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ABSTRACT

Groundwater contamination was characterised using a methodology which combines shallow groundwater geochemistry data from 17 piezometers over a 2 yr period in a statistical framework and hydrogeological techniques. Nitrate-N (NO₃-N) contaminant mass flux was calculated across three control planes (rows of piezometers) in six isolated plots. Results showed natural attenuation occurs on site although the method does not directly differentiate between dilution and denitrification. It was further investigated whether NO₃-N concentration in shallow groundwater (<5 m below ground level) generated from an agricultural point source on a 4.2 ha site on a beef farm in SE Ireland could be predicted from saturated hydraulic conductivity ($K_{sat}$) measurements, ground elevation (m Above Ordnance Datum), elevation of groundwater sampling (screen opening interval) (m AOD) and
distance from a dirty water point pollution source. Tobit regression, using a
background concentration threshold of 2.6 mg NO3-N L⁻¹ showed, when assessed
individually in a step wise procedure, \(K_{sat}\) was significantly related to groundwater
NO3-N concentration. Distance of the point dirty water pollution source becomes
significant when included with \(K_{sat}\) in the model. The model relationships show areas
with higher \(K_{sat}\) values have less time for denitrification to occur, whereas lower \(K_{sat}\)
values allow denitrification to occur. Areas with higher permeability transport greater
NO3-N fluxes to ground and surface waters. When the distribution of Cl⁻ was
examined by the model, \(K_{sat}\) and ground elevation had the most explanatory power but
\(K_{sat}\) was not significant pointing to dilution having an effect. Areas with low NO3
concentration and unaffected Cl⁻ concentration points to denitrification, low NO3
concentration and low Cl⁻ chloride concentration points to dilution and combining
these findings allows areas of denitrification and dilution to be inferred. The effect of
denitrification is further supported as mean groundwater NO3-N was significantly
\((P<0.05)\) related to groundwater N₂/Ar ratio, redox potential (Eh), dissolved O₂ and
N₂ and was close to being significant with N₂O \((P=0.08)\). Calculating contaminant
mass flux across more than one control plane is a useful tool to monitor natural
attenuation. This tool allows the identification of hot spot areas where intervention
other than natural attenuation may be needed to protect receptors.

**Keywords:** nitrate; shallow groundwater; saturated hydraulic conductivity;
contaminant mass flux; denitrification; natural attenuation; Ireland; grassland.

1. INTRODUCTION
Delineation of an elevated nitrate (NO$_3$-N) plume in shallow groundwater is difficult as NO$_3$-N concentration differences may be prevalent over short distances. As a result of high denitrification capacity, NO$_3$-N concentration may be low at the centroid of the plume. Contaminated groundwater in aquifers with low hydraulic conductivity ($K_{sat}$) may represent a long-term threat to groundwater due to long travel times from source to receptor. A shallow watertable allows reduction of nitrate through denitrification before recharge reaches deeper groundwater (Boland et al., 2002). The thickness and permeability of subsoil can control groundwater vulnerability (Lee, 1999). In such shallow groundwater sites reduction of NO$_3$-N through denitrification may provide the basis for remediation. Monitored natural attenuation is a valid method in sites with low permeability and high denitrification capacity, leading to a low vulnerability status. In such scenarios surface water and not deeper groundwater may be a potential receptor for NO$_3$-N pollution.

In spite of efficient nutrient management practices, agricultural activities, such as application methods and storage, are probably the most significant anthropogenic sources of NO$_3$-N contamination in groundwater (Oyarzun et al., 2007). Current agricultural practices (application methods, application rates and storage) while achieving high nutrient efficiency and nutrient management cannot avoid some nutrient losses to surface and groundwater. Contamination of shallow groundwater (<30 m bgl) with NO$_3$-N has been documented in a large number of studies (C. D. A. McLay et al., 2001; Harter et al., 2002; Bohlke et al., 2007; Babiker et al., 2004). To relate different forms of landuse to different shallow groundwater NO$_3$-N concentrations spatially, a variety of statistical techniques, such as multivariate cluster analysis (Hussain et al., 2008; Ismail et al., 1995; Yidana et al., 2008), Tobit and
logistic regression using mean nutrient data (Gardner and Vogel., 2005; Kaown et al., 2007), weights of evidence modelling techniques (Masetti et al., 2008), and ordinary kriging methods (Hu et al., 2005), have been used. Other tools, such as regression models based on conceptual models, link shallow groundwater NO$_3$-N concentration with inventories such as landuse and cattle density (Boumans et al., 2008). Other techniques are employed when both spatial and temporal relationships are considered such as the vulnerability of an aquifer to nitrate pollution through the use of DRASTIC and GLEAMS models (Almasri, 2008; Leone et al., 2007). Spatial and temporal correlations of surface and groundwater were described using t-test analysis to show that surface and groundwater management should be integrated (Kannel et al., 2008). Agri-environmental indicators (AEIs) provide information on environmental as well as agronomic performance, which allows them to serve as analytical instruments in research and provide thresholds for legislation purposes.

Langeveld et al. (2007) investigated AEIs used in various studies: nitrogen use efficiency, nitrogen surplus, groundwater nitrate concentration and residual nitrogen soil concentration, to explain nitrogen management. Results indicated an integrated approach at an appropriate scale should be tested, not forgetting that indicators are simplifications if complex and variable processes.

The land surface around a well which contributes to the water quality at that well may be calculated from: aquifer discharge ($m^3$ day$^{-1}$), aquifer thickness (m) and effective Darcian velocity (m day$^{-1}$). This circular buffer zone contributes direct recharge to a specific monitoring point, such as a borehole or piezometer (Kolpin, 1997). The circular shape is assumed to be homogenous according to its physical properties. If groundwater flow direction is known, any pollution sources down-gradient of the
monitoring point may be discounted. The size of the buffer zone is an important factor and many studies have used different buffer zone radii: (Eckhardt et al., 1995) - 800 m; (Kolpin, 1997) - 200 to 2000 m; (Barringer et al., 1990) – 250 m to 1000 m, (McLay et al., 2001)- 500 m and (Kaown et al., 2007) – 73 to 223 m. A mean diameter is often taken where a large range occurs. In an area with a common landuse nutrient management within this area will be an important factor as well as identifying potential point sources in this zone.

