 20 analyser (Technical Laboratory Services, Ontario, Canada) for NO_2-N, total oxidised N (TON-N), ammonium-N (NH_4-N), chloride (Cl^-), total dissolved nitrogen

(TDN), total phosphorus (TP) and calcium (Ca^{2+}). NO_3-N was determined by subtracting NO_2-N from TON. Water samples were collected in polyethylene screw top bottles and filtered through a 0.45 μm filter membrane. In addition, other parameters were taken to investigate if denitrification is a viable pathway for NO_3^- reduction. pH, conductivity (cond, μS cm^{-1}) and temperature (temp, ºC) were measured in the field using a multi-parameter Troll 9500 probe (In-situ, Colorado, U.S.A.) with a flow through cell. Dissolved organic carbon and TOC were also measured using a TOC-V Series (Shimadzu, Kyoto, Japan). The metal content of the water samples (copper (Cu), iron (Fe), magnesium (Mg), potassium (K) and zinc (Zn)) were determined by aqua regia digestion using a Gerhard Block digestion system (Cottenie and Kiekens, 1984) and analysed using an ICP VISTA-MPX (Varian, California, U.S.A.).

2.5 Solid carbon enhancement

Washed, untreated woodchip (WC) (10 g, 1-2 mm in length) was packed loosely into a filter sock (Eijelkamp, the Netherlands) approximately 0.2 m in length and 0.02 m thick. This was cable tied and installed in the screened interval of two wells (L1 (WC) and L3 (WC)) with high NO_3^- concentration, a 'low denitrification potential' signal from N_2/Ar analysis and with low (L1 (WC)) and high (L3 (WC)) K_{sat} with moderate permeability tills.

2.6 Statistical analysis

To explain the spatial and temporal distribution of NO_3^- and other parameters on site, the development of predictive models using the available datasets for this field site was examined for NO_3^-, Cl^-, N_2/Ar and DOC. As a first step, statistical analysis was directed towards the testing of the effect of woodchip enhancement in Wells L1 (WC) and L3 (WC). The analysis was formulated as a repeated measures analysis of the factorial structure for treatment and time. Statistical analysis was undertaken with group variables: WC (L1 (WC) and L2 (WC)) and all other wells were set up as a fixed, treatment effect in the analysis using SAS V.9 (2003) software. A factorial model with days and treatment (WC or other wells) and their interaction was developed. As readings within each well were correlated and as the time between sampling events varied, a spatial type covariance structure was fitted across days (14 days in total, between 24th August 2008 and 5th November 2009). Mixed models were used to account for the repeated measures in each well and for heterogeneous variance within treatments. As previous work (Fenton et al., 2009) correlated K_{sat} as an important parameter to explain denitrification, testing it for inclusion as a covariate in any analysis was essential for an unbiased test of the treatment effect. Other covariates were also tested.

A number of covariates were available (K_{sat}, O_2 and depth to watertable) and these were tested for inclusion in the model to remove possible bias and for their potential role in a predictive model. As the number of K_{sat} values varied spatially but not temporally, and the relationship between variables examined and K_{sat} was statistically significant, apparent non-linearity in the examined relationships was modelled by a nonlinear regression fitted with mixed model equations using Proc Nlmixed (SAS, 2003). Residual checks were made to ensure the approach used, but did not violate the assumptions of the analysis. Transformation was used as required for the variable being analysed.

3. Results

3.1 K_{sat}, watertable depth and effective rainfall

The K_{sat} on site for each well is presented in Table 2. Combining such results with isotopic data from Table 1 allowed the wells to be paired, e.g. Wells L1 (WC) and L2. Both wells had the same ‘low denitrification potential’ signal and both had a low K_{sat} of 0.06 m day^{-1}. Similarly, Wells L3 (WC) and L4 had a ‘low denitrification potential’ signal, but had a high K_{sat} of 0.13 m day^{-1}. Wells H1-H3 were identified by isotope analysis as ‘high denitrification potential’ wells and had a very low K_{sat}, allowing enough time for denitrification to occur. The depth to watertable during the experiment was consistently above the screened interval depth, ensuring the woodchip was saturated throughout the experiment (Table 2).

Using the K_{sat} of each well, a uniform hydraulic gradient of 1% and effective porosity of 5%, effective velocity ranged from 0.001 to 0.02 m day^{-1}. This is the equivalent of 0.05 to 0.78 years required to travel 5 m down gradient of the well network. The experiment lasted for 0.24 years and water movement in each well was very slow during this period.

3.2 Water samples

The N_2/Ar signal of ‘low denitrification potential’ was changed in well L1 (WC) by woodchip addition. This was associated with an unchanged mean Cl^- concentration and a pronounced decrease in NO_3^- concentration during the experiment, indicating denitrification. Chloride release from the woodchip was also expected, showing interaction with the contaminated water and the well. Despite the N_2/Ar signal of ‘low denitrification potential’ in wells L2 – L5, low mean Cl^- concentration with pronounced decreases in NO_3^- concentration was observed. This indicated possible dilution in ‘low denitrification potential’ wells L2-L5 (Table 2). The isotope data from April to August, the ‘low denitrification potential’ well L1 (WC) and all ‘high denitrification potential’ wells had composition values higher in August than in April. For ‘low denitrification potential’ wells L2, L4 and L5, this decreased, with no change in L3 (WC). Therefore, some dilution occurred in Wells L2, L4 and L5. Recharge occurred from day 5 to 24. N_2/Ar ratios, NO_3^- and Cl^- concentration throughout the experiment for all wells are presented in Fig 2. Looking at isotopic compositions from Table 1, values tended to be higher in the N_2/Ar results for ‘low denitrification potential’ well L3 (WC), with high K_{sat}. As expected from the isotopic results, ‘high denitrification potential’ wells (H1-H3) had low mean Cl^- and NO_3^- concentrations, confirming natural abundance results i.e. transformational process signal of denitrification (Table 2).