Both qualitative and quantitative methods need to be applied to investigate contaminant concentration patterns and to calculate contaminant mass flux. Contaminant flux can prove that natural attenuation occurs on a site but does not differentiate between dilution and denitrification. Contaminant mass flux across a transect of wells, known as a control plane, has been used to quantify the contaminant load leaving a system (Basu et al., 2006; Bockelmann et al., 2001; Bockelmann et al., 2003; Brusseau et al., 2007; Campbell et al., 2006; Duncan et al., 2007; Hatfield et al., 2004; Kubert et al., 2006). This method allows a quantifiable load of NO$_3$-N leaving a system to be calculated, rather than focusing on a point where shallow groundwater exceeds target or legislative concentration limits such as 11.3 mg NO$_3$-N l$^{-1}$.

Traditional source treatment assessment has focused on the pollution source zone, partial mass removal and the calculation of the source strength (contaminant mass discharge and mass flux). Contaminant plume properties are a combination of source strength, assimilative capacity (differential mass discharge with distance along a plume) and time. This procedure is based on the assumption that source treatment results in a contaminant mass reduction in the source zone. It gives an incomplete
view of potential impacts and there is uncertainty regarding the plume response to partial mass removal (source treatment). Risk reduction is, therefore, uncertain and the associated costs are difficult to ascertain (Jarsjö et al., 2005). The source strength is calculated from groundwater samples, taken at specified time intervals, and the water flow velocity calculated for each well. These data are then inputted into predictive models and the down-gradient concentration in a sentinel well is predicted. The sentinel well is positioned along a compliance plane down-gradient of the control plane and up-gradient of a potential receptor. For the calculation of contaminant mass flux, a number of screened wells along a control plane, which transect the entire contamination plume perpendicular to groundwater flow direction downstream of the pollutant source, are used, as opposed to the standard central line cross section parallel to groundwater flow direction of the plume (Bockelmann et al., 2003). Longitudinal cross sections may over- or underestimate the contaminant mass flux value and this method requires a larger number of piezometers. The contaminant mass flux is then measured directly from the contaminant flow and concentration in the monitoring piezometers. The source strength is interpolated and then inputted into a model for the prediction of down-gradient contaminant concentrations. Natural attenuation rates (dilution and denitrification) may be achieved by the use of two control planes: a control plane to calculate contaminant mass flux (influent) and a compliance plane down-gradient (Kao et al., 2001). Flux-averaged concentrations along the compliance plane must adhere to specified water quality targets.

The aim of this study was to investigate the factors contributing to the occurrence of elevated NO₃-N concentration in shallow groundwater (<10 m) on a section of a beef farm in SE Ireland. A statistical framework, combining mean geochemical and physical data (saturated hydraulic conductivity ($K_{sat}$) measurements, ground elevation
(m Above Ordnance Datum), elevation of groundwater sampling (screen opening interval) (m AOD) and distance from point pollution source (m)) from a grid of 17 piezometers over a 2 year period, was used to identify factors affecting the occurrence of NO₃-N concentration on site.

The contaminant mass flux entering and leaving the site is also assessed through rows of piezometers called control planes to assess the amount of natural attenuation due to dilution and denitrification combined on site. To differentiate between dilution and denitrification occurrence on site chloride (Cl⁻) was also inputted into the model and NO₃/Cl⁻ ratios investigated. Other parameters were sampled on a random date to confirm areas indicative of denitrification.

1.1 INTRODUCTION TO THE STUDY SITE

A 4.2 ha gently sloping (2%) study site, comprising six study plots, was located on a beef farm at the Teagasc, Johnstown Castle Environmental Research Centre, Co. Wexford, Ireland (Figure 1).

The field site is bound to the north by an elevated 3.2 ha grassland sandhill area (71-75 m above ordnance datum (AOD), slope 5%), to the northwest by a 2.8 ha grassland site (71-72 m AOD, slope 2%), and on all other sides by agro-forestry. The dirty water point source was located in this sandhill area. Possible receptors on site are a narrow contour stream and the larger Kildavin River boarding the site (Figure 2). The sandhill and northwest areas are up-gradient and hydrologically connected through shallow flow lines to the 4.2 ha study site approximately 200 m away. Groundwater head contours show groundwater flow direction is towards the six isolated plots (Figure 2).
Two shallow, unlined trapezoidal drains, excavated to a depth of 1 m, with bases ranging from 71.08 m AOD to 70.2 m AOD and 71.10 m AOD to 70.30 m AOD, respectively, were constructed along the northern edge of the plots. This prevents runoff from entering the plots from the elevated up-gradient area. Runoff from the point source flowed directly into these drains. The plots were also isolated laterally to 1 m bgl to prevent cross flows from one plot to the other.

Heterogeneous glacial deposits on the farm vary in thickness from 1-20 m. On site the glacial deposits are < 10 m, underlain by Pre-Cambrian greywacke, schist and massive schistose quartzites, which have been subjected to low grade metamorphism. Outcrop appears just south of the plots and confirms with the shallow nature of the glacial deposits. This results in a differential $K_{sat}$ at depth. The topography is morainic and, in the area of the point source pollution where the elevation is greater than 71 m AOD, consists of both sand and fine loamy till, and has different topographical form and drift composition. Some of this sand may have been soliflucted downslope, resulting in stratification between sand and underlying fine till. The sandhill is well- to excessively drained and consists of deep loamy sands (Figure 2). A sandpit of industrial grade sand is in operation in the area.

Topsoil samples (0 to 0.4 m) contained 22 ± 3.7 % coarse sand, 26 ± 3.6 % fine sand, 34 ± 5.1 % silt and 18 ± 2 % clay and subsoil samples (0.4 to 1.0 m) contained 18 ± 5.3 %, 22 ± 4.2 %, 34 ± 4.5 % and 25 ± 4 %, respectively (Diamond, 1988). Clay content increases with depth on site as sand decreases. Silt content remains the same. Textural changes are not due to pedological processes but to small scale sorting of glacial till. It is this transition between sand and clay that governs $K_{sat}$ heterogeneity at
depth. Subsoils with a high percentage of fines (clay and silt) are classed as having low permeability, poorly sorted subsoils are assigned as having moderate permeability and well sorted coarse grained subsoils (glaciofluvial sand and gravel) have high permeability (Swartz et al., 1999).

In 2005, the first groundwater samples were taken. (The study site was instrumented with piezometers in 2003.) Initially, 30% of all shallow groundwater samples (< 5 m) exceeded NO$_3$-N drinking water quality targets (11.3 mg NO$_3$-N l$^{-1}$). The present model is only applicable to shallow flow lines of the same groundwater age connecting the pollution source to the 1 m screen intervals in all 17 piezometers. (Fenton et al., 2008) investigated the source of pollution and proposed the use of a continuous shallow denitrification trench to intercept contaminated shallow groundwater. A stationary beef dirty water irrigation system, operated on the sandhill for decades until 2004, and was identified as a pollution point source (Figure 2). This small area has been treated uniformly over a long period of time, before and after implementation of the irrigation system. Currently, the site is cut for silage twice a year and is being used to monitor natural attenuation of the elevated groundwater NO$_3$-N plume migration, position and concentration on site.

2. MATERIALS AND METHODS

2.1 NUTRIENT MANAGEMENT

A detailed account of organic and inorganic application and silage production on the sandhill, northwest and field site was kept for 2006-2007. Nutrient records confirm uniform treatment in subsequent years. The nitrogen (N) surplus was calculated for each area. These areas are not grazed.
2.2 MONITORING ON SITE

Partially penetrating piezometers (n=17) (25 mm LDPE casing; Van Walt Ltd, Surrey, U.K.) were installed in a grid to shallow groundwater of multilevel depths using rotary drilling (60 mm) (Giddings soil excavation rig, Colorado, USA) to several metres below the groundwater table. The average piezometer drilling depth was 3.2 m bgl (Table 3), with a 1 m screen at the bottom of each well. The screen was covered with a filter sock, surrounded with washed pea gravel, and sealed with bentonite above the gravel. Two multi level drilling depths were used, from 63 m to 67 m above ordnance datum (AOD), and from 67 m to 70 m AOD, respectively, were drilled.

Drilled holes were back-filled with gravel (3-6 mm diameter) to 0.5 m above the screen, sealed with bentonite (1 m-deep), and then backfilled to the land surface to avoid contamination. All piezometers were surveyed using GPS (X-Y survey only) and the locations of the piezometers were recorded using digital mapping software (ArcGIS™ 9.1, ESRI, Ireland). The site and monitoring network was then digitised using a DGPS antenna, MG-A1 equipment (TOPCON, Ireland) and the site elevations were obtained (Z survey). The depth to the water level in each monitoring well was measured using an electric water-level indicator (Van Walt Ltd, Surrey, U.K.) and groundwater heads were determined using ordnance survey data. Data are described using m AOD to allow comparisons of plume position, thus eliminating topographical differences.

Surface water features, such as streams, drains and lagoons, were also levelled on the same date. The maps were used to construct groundwater maps and elucidate
groundwater flow direction. A topographic base map with a field boundary overlay was generated using ArcGIS™ and merged with well location and groundwater head input files. 2-dimensional groundwater data models were generated using GW-Contour 1.0 software (Waterloo Hydrogeologic, Canada).

Watertable levels were measured weekly using an electronic dipper (Van Walt Ltd, Surrey, U.K.) and groundwater was sampled in duplicate using a Waterra hand-held pump (Van Walt Ltd, Surrey, U.K.) Nutrient concentrations were analysed (in duplicate) monthly with a Thermo Konelab 20 (Technical Lab Services, Ontario, Canada) for nitrite-N (NO₂-N), total oxidised N (TON-N), ammonium-N (NH₄-N) and chloride (Cl⁻).

2.3 WATER BALANCE

A water balance of the site was used to calculate the travel time from surface level to the watertable in the six isolated plots. Daily weather data, recorded at the Johnstown Castle Weather Station, were used to calculate daily soil moisture deficit (SMD) using a Hybrid model for Irish grasslands. Potential evapotranspiration, $ET₀$ (mm day⁻¹), was calculated using the FAO Penman-Montieth equation (Allen et al., 1998):

$$ET₀ = \frac{0.408Δ(R_n - G) + \gamma \frac{900}{T + 273} u_2(e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)}$$ (1)

where $R_n$ is the net radiation at the crop surface (m² day⁻¹), $T$ is the air temperature at a 2 m height (°C), $u_2$ is the wind speed at a 2 m height (m s⁻¹), $e_s$ and $e_a$ are the saturation and the actual vapour pressure curves (kPa °C⁻¹), and $\gamma$ is the psychrometric
constant (kPa °C⁻¹). $ET_0$ was then converted to actual evapotranspiration ($Ae$) using an Aslyng scale recalibrated for Irish conditions (Schulte et al., 2005). Effective rainfall was calculated by subtracting daily actual evapotranspiration from daily rainfall (assuming no overland flow losses due to the high infiltration capacity of the soil on this site). Higher $K_{sat}$ zones were found in the topsoil, even in the poorly drained plot. SMD on day one (January 1st, 2006 and 2007) was set to zero and effective drainage was estimated for each subsequent day. Modelling the effective drainage enables the infiltration depth of water to be calculated at specific hydraulic loads where the soil effective porosity is known. This infiltration depth may be compared to watertable data to investigate if recharge to groundwater in that particular year affects water quality.