A denitrification potential background N_2/Ar ratio based on minimum dissolution of entrapped air in the groundwater sample was found to be 37.68 (Weymann et al., 2008). Denitrification occurs above this value in the groundwater. Between ‘low denitrification potential’ wells L1 (WC) and L2, well L1 (WC) after C enhancement consistently demonstrated higher denitrification potential. Again, between ‘low denitrification potential’ wells L3 (WC) and L4, well L3 (WC) consistently demonstrated higher denitrification potential. Both groups had different K_{sat}, but K_{sat} was the same within each group. Among the wells with low K_{sat}, well L1 (WC) showed greatest denitrification potential. In ‘high denitrification potential’ wells, the N_2/Ar ratios were consistently above 40.

The extent of denitrification in a water sample is the excess N_2, accounting for the solubility and excess air. Conforming to results derived from isotopic signatures, the average NO_3-N, represented as excess N_2, was found to be higher in ‘high denitrification potential’ wells compared with ‘low denitrification potential’ wells. However, the mean amount of NO_3 removal due to denitrification in all wells was small (Table 3). For C enhanced wells and ‘high denitrification potential’ wells, this mean NO_3^- removal due to denitrification was approximately 1 mg NO_3-N L^{-1}. Solid C emplacement in ‘low denitrification potential’ wells L1 (WC) and L3 (WC) only resulted in a small increase in the denitrification potential. Denitrification progress reduces the amount of NO_3^-, but calculated RP mostly produced similar results for the full extent of NO_3^- elimination (Table 3). In ‘low denitrification potential’ wells, the RP varied from 0 to 0.06 and was highest in the wells containing WC. It increased the most in ‘high denitrification potential’ wells, which enhanced reduction of NO_3^- from 18 (H2) to 91% (H3).

In Fig. 3a, the ‘low denitrification potential’ wells reached steady state early in the experiment, with no changes after approximately 10 days. The ‘low denitrification potential’ well L1 (WC), however, continued to increase throughout the experiment. For the ‘high denitrification potential’ wells in Fig. 2, well H2 showed a constant reduction of NO_3^- throughout the experiment, with wells H1 and H2 showing reduction at lower rates. The ‘low denitrification potential’ well L5 showed high NO_3^- reduction and this well was an intermediary between ‘low denitrification potential’ and ‘high denitrification potential’ wells.

Dissolved oxygen in ‘high denitrification potential’ wells were generally below 5 mg L^{-1}, with well L1 (WC) also falling within the low DO group. As a result of low DO, Fe and Mn in these wells can dissolve more readily. Fe and Mn concentration was highest in these wells (> 0.01 mg L^{-1}). In the ‘low denitrification potential’ wells, DO ranges varied considerably, and Fe and Mn were generally at this 0.01 mg L^{-1} concentration (Table 3). The pH ranges for the wells in this study ranged from 5.5 to 7.5. Conductivity and temperature ranged from 200 to 500 µS cm^{-1} and from 10ºC to 15ºC, respectively. Mean concentration of DOC in all wells, except well L3 (WC), was below 5 mg L^{-1}.

3.3 Identification of covariates of importance in predictive models for NO_3-N, Chloride, N_2/Ar and DOC.

Covariates were tested and K_{sat} and water level in the well at the time of sampling were found to be important and required for unbiased estimation of NO_3-N, Cl, N_2/Ar and DOC. Plotting of the responses (NO_3-N, Cl, N_2/Ar and DOC) against K_{sat} comfirmed its importance, and the water level in the well at time of sampling proved important for only some variables (i.e. NO_3-N and TOC). For a K_{sat} adjusted test of the treatment effect (C enhanced wells versus all other wells), an ANOVA-type model was used with those values of K_{sat} that were replicated in the observations (one for each well). This gave the most general adjustment for K_{sat} fitted as a categorical covariate. For NO_3-N, K_{sat} and a quadratic effect of water level were found to be important ($p<0.0001$ and $p=0.02$ respectively), but there was no evidence for a C enhancement treatment effect ($p=0.09$). This relationship applies to all wells as covariates were fitted to an analysis model containing the experiment structure (treatment and day). Therefore, data from wells with and without C enhancement are included. Where a covariate is significant, this adds some explanation over and above such structural factors. Although the denitrification potential in the C enhanced wells changed, the nitrate removal was small during the study period.

The observed means, adjusted for covariates, for NO_3-N were 4.8 mg L^{-1} for woodchip wells (L1 (WC) and L3 (WC)) and 4.0 mg L^{-1} all other wells in the ‘low denitrification potential’ category. Interpretation of the outcome for the treatment is not straightforward as replication of the woodchip addition was limited to two, but the outcome of the test could be regarded as marginally significant.

From a previous study (Fenton et al., 2009), it was clear that K_{sat} is important to explain the spatial pattern of NO_3-N in glaciated till subsoils, therefore it was necessary to include it in the exploratory analysis models to reduce the danger of spurious relationships emerging for other factors. In order to use all the K_{sat} information, a nonlinear regression was used to fit K_{sat}. Smooth curves proved unsatisfactory because of the small number of K_{sat} values (this parameter does not change over time in saturated conditions and is, therefore, limited to the number of well screens used within an experiment i.e. eight) relative to the number of parameters required, and, ultimately, a broken straight line fit was used to capture the information. Having accounted for K_{sat} in this way, a significant fit for a curved (quadratic) relationship between NO_3-N and water level (likelihood ratio test, p=0.007) was found. As there is no underlying theoretical relationship in the nonlinear model, its form is not expected to apply generally beyond this experiment, but the model serves to highlight interesting facets of the relationships identified. Fig. 4 shows a plot of the predicted surface defined by K_{sat} and water level for day 54 for wells L1 (WC) and L3 (WC). A plot for untreated wells or any other day would be parallel to this. For Cl, the ANOVA-type analysis showed no treatment effect (p=0.18) and no effect of the covariates tested. The analysis for N_2/Ar showed no effect of the treatment, but a clear quadratic relationship with K_{sat} (p=0.44 and p=0.007, respectively). There was no evidence that water level played a role in explaining the observations for this ratio. The decreasing magnitude of this ratio with increasing K_{sat} (raw data in Fig. 5) appears to reflect the behaviour of NO_3-N. In this case, a nonlinear fit does not offer any more information. For the natural logarithm of DOC, there was a significant treatment effect (p=0.04) with both K_{sat} and water level non-significant. The back-transformed, bias-corrected DOC means were 2.9 mg L^{-1} for woodchip amended wells and 1.85 mg L^{-1} for other wells.

4. Discussion

4.1. N_2/Ar ratio after carbon amendment.

Agriculture, specifically intensively grazed grassland, receiving high loads of organic and inorganic forms, is prone to elevated NO_3^- losses. Molecular N_2 is a benign end product of denitrification, and completes the N cycle in terrestrial and aquatic ecosystems. The interactive effects of C and N sources are important to reduce the knowledge gap associated with denitrification potential in soils, subsoil and waterbodies. The identification of how denitrification changes spatially in subsoil will have consequences for groundwater and surface water protection (Hill et al., 2004). Such information allows the identification of areas where natural NO_3^- reduction in subsoils can actually protect a waterbody (Khalil and Richards, 2010).

Based on chemical stoichiometric relationships, denitrification of one mole of NO_3^- will require 1.25 moles of C. This equates to a mass balance of 1.07 kg of available C per 1 kg of NO_3^-. With approximately 50% of C availability in woodchip (based on bulk density), the treatment of 1 kg of NO_3^- will be approximately 2 to 2.5 kg of woodchip (Fahner, 2002). The woodchip amount used in the current study was considerably less at 10 g and was still limiting, therefore, N_2/Ar ratios with higher peaks could be expected in a bioreactor study. As woodchip amounts used were small, denitrification potential remained similar to ‘high denitrification potential’ wells throughout the experiment. Even at this low amendment rate, the denitrification potential changes were significant. The use of natural abundance and denitrification potential techniques could be used to track the NO_3^- removal efficiency of the reactive media over time. A drop in denitrification potential and NO_3^- removal due to denitrification could indicate a replenishment of media is needed.

Although redox conditions are favourable for denitrification processes in shallow groundwater and riparian areas, there is very little denitrification potential data in the literature (Ross, 1995). In particular, such data is lacking for saturated zones within glaciated subsoils and C enhanced subsoils. On glaciated till subsoils (maximum depth of 0.7 m), a mean N_2/Ar ratio of 40 was found during a C-enhanced incubation study (Khalil and Richards, 2010). In the present study, samples were taken at an average depth of 3 m and N_2/Ar ratios ranged from background (37.6) to 45. Such results were comparable to a nearby shallow groundwater investigation carried out within heterogeneous glacial tills (Fenton et al., 2009). In that study, N_2/Ar ratios ranged from background to 44 at a mean depth of 3.6 m. Jahangir et al. (2010) found N_2/Ar ranges from 40.7 to 52.0, 39.0 to 48.1, 38.5 to 41.9 and 37.8 to 40.4 in subsoils of the present study site, poorly drained grassland site, sand and gravel tillage site and free draining grassland site underlain by limestone, respectively. Wilson et al. (1990) identified the following sequence of N_2/Ar ratios within the Lincolnshire limestone aquifer: atmospheric equilibrium: N_2/Ar = 38, extra air entrainment: N_2/Ar = 41 and denitrification: N_2/Ar = 42 to 55.

4.2. Conditions found in aquifers for denitrification to occur.

Heterotrophic denitrification is controlled by the concentrations of oxygen, NO_3^- and C in shallow groundwater. Where high NO_3^- concentrations are present in such a waterbody (e.g. below an agricultural landscape), the availability of degradable C becomes critical for denitrification to occur. Aerobic microorganisms utilise this labile C to consume oxygen. Huge spatial and temporal variation in N_2O measurements from soil have been found due to changes in soil and subsoil properties such as availability of mineral N (which is a substrate for nitrification and denitrification), oxygen, water content, temperature, pH, redox conditions and the availability of labile carbon (Chapuis-Lardy et al., 2007). In the current study, isotopes identified organic fertilizer as the source of pollution on site from dairy dirty water irrigation (Table 1). After removal of such a point pollution source, on site NO_3^- concentration is maintained though mineralisation in the soil. While N inputs are responsible for NO_3^- concentrations, the proportion of N to be denitrified is controlled by the hydrology and geomorphology (Seitzinger et al., 2006). The kinetics of denitrification at N concentrations >1 mg L^{-1} are independent of concentration. This implies that the rate of denitrification is limited by donor availability. Carbon limitation is evident in the low denitrification potentials of all wells on the site. Total organic carbon concentration decreases with soil depth on site. Ryan et al. (1998) found soil and subsoil denitrification rates varied spatially and temporally soil depths due to the changes in soil moisture and soil NH_4^+-N. Such facts lead to differential denitrification potentials with depth both spatially and temporally, and may be the controlling factor for varied groundwater NO_3^- recharge concentrations.