2.4 HYDRAULIC CONDUCTIVITY DETERMINATION

$K_{sat}$ for the open screen area of each piezometer was estimated in slug tests using an electronic diver (Eijkelkamp, the Netherlands) set to record heads at 1-sec time intervals in each piezometer. The diver measures the initial head of water in the piezometer before, during and after the test until full recovery occurs in the piezometer. A slug of 1 L of water was placed instantaneously into the piezometer. The start time ($t_0$) for the test was noted. Data was downloaded and analysed after (Bouwer et al., 1976) method as outlined in (ILRI, 1990) for unconfined aquifers in steady-state flow conditions:

$$K_{sat} = \frac{r_c^2 \ln \left( \frac{R_{eu}}{r_w} \right)}{2d} \frac{1}{t} \ln \left( \frac{h_0}{h_r} \right)$$

(2)

where $r_c$ is radius of the unscreened part of the well where the head is rising, $r_w$ is the horizontal distance from the well centre to the undisturbed aquifer, $R_{eu}$ is the radial
distance over which the difference in head, \( h_o \), is dissipated in the flow system of the
aquifer, \( d \) is the length of the well screen, \( h_o \) is the head in the well before the start of
the test and \( h_t \) is the head in the well at time \( t>t_o \).

As the wells on site are partially penetrating, the following equation was used:

\[
\ln \frac{R}{r_w} = \left[ \frac{1.1}{\ln \left( \frac{D}{r_w} \right)} + \frac{A + B \ln \left( \frac{D-b}{r_w} \right)}{\frac{D}{r_w}} \right]^{-1}
\]  

(3)

where \( b \) is the distance from the watertable height to the bottom of the well, \( D \) is the
distance from the watertable to the impermeable zone, and \( A \) and \( B \) are dimensionless
parameters, which are function of \( d/r_w \). If \( D\gg b \), the effective upper limit of \( \ln \left( \frac{(D-b)}{r_w} \right) \) may be set to 6. A spatial \( K_{sat} \) map was developed in ArcGIS\textsuperscript{TM} and merged
with well location and groundwater head input files. \( b \) is measured by an electronic
dipper before commencement of the slug test.

2.4.1 DISCHARGE AND DARCIAN VELOCITY

The quantity of water discharging from each plot (a known width of aquifer), \( Q \) (m\(^3\) day\(^{-1}\)), was determined using (Darcy, 1856):

\[
Q = -K_{sat} A \frac{dh}{dx}
\]  

(4)

where \( A = bw \), where \( b \) is the aquifer thickness (m), \( w \), the width (m), and \( dh/dx \) is the
hydraulic gradient. \( w \) is taken as the combined diameter of the plots.

The average effective Darcian linear velocity, \( v \) (m day\(^{-1}\)), was calculated from:

\[
v = -K_{sat} \frac{1}{n} \frac{dh}{dx}
\]  

(5)
where \( v \) is equal to \( Q/A \), and \( n \) is effective porosity calculated in a previous study by (Fenton et al., 2008)

The transmissivity, \( T \ (m^2 \text{ day}^{-1}) \), was calculated using the aquifer thickness, \( b \):

\[
T = K_{sv} b
\]

\[ (6) \]

2.4.2 BUFFER ZONE DIAMETER AND CONTAMINANT MASS FLUX

A land use circular buffer zone around each piezometer was previously used to correlate a landuse area that contributes to groundwater quality (Koun et al., 2007) where the diameter \( D \) (m) of the buffer zone in the direction of groundwater flow was approximated by:

\[
D = \frac{Q}{bv}
\]

\[ (7) \]

where \( Q \) is calculated using equation 4, \( b \) is the aquifer thickness as used in equation 6 and \( v \) is calculated using equation 5. The central piezometer in each plot was taken as the centre of the buffer area. In areas where groundwater flow direction is known the buffer zone method over estimates the groundwater contribution down hydraulic gradient, while underestimating the area of contribution up hydraulic gradient, which should extend to a groundwater divide. When groundwater flow direction is known the buffer zone becomes a true zone of contribution (ZOC). This is then defined as the area surrounding the piezometer that encompasses all areas or features that supply groundwater recharge to the piezometer up hydraulic gradient to the groundwater divide. In this case the groundwater divide is represented by the brow of the sandhill. Over a period of time, determined by effective Darcian velocity, groundwater within the ZOC will flow past the piezometer monitoring point and thus will affect the
hydrochemistry at that point. In this study land use management within the entire ZOC, was assessed.

To evaluate the contaminant mass flux (g m\(^3\) day\(^{-1}\)) of a dissolved contaminant, the mass flux was measured across a control plane (row of piezometers). The total contaminant mass flux across a control plane was determined by summing the mass flux of the individual cells along this plane. Each cell was assigned a unique depth of saturated zone, mean NO\(_3\)-N concentration, and groundwater-specific discharge (calculated using mean \(K_{sat}\) values at each piezometer and mean hydraulic gradient in each plot). The total mass flux across the plane was determined by summing the mass flux of the individual plots according to (API, 2003):

\[
w = \sum_{i=1}^{i=n} C_i q_i A_i
\]

where \(w\) is total mass flux across a control plane (g m\(^3\) day\(^{-1}\)), \(C_i\) concentration of constituent in \(i\)th plot (g l\(^{-1}\)), \(q_i\) is specific discharge in \(i\)th plot (m day\(^{-1}\)) and \(A_i\) is area of \(i\)th plot (m\(^2\)). Within the plots, three control planes were assigned using the top (3, 5, 8, 11, 14, 17), middle (2, 7, 10, 13) and bottom (1, 4, 6, 9, 12 and 15 form the compliance control plane) piezometers (Figure 2). The contaminant mass flux passing through each control plane was calculated and the natural attenuation process assessed.