As the oxygen levels decrease, the pH becomes more acidic, metals (micronutrients Fe and Mn) dissolve, and denitrifying organisms utilise the remaining C as an electron donor. Rivett et al. (2008) found denitrification occurs in aquifers when DO is 2 mg L^{-1} or less, and heterotrophic denitrifying bacteria prefer a pH range from 5.5 to 8.0. Significant denitrification only occurred in the current study below this DO concentration, which is agreement with many studies dealing with agricultural derived NO_3^- plumes (full list in Rivett et al., 2008). The DO values in all wells were much lower than 2 mg L^{-1}, which shows that DO is not limiting for denitrification to occur. The optimum temperature for denitrification to occur is from 25ºC to 30ºC, but studies show a larger range from 2 ºC to 50 ºC (Rivett et al., 2008). Bailey et al. (submitted) argued that low temporal variability in NO_3^- on this site was due to rainfall distribution throughout the year being constant, and a temperate climate allowed microbial process of nitrification and denitrification to continue all year round.

The woodchip used in this study degraded rapidly increasing the DOC concentrations in the C-enhanced wells. With high NO_3^- concentrations also present in these wells, the denitrification potential increased turning such wells from a ‘low denitrification potential’ signal to a ‘high denitrification potential’ signal. Laboratory column tests have shown that DOC released from aged woodchips of two years can deplete O_2 in DO saturated water in 1 hour (Robertson, 2010). In preliminary batch experiments on this site, the DOC release in 24 h reached 50 mg L^{-1} in shaken tests and 40 mg L^{-1} in unshaken tests. In the field, DOC levels of 15 mg L^{-1} and 14 mg L^{-1} were found in wells L3 (WC) and L1 (WC), respectively, in the same period. Rivett et al. (2008) found that DOC in most aquifers is < 5 mg L^{-1}. DOC is first oxidised by DO in the system and any remaining DOC can fuel denitrification. It takes 1 mg C L^{-1} to convert 2.7 mg O_2 L^{-1}. Below 1 mg O_2 L^{-1} denitrification can occur. Dissolved organic carbon requirements to fuel denitrification in each well are presented in Table 3. Dissolved organic carbon deficiencies are present in 'low denitrification potential' wells L2 and L4. Before C enhancement, well L1 (WC) and L3 (WC) had DOC concentrations of 1.1 and 1.4 mg L^{-1}, respectively, and had a 'low denitrification potential' signal. After solid C enhancement, these wells had enough DOC to fuel denitrification.

4.3. K_{sat}

In the saturated zone, K_{sat} remains constant at a particular location but varies spatially, due to the heterogeneity of the aquifer, and between different aquifers and geological units. It may also vary due to anisotropies in the aquifer. The K_{sat} of glaciated tills varies considerably e.g. sandy silty tills in Scandanavia range from 5 x 10^{-9} to 5 x 10^{-4} m s^{-1} (Lind and Lundin, 1990). Clay tills have very low permeability of < 10^{-9} m s^{-1} or, in some Canadian examples, vary from 10^{-11} to 10^{-12} m s^{-1}. Areas of naturally high or enhanced denitrification potential, referred to as 'denitrification hotspots', may in part be due to differential K_{sat}, mobile fractions of groundwater and slow diffusion into the immobile fraction where denitrifiers are active (Schipper et al., 2005). The extent to which K_{sat} controls such processes is unknown. On a mature glacial till field site, Fenton et al. (2009) found that K_{sat} was positively related to mean shallow groundwater (< 10 m below ground level) NO_3^- concentration, i.e. areas with higher K_{sat} values have less time for denitrification to occur and vice versa. Gurwick et al.

(2008) reported that low K_{sat} areas can also be associated with buried organic matter in riparian soil, which transmits water more slowly. These buried layers, in turn, provide a supply of organic matter as an energy source for denitrification. In an enhanced denitrification bioreactor scenario, a solid C source is mixed with soil, which decreases subsurface K_{sat} in the trench. This may occur during construction when compaction or insufficient mixing of soil and C material occurs. The interface between the soil and the denitrification trench may also create preferential flow paths into the reactive media. However, lower K_{sat} zones may establish 'denitrification hotspots' (Parkin, 1987; Jacinthe et al., 1998; Schipper et al., 2005). Another interesting aspect of K_{sat} related research is how it changes within a denitrification wall over time, due to degradation of reactive material and/or changes in overburden (Schipper et al., 2010). Interestingly, high K_{sat} may reduce denitrification due to lower retention times but also it can increase recharge rate, C availability and O_2 supply. Based on K_{sat}, uniform hydraulic gradient (1%) and N removal due to denitrification in each well, the volume of water treated during the duration of the experiment varied in each well as follows: L1 (WC) - 42 L, L2 - 21 L, L3 - (WC) 91 L, L4 - 91 L, L5 - 70 L and H1-H3 - 21 L. Such volumes corresponded with low N removal rates of 0.90, 0.01, 3.20, 0.00, 0.70, 1.08, 0.74 and 2.70 mg NO_3 m^3 for the duration of the experiment passing through a bioreactor 0.02 m in diameter, respectively.

Fenton et al. (2009) showed that mean groundwater NO_3^- was significantly ($p<0.05$) related to groundwater N_2/Ar ratio, redox potential, DO and N_2, and was close to being significant with N_2O ($p=0.08$). In this study, both spatial and temporal data was utilised for NO_3^- prediction, K_{sat} and a quadratic effect of water level were both statistically significant. When amended and no amended wells were compared, this was marginally significant. Other good relationships were found between denitrification potential (N_2/Ar ratio) and K_{sat}.

5. Conclusions

1. Isotopic ratios can be used to select indicative source and transformational processes responsible for NO_3^- occurrence in a well, whereas N_2/Ar ratios can differentiate such wells into ‘high denitrification potential’ and ‘low denitrification potential’ categories. Saturated hydraulic conductivity (K_{sat}) can divide these wells further into different permeability classes.
2. Groundwater samples retrieved using impermeable tubing and a syringe can be analysed quickly, whilst avoiding de-gassing for N_2/Ar ratios using membrane inlet spectroscopy (MIMS). Using this method, the denitrification potential of ‘low denitrification’, ‘high denitrification’ and ‘enhanced denitrification’ wells can be tracked spatially and temporally.
3. Data generated can then be used to develop site specific relationships and predictive models for nitrate, chloride, dissolved organic carbon and N_2/Ar ratios.
4. Such a methodology could be applied to monitored denitrifying bioreactors to identify denitrification hotspots and to examine the denitrification potential of reactive media over time.

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Captions for Figures

Fig 1. Schematic of Dairy farm site with location of woodchip (WC) wells, wells with high (H) and low (L) denitrification potential, NO_3^- ranges and K_{sat} for each well.

Fig 2. Groundwater N_2/Ar ratios, NO_3-N (mg L^{-1}) and Cl (mg L^{-1}) concentrations for low (L1-5) and high (H1-H3) denitrification potential wells over time. WC here signifies presence of woodchip.

Fig 3. A and B Cumulative Excess N_2 in low and high denitrification potential wells

Fig 4. Predicted NO_3-N model using K_{sat} and water level.

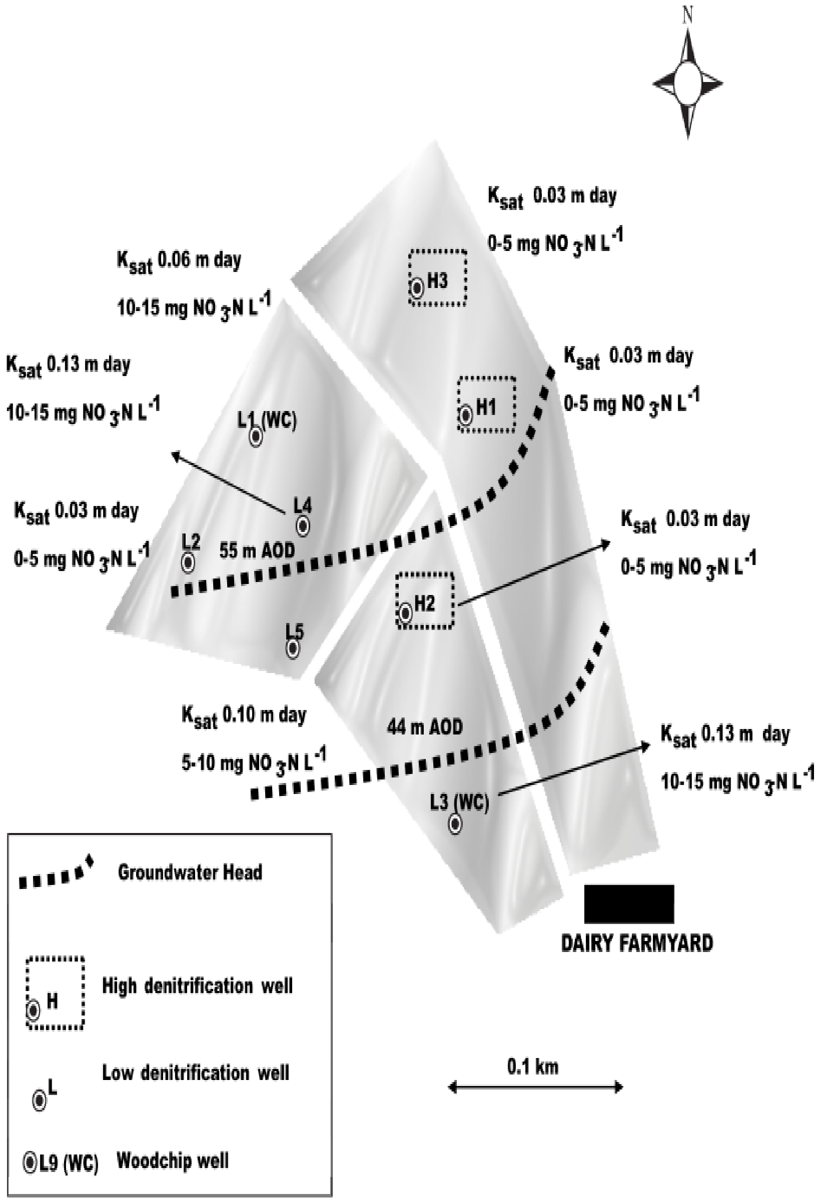
Fig 5. Relationship between physical (K_{sat}) and denitrification (N_2/Ar ratio) parameters

Captions for Tables

Table 1 Background isotopic data, source identification and processes in each well chosen for the present study.