The overall efficiency of NO\(_3\)-N attenuation between control planes has been used in riparian studies (Orleans et al., 1994; Dhondt et al., 2006) and may be calculated by the following equation:

\[
Efficiency = \frac{N_{IN} - N_{OUT}}{N_{IN}} \times 100\%
\]
where \( N_{IN} \) is the up-gradient NO\(_3\)-N contaminant mass flux and \( N_{OUT} \) is the down

\[ \text{gradient contaminant mass flux.} \]

\[ \text{3.5 TOBIT REGRESSION} \]

The effects on groundwater NO\(_3\)-N concentration of \( K_{sat} \) (m day\(^{-1}\)), elevation, screen

opening elevation and distance from pollution source were assessed using a Tobit

regression model (Tobin, 1958). The NO\(_3\)-N concentration was left censored using a

background concentration threshold of 2.6 mg L\(^{-1}\). Model selection was performed

using a forward selection stepwise procedure. Due to the grid layout of the

piezometers, residuals could not be assumed to be independent and their spatial

dependence was modeled using an anisotropic power covariance structure. The

anisotropic power correlation model depends on two parameters: one that represents

the correlation between piezometers in the direction of rows and the other that

represents the correlation in the direction of columns. Models were fitted using the

MIXED procedure (SAS, 2003). To separate the effect of groundwater NO\(_3\)-N

denitrification from dilution, groundwater NO\(_3\)-N retention is studied by evaluating

concurrently groundwater NO\(_3\)-N and Cl\(^-\) concentration (Altman et al., 1995). To

investigate the effect of dilution on the study area Cl\(^-\) was also inputted into the

model. Cl\(^-\) is considered a conservative tracer.

\[ \text{3.6 DENITRIFICATION} \]

Denitrification is considered the most important reaction for NO\(_3^-\) remediation in

aquifers. The process of denitrification occurs in O\(_2\) depleted layers with available

electron donors and in agricultural environments with N nutrient losses considerable

NO\(_3^-\) reduction is possible. To investigate further if denitrification is a viable pathway
for NO$_3^-$ reduction some additional water quality measurements were taken on a
random date. Physio-chemical parameters- pH, redox potential (Eh (mV)),
conductivity (cond ($\mu$S cm$^{-1}$)), temperature (temp ($^\circ$C)) and rugged dissolved oxygen
(RDO ($\mu$g L$^{-1}$)) were measured in the field using a multi parameter Troll 9500 probe
(In-situ, Colorado, U.S.A) with a flow through cell.

To elucidate the locations of potential denitrification during groundwater sampling
based on dissolved N$_2$ and the N$_2$/Ar ratio, three water samples were taken from each
piezometer mid way within the screened interval using a 50 ml syringe and gas
impermeable tubing. Samples were transferred from the syringe to a 12 ml
Exetainer® (Labco Ltd, UK) and sealed to avoid any air entrapment with a butyl
rubber septum. Samples were then placed under water in an ice box, transported to
laboratory and kept in a cold room at 4$^\circ$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$^\circ$C) during groundwater sampling (Kana et al. 1994). For N$_2$O
concentration, three additional samples were taken in glass bottles for degassing.
Eighty ml collected water was injected into a pre-evacuated 160 ml serum bottle
followed by 80 ml pure helium. The bottles were shaken for 5 minutes and then 15 ml
equilibrated gas in the headspace was collected using an air-tight syringe and
transferred into a 12 ml Exetainer for the analysis of dissolved N$_2$O using a gas
chromatography (GC; Varian 3800, USA) equipped with electron capture detector.
The concentration of dissolved N$_2$O was calculated by using the Henry’s law constant,
the concentration of the gas in the head space, the bottle volume, and the temperature
of the sample but the lowest 14$^\circ$C was taken due to limitation in gas solubility
coefficient to calculate Henry’s law constant (Hudson, 2004).
3 RESULTS

3.1 NUTRIENT MANAGEMENT

In 2006 as in previous years after the point source was removed, the sandhill area, the northwest area and the isolated plots received the same N application (Table 1). What about previous years e.g. before 2003-2005. Comment here. These areas were cut for first cut silage at the end of May and for second cut silage in July but they were not grazed by cattle for the duration of this study. Half of the fertiliser N was applied as urea in late-February and April and the remaining N was applied in June and August as calcium ammonium nitrate (CAN). Loss of N to the environment from urea would tend to be atmospheric ammonia (NH₃) losses as urea tends to be immobile and is retained in the soil by cation exchange capacity (CEC). Whereas N applied as CAN is already partially nitrified and would be susceptible to leaching and denitrification.

At a crop uptake rate of 2 kg N ha⁻¹ day⁻¹ from March – May, a surplus of approximately 75 kg N ha⁻¹ remained after first cut silage. The grass needed approximately 80 kg N ha⁻¹ before second cut silage at the end of July. Therefore, no N leaching losses would be expected from this surplus. In August 2006, the six isolated plots received a higher application of CAN (83.7 kg N ha⁻¹) for the third cut silage in early October. The grass requirement for third cut silage matched the fertilizer application rate (approximately 90 kg N ha⁻¹).

In June 2007, in addition to fertilizer application (Table 1), the sandhill and northwest area received 118 kg N ha⁻¹ as cattle slurry. The sandhill area was N-deficient by approximately 24 kg N ha⁻¹ for first cut silage in May. With addition of CAN and slurry in June, there was an N-surplus of approximately 70 kg N ha⁻¹ after second cut
silage. In July and August 2007, there was a large increase in effective drainage. With the time lag between second cut silage and the final application of CAN in the middle of August, there was just enough N available for grass recovery. The same was true for the northwest site but there was a surplus after first cut silage in May.