Table 2 Nitrate, chloride and N_2/Ar min, max and mean for all wells during the study period.

Table 3. DO, Fe, Mn, DOC and mean denitrification data for all wells during the study.



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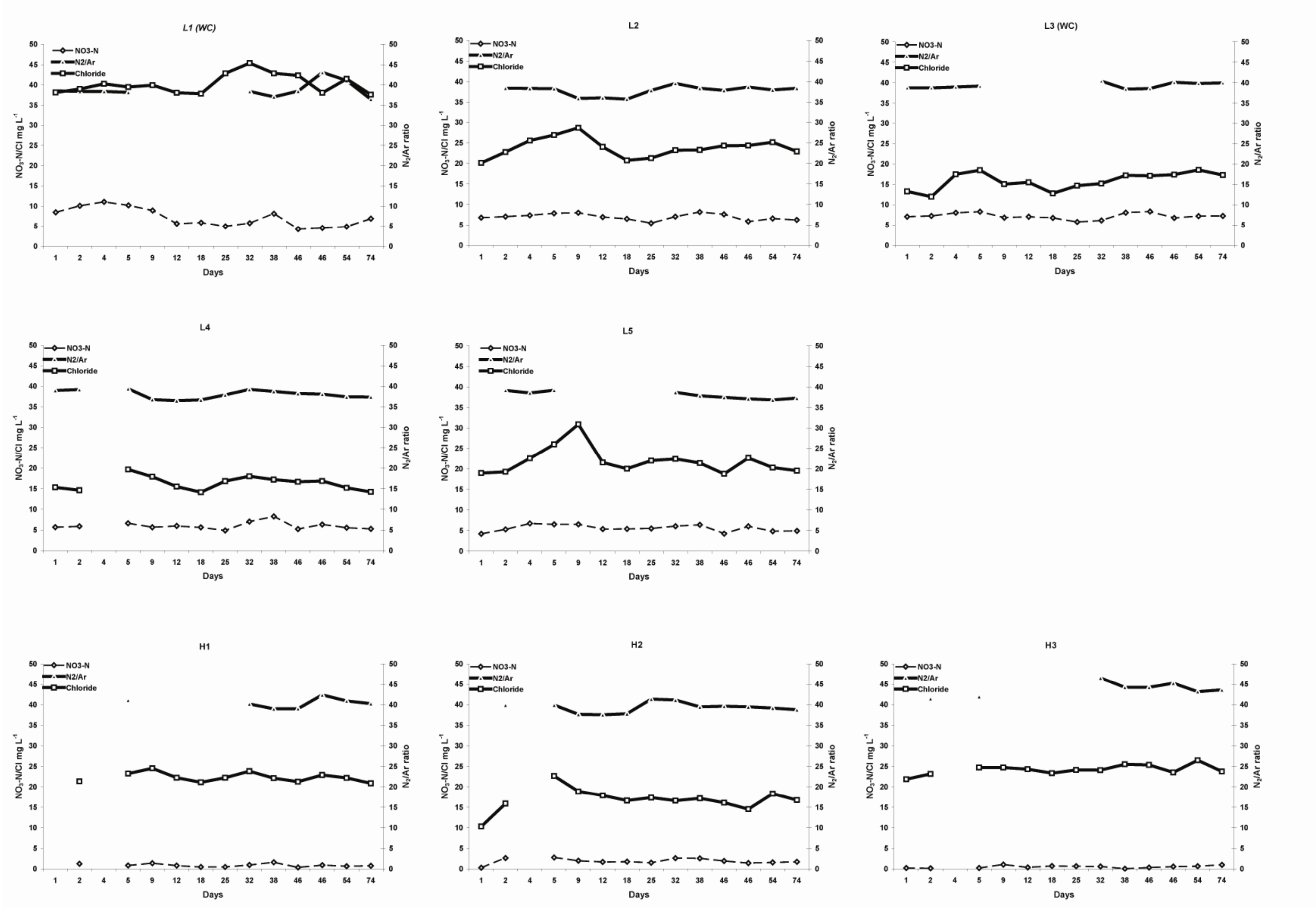

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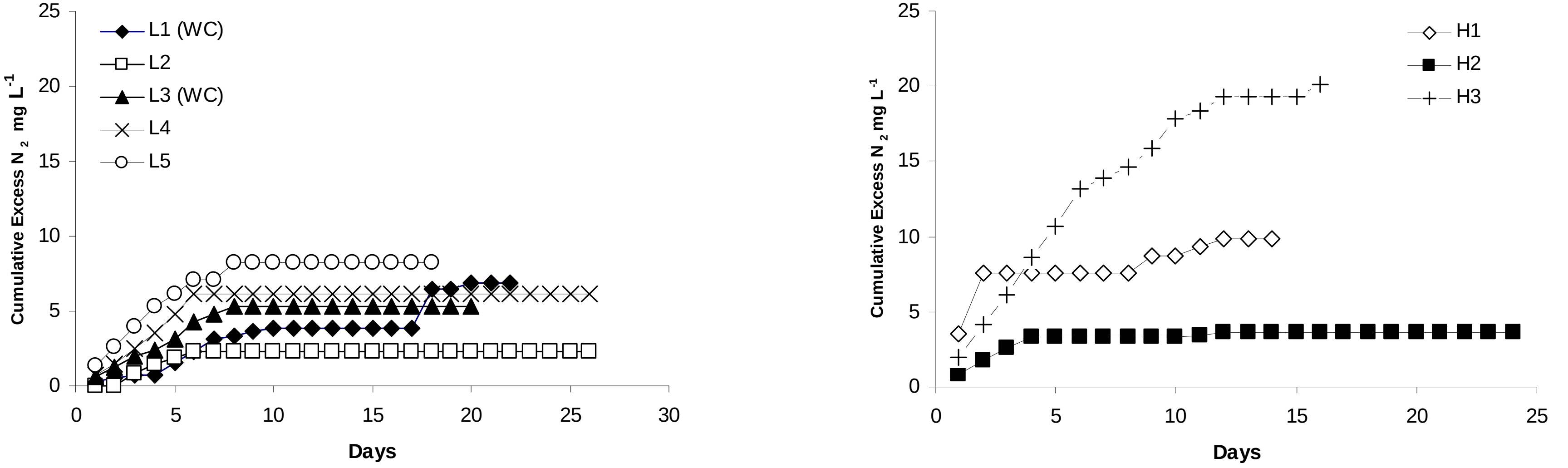
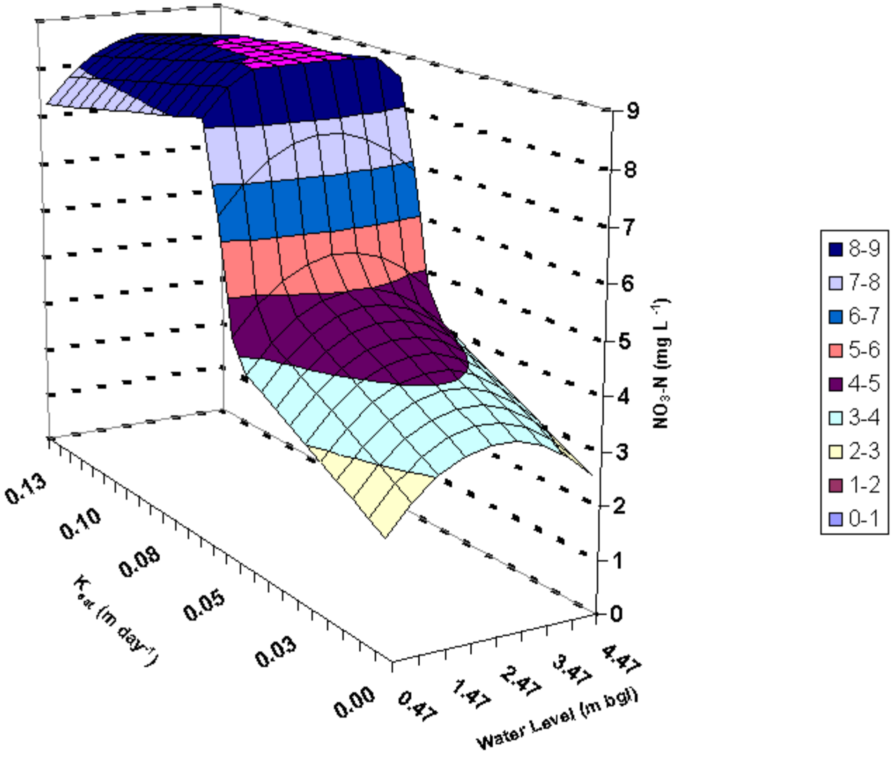


A) 'Low denitrification potential' wells

B) 'High denitrification potential' wells

Fig 3. A and B Cumulative Excess N_2 in low and high denitrification potential wells



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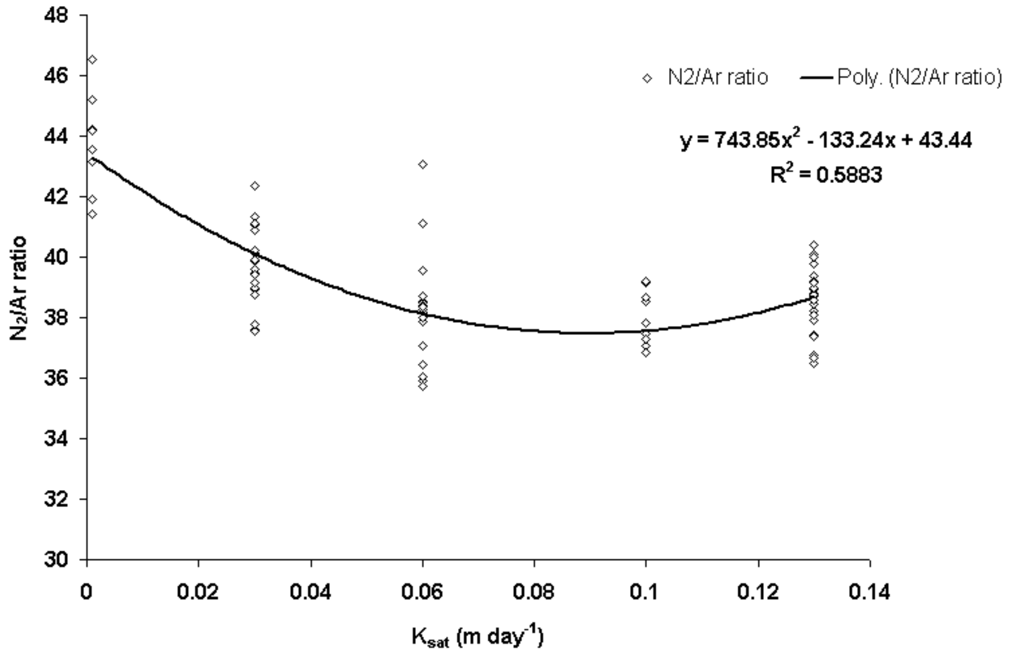

Fig 5. Relationship between physical (K_{sat}) and denitrification (N_2/Ar ratio) parameters.