3.2 WATER BALANCE

A water balance for the site showed total precipitation of 992.6 mm and 889.1 mm for 2006 and 2007, respectively. For the two years, the Hybrid model calculated 483 mm and 335 mm drainage through the root zone in a process known as effective drainage. It was assumed that all of this direct recharge reached the watertable as the rainfall intensity is generally lower than the soil infiltration capacity. Model output showed effective drainage occurred on 87 and 74 days, giving an average recharge rate of 5.5 and 4.5 mm day\(^{-1}\), respectively. Cumulative drainage for both years is presented in Figure 3. The mean soil total porosity was 32.2±4.9%. The average pore velocity was estimated to be 17.3 and 14.1 mm day\(^{-1}\), giving an approximate mean travel depth of 1.5 and 1.04 m in a moderately-drained soil for 2006 and 2007. The mean watertable depth for 2006-2008 on site was 2.2 m bgl. This is the unsaturated zone vertical travel time (approx 2 years) achievable due to effective drainage, representative of drainage during the winter period. Lateral migration of the nutrients is with groundwater flow direction under the experimental plots.

Accumulative effective drainage shows differential recharge each year and seasonal differences in recharge led to differential NO\(_3\)-N dilutions over time. Both years had wet winters but 2006 had a dry summer period (Figure 3). Slurry was only spread in times of dry weather. This contributed to higher mean site NO\(_3\)-N concentrations for
sampling events in early 2006. The dry summer of 2006 halted significant recharge
and NO$_3$-N concentrations reached steady state. As effective drainage increases,
overall mean NO$_3$ concentration on site increases.

Each piezometer followed the same pattern for mean NO$_3$-N concentration, with some
piezometers falling below the 11.3 mg L$^{-1}$ threshold for drinking water quality within
1 year. There was no increase in the shallow groundwater NO$_3$-N concentration, after
the slurry application in June 2007 due to a combination of slow groundwater
transport ($K_{sat}$ ranges from 0.001 – 0.016 m day$^{-1}$ with subsequent travel distance of
2.9 and 4.5 m yr$^{-1}$) (Table 2) and gaseous losses of NH$_3$.

3.3 BUFFER ZONE AND CONTAMINANT MASS FLUX

Buffer zone diameter for plots 1-6, using equation 7, was 193, 178, 195, 195, 148 and
120 m respectively. A mean area of 2.4 ha for the ZOC was calculated. The buffer
zones can extend beyond the isolated study site to the groundwater divide in the
sandhill area. Therefore, land management and recharge in the entire ZOC area can
contribute to shallow groundwater NO$_3$-N contamination within the study site. The
historical stationary dirty water point source pollution occurred within this ZOC.
The contaminant mass fluxes calculated for three control planes are presented in Table
2. Influent contaminant mass flux through the upper control plane cells ranged from
0.0008 to 0.0016 g N m$^3$ day$^{-1}$ and the contaminant mass fluxes leaving the site at the
compliance plane ranged from 0.00001 to 0.0007 g N m$^3$ day$^{-1}$. Total contaminant
mass flux on a plot basis was as follows: Plot 3>1>5>4>6. Total contaminant mass
flux decreased from the top plane to the central plane to the compliance plane
demonstrating natural attenuation. Using equation 9, a 42 % contaminant mass flux
reduction efficiency was calculated from the influent control plane to the central plane. From the central plane to the compliance plane a 64% reduction occurred. Plot 3 contributed the greatest contaminant mass flux. The load transfer from the influent control plane to the central control plane showed a reduction of 33.6%, with a subsequent reduction of 69.5% at the compliance control plane. Plot 4 showed a 96% reduction in contaminant mass flux from the influent control plane and the central control plane. Plot 1 doubled its contaminant mass flux from the influent control plane to the central control plane, but then decreased by 51.2% downgradient at the compliance control plane. The upper, middle and lower control planes are 18%, 44% and 76% below the compliance control plane threshold (11.3 mg l⁻¹ with present flux) respectively.

4 TOBIT REGRESSION

Selected piezometer parameters are presented in Table 3. In each step of the procedure, a series of regressions are fitted (Table 4). Each model includes random effects to account for the spatial dependence of model residuals. Type III F-tests for the fixed effects are presented for each model accompanied by Akaike's Information Criterion (AIC). The AIC is a model selection tool that compares the Log Likelihood of models while penalising for the number of parameters in the model. The model with the lowest AIC is the best fitting model.

When assessed individually, \(K_{sat}\) \((p=0.0004)\) had significant impacts on \(\text{NO}_3-\text{N}\) concentrations. However, \(K_{sat}\) \((p<0.001)\) and distance from point source \((p=0.0014)\) are significant when \(K\) is already in the model. The stepwise procedure selected the \(K_{sat}\) and distance from point source as having more explanatory power than when
other parameters are inputted into the model. The final model contains only $K_{sat}$ and distance from point source. The final model is presented in Figure 4.

Estimated model coefficients for final model from the Tobit regression are presented in Table 5. The model describes the relationship between mean groundwater NO$_3$-N concentration and the explanatory variables $K_{sat}$ and distance from pollution source. The percentage variation explained by different factors is presented in Table 6.

Dilution due to recharge occurred for all piezometers within the contamination plume on site (NO$_3$-N/Cl$^-$ ratio), but at the same rate for each piezometer. Therefore, dilution did not account for differences in NO$_3$-N concentration within the contamination plume. Therefore, diffuse pollution due to fertiliser application within the field site may be discounted. A two-layered conceptual model represents a shallow zone of higher $K_{sat} \geq 0.01$ m day$^{-1}$ with higher NO$_3$-N concentrations and a deeper low $K_{sat}$ zone $< 0.01$ m day$^{-1}$ with lower NO$_3$-N concentrations. In the shallow layer, $K_{sat}$ values ranged from 0.01 – 0.016 m day$^{-1}$ but were not consistent with depth, indicating heterogeneity.