Table 1 Background isotopic data, source identification and processes in each well chosen for the present study.

Well	NO_3-N	δ^{15}N	δ^{18}O	NO_3-N	δ^{15}N	δ^{18}O	NO_3-N	δ^{15}N	δ^{18}O	Source of Nitrate	Transformational Process
	mg L^{-1}	‰	‰	mg L^{-1}	‰	‰	mg L^{-1}	‰	‰		
	April 2008			August 2008			December 2008				
L1 WC	9.8	6.8	5.3	12.9	7.1	5.7	12.7	8.9	8.7	Manure	Nitrification but no denitrification
L2	8.4	7.3	4.6	8.5	6.7	4.1	8.6	7.7	5.6	Manure	Nitrification but no denitrification
L3 WC	12.9	6.8	1.4	13.0	6.6	1.4	10.7	7.3	3.7	Low manure signal	Nitrification but no denitrification
L4	13.5	7.6	5.4	11.4	7.7	4.8	11.1	8.2	9.6	Manure	Nitrification but no denitrification
L5	7.3	9.1	8.1	7.6	7.8	4.4	7.3	8.4	5.7	Manure/sewage	Soil nitrification
H1	3.7	9.2	6.1	1.8	11.4	8.1	0.8	11.7	7.9	Manure	Denitrification
H2	4.2	11.7	9.6	3.3	13.1	11.6	2.6	16.2	14.7	Manure	Lots of denitrification
H3	0.3	7.6	4.6	0.3	16.2	14.2	0.1	16.7	16.1	Manure	High nitrification, volatilisation and denitrification

Table based on Baily et al. (submitted)

Table 2 Nitrate, chloride and N_2/Ar min, max and mean for all wells during the study period.

Well	WT[b]	Screen[c]	Nitrate	Nitrate	Nitrate	Chloride[a]	Chloride	Chloride	N_2/Ar	N_2/Ar	N_2/Ar	DOC	TOC
	Mean		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Mean	Mean
	m bgl	m bgl	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	ratio	ratio	ratio	mg L^{-1}	mg L^{-1}
‘low denitrification potential’ wells													
L1 (WC)	2.6	3.4	4.2	11.0	7.1	37.6	45.3	40.2	36.4	43.0	38.8	2.9	30.9
L2	2.9	5.9	5.4	8.1	6.9	20.0	28.6	23.8	35.7	39.5	37.8	1.2	7.1
L3 (WC)	2.5	4.9	5.7	8.3	7.1	11.8	18.5	15.8	38.5	40.4	39.3	7.0.	57.1
L4	1.3	3.0	4.8	8.2	5.9	14.1	19.6	16.3	36.5	39.4	38.0	1.4	6.2
L5	4.6	7.8	4.1	6.7	5.5	18.7	30.8	21.6	36.8	39.2	38.0	3.2	12.8
‘high denitrification potential’ wells													
H1	7.4	8.1	0.3	1.5	0.8	20.8	24.5	22.3	39.0	42.4	40.4	1.7	5.8
H2	0.9	2.5	0.2	2.7	1.8	10.3	22.6	16.8	37.5	41.3	39.3	1.4	6.6
H3	4.0	4.5	0.003	1.0	0.4	21.9	26.5	24.2	41.4	46.5	43.8	1.9	4.7

[a] In Ireland natural background levels of Chloride in groundwater are 18 mg L^{-1}. Concentrations above this are due to influences from the pollution sources on the far

[b] Mean Watertable Height

[c] Top of screen, total Well depth + 1m

Table 3. DO, Fe, Mn, DOC and mean denitrification data for all wells during the study.

Well	DO[a]	Fe[b]	Mn[c]	DOC[d]	DOC[e]	Mean Excess N_2	Reaction Progress
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	Ratio
‘low denitrification potential’ wells							
L1 WC	0.6	3.4	0.7	1.2	2.9	0.55±0.30	0.05±0.06
L2	1.7	10.5	0.0	3.8	1.2	0.02±0.13	0.01±0.03
L3 WC	0.3	5.2	0.0	1.9	7.3	0.88±0.12	0.06±0.06
L4	0.7	8.8	0.0	3.2	1.4	0.00±0.12	0.00±0.02
L5	0.5	6.8	0.0	2.5	3.2	0.25±0.18	0.03±0.05
‘high denitrification potential’ wells							
H1	0.4	0.9	0.0	0.3	1.7	1.29±0.20	0.26±0.26
H2	0.3	4.0	0.0	1.4	1.4	0.89±0.13	0.18±0.18
H3	0.3	4.8	0.2	1.7	1.9	3.22±0.28	0.90±0.91

[a]min, [b]max, [c]mean, [d]required for denitrification, [e]available for denitrification.