4.1 DILUTION AND DENITRIFICATION DIFFERENTIATION

In some locations the Cl$^-$ concentration is representative of natural background levels (NBL). In Ireland groundwater has a median NBL of 18 mg L$^{-1}$. Some points therefore were not included in the regression process. Plots 1, 2, 4, 5 and 6 have the highest ratio in the top of the plots nearest the source but standard deviation shows some change over time (Table 3).
The model was run a second time to explain Cl\(^-\) occurrence using the same parameters as before. Here K\(_{\text{sat}}\) and ground elevation have the greatest explanatory power but K\(_{\text{sat}}\) is not significant. As shown previously, NO\(_3\)-N occurrence in the same piezometers was explained by K\(_{\text{sat}}\) and distance from the dirty water point pollution source. Due to the fact that K\(_{\text{sat}}\) influences NO\(_3\)-N occurrence but not Cl\(^-\) occurrence denitrification can be inferred. But distances from the dirty water source and ground elevation are linked due to the nature of the sloped site and therefore dilution is a factor for Cl\(^-\) occurrence. In general on site:

- Low NO\(_3\) concentration and unaffected Cl\(^-\) concentration points to denitrification (Figure 5a)
- Low NO\(_3\) concentration and low Cl-chloride concentration points to dilution (Figure 5b)
- Over lying Figure 6a and 6b allows areas of denitrification and dilution to be inferred (Figure 5c)

The Nitrate/chloride ratio identifies two zones where the present plume position is evident. This ratio is low in plot 4 and in the southern part of the site where the plume has not reached. This infers denitrification in the central part of the site (plot 4) and dilution in other areas.

To further elucidate the effect of groundwater denitrification on NO\(_3\)-N occurrence on the site, dissolved gases and physiochemical properties of groundwater collected on a random date were determined and related to the mean groundwater NO\(_3\)-N concentration during the study. Average groundwater NO\(_3\)-N was significantly \((P<0.05)\) related to groundwater N\(_2\)/Ar ratio, redox potential (Eh), dissolved O\(_2\) and N\(_2\) and was close to being significant with dissolved N\(_2\)O concentration \((P=0.08)\)
Based on the AIC score $N_2/Ar$ ratio and redox potential (Eh) were the best fitting models of groundwater NO$_3$-N occurrence. The higher ratio of $N_2/Ar$ directly indicates that denitrification is occurring on the site (Figure 5d) and that lower redox potentials and dissolved oxygen are related to lower groundwater NO$_3$-N occurrence (Table 7).

5 DISCUSSION

Documented nutrient management of the study site, while contributing to the elevated NO$_3$-N concentration in shallow groundwater, could not solely account for NO$_3$-N distribution on site. Surplus nutrients calculated for 2007 in the sandhill area had not yet reached the shallow groundwater under the plots due to slow travel times. Historic dirty water irrigation occurred on the sandhill site for decades prior to this study with excessive hydraulic loads leading to elevated infiltration on the sandhill.

Vertical unsaturated zone travel time was not within a single drainage season. Saturated shallow groundwater and contamination plume migration time was from 2.92 to 4.50 m yr$^{-1}$ underneath the plots. The travel time from the sandhill (source) to the plots approximately 200 m away was much quicker due to the sand. Dilution of the groundwater NO$_3$-N concentrations by recharge to the shallow watertable occurred in both study years. A two-layered conceptual model of the site emerged, where higher NO$_3$-N concentrations existed in the shallower, high $K_{sat}$ subsurface. The model describes the relationship between mean groundwater NO$_3$-N concentration and the explanatory variables $K_{sat}$ and distance of the piezometers from
the point pollution source. To account for bias due to the distance of each piezometer within the grid pattern from the pollution source, the spatial dependence of residuals was modelled using an anisotropic power covariance structure. Higher $K_{sat}$ zones in the subsurface allow faster migration of contaminated groundwater, resulting in shorter retention time. The shorter retention time in the high $K_{sat}$ zone decreases the opportunity for denitrification to occur. Lateral flow in higher $K_{sat}$ layers may result in surface water pollution. The opposite is true of lower $K_{sat}$ zones, where a longer retention time is available for denitrification to occur. This is why low NO$_3$-N concentrations may be present at the plume centroid. In elevated areas, the watertable mirrors topography and has a greater hydraulic gradient and higher $K_{sat}$ values.

Groundwater NO$_3$-N occurrence was statistically related to topsoil denitrifying enzyme activity, topsoil inorganic N content, depth to water table and a stronger relationship was observed with vadose zone permeability (McLay et al., 2001). The effect of vadose zone permeability on groundwater NO$_3$-N distribution was recognised by (Vellidis et al., 1996) who observed low N leaching associated with low subsoil permeability and (Hansen et al., 1996) observed high N leaching with high subsoil permeability. (Richards et al., 2005) observed lower groundwater NO$_3$-N occurrence in deeper wells with clay soils with no cropland nearby but they could not separate the effect of $K_{sat}$ from landuse or well depth. In Ireland (Ryan et al., 1996) also highlighted the importance of soil type and permeability with lower NO$_3$-N losses from soil with the percentage fines (silt and clay) $>$75% estimated mean subsoil travel times of 0.01 m day$^{-1}$ on a site with elevated groundwater NO$_3$-N concentrations. The unsaturated vadose zone transport of NO$_3$-N is clearly influenced by the permeability and thus longer residence time in lower permeability subsoil
favouring NO$_3$-N reduction through denitrification. The strong relationship observed in this work also clearly identifies the importance of the saturated subsoil zone in favouring NO$_3$-N reduction by denitrification in low subsoil permeable zones. Also importance is the exact location of the point pollution source. The strong correlations between mean groundwater NO$_3$-N and denitrification end products (N$_2$O and N$_2$) and physiochemical properties favouring denitrification (dissolved O$_2$ and Eh) further supports that denitrification is the dominant process controlling groundwater NO$_3$-N occurrence and transport on the study site. The relationship between subsoil/aquifer $K_{sat}$ and denitrification requires further investigation.

In Ireland, groundwater protection is based on the mapping of vulnerability zones for the protection of groundwater source (wells and springs) and the groundwater resource. Irish aquifers are deemed to have low attenuation potential due to there fractured and karstified nature and thus they are mainly protected by the overlying glacial tills. Vulnerability zones are ranked in four classes from extreme to low vulnerability based primarily on the thickness and lithology/permeability of the Quaternary subsoil deposits (Daly et al., 1988). Vulnerability decreases with increasing thickness and decreasing permeability of subsoil. The definition of groundwater in Ireland often excludes the shallow groundwater in subsoils (with the exception of sand and gravel aquifers) as it is not valued as a potential source of water for human consumption. Although not sufficient for consumption shallow subsoil groundwater is environmentally important as it contributes to through flow and drain flow to surface waters bypassing any potential for abatement when transported through deeper aquifers.
Groundwater protection in Ireland for subsoil permeability is not routinely measured in Irish subsoils, (Fitzsimons et al., 2006) classified Irish till permeability as being highly permeable $K_{sat} = 10$ m day$^{-1}$, moderately permeable when $K_{sat} = 0.004$ to 0.009 m day$^{-1}$ and low permeability (clay content $>13\%$) when $K_{sat} = 0.0004$ to 0.0009 m day$^{-1}$. Mean plot $K_{sat}$ values on site range from 0.008 – 0.01 m day$^{-1}$. This suggests further classification may be needed from moderate to highly permeable classes.

Contaminant mass flux calculations show that the load of NO$_3$-N passing through parallel control planes perpendicular to groundwater flow was uneven across the site. A 96% reduction in contaminant mass flux occurred across the control planes in Plot 3. This leads to groundwater NO$_3$-N loads of acceptable quality leaving the site. Natural attenuation occurred down-gradient in all plots except Plot 1.

In this study subsoil permeability and distance from point source pollution have been clearly identified as significant factors in determining the occurrence of NO$_3$-N in groundwater. The subsoil on the study classified as moderate permeability and this study highlights the need to further subdivide this category for risk assessment of NO$_3$-N occurrence in groundwater and transport to surface waters via through flow or artificial drainage. Furthermore as subsoil $K_{sat}$ is incorporated in the contaminant mass flux calculation, particular hot spot locations may be identified, which contribute significantly more contaminant flux per unit area to potential down-gradient receptors. The identification of hot spots of groundwater contaminants may be used to target areas for locating an environmental remediation technology to reduce contaminant fluxes to sensitive receptors.
**6 CONCLUSION**

$K_{sat}$ and distance from point source are important when assessing the spatial distribution of NO$_3$-N in shallow groundwater. Within subsoils classified as moderately permeable subsoil saturated hydraulic conductivity was significantly related to groundwater NO$_3$-N occurrence and slight differences in permeability greatly influenced the concentrations on site. Groundwater denitrification is likely to be the dominant process influencing groundwater NO$_3$-N occurrence and transport at this site. Calculating contaminant mass flux across more than one control plane is a useful tool to monitor natural attenuation. This tool allows the identification of hot spot areas where intervention other than natural attenuation may be needed to protect receptors.

**ACKNOWLEDGEMENTS**

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FIGURE 1. Field site and northwest and elevated sandhill locations.

FIGURE 2. Field site and elevated sandhill. Groundwater flow map. Sandhill groundwater head contours are based on watertable data from 3 wells drilled in this area. Wells 1, 4, 6, 9, 12 and 15 form the compliance control plane. Wells 3, 5, 8, 11, 14, and 17 form the first control plane. Wells 2, 7, 10, 13 1and 16 form the intermediate control plane.

FIGURE 3. Calculated cumulative effective drainage (mm) from 2006 to 2007.

FIGURE 4. Predictions of NO3-N from fitted model.

FIGURE 5 Spatial distribution across the six plots (x axis) of groundwater a) Mean NO3-N concentration b) Mean Cl concentration c) mean NO3/Cl ratio and d) N2/Ar ratio on a random date.
Table 1. Nutrient management of the sandhill, northwest and field site for 2006 and 2007.

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Area (ha)</th>
<th>Month</th>
<th>N fertiliser application rate (kg N ha⁻¹)</th>
<th>Nitrogen fertiliser type</th>
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<td>June</td>
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<td>CAN†</td>
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<td>Aug</td>
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<td>CAN</td>
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<td>Feb</td>
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<td>Urea</td>
</tr>
<tr>
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<td>Urea</td>
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<tr>
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<td>June</td>
<td>102.1</td>
<td>CAN</td>
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<td></td>
<td>Aug</td>
<td>51.1</td>
<td>CAN</td>
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<td>Urea</td>
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† Urea is 46% nitrogen
† Calcium Ammonium Nitrate (CAN) is 27% nitrogen
Table 2. Contaminant mass flux calculation for six isolated plots

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<th>Parameters</th>
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<td>Area (ha)</td>
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<td>Width of plot (m)</td>
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<td>Mean effective velocity v (m day⁻¹)</td>
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<td>Hydraulic conductivity K (m day⁻¹)</td>
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<tr>
<td>Transmissivity T (m² day⁻¹)</td>
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</tr>
<tr>
<td>Mean hydraulic head (Top) (m AOD)</td>
<td>67.13</td>
</tr>
<tr>
<td>Mean hydraulic head (Bottom) (m AOD)</td>
<td>63.31</td>
</tr>
<tr>
<td>Mean Travel Distance in 1 year</td>
<td>3.92</td>
</tr>
</tbody>
</table>

| Q m³ day⁻¹ | Top Control Plane Nodes | 0.15  | 0.15  | 0.15  | 0.15  | 0.12  | 0.09  |
|           | Middle Control Plane Nodes | 0.15  | -     | 0.15  | 0.20  | 0.11  | 0.07  |
|           | Bottom Control Plane Nodes | 0.11  | 0.01  | 0.22  | 0.19  | 0.04  | 0.01  |

| Contaminant Mass Flux g m³ day⁻¹ | Top Control Plane Nodes | 0.0009 | 0.0017 | 0.0016 | 0.0009 | 0.0015 | 0.0008 |
|                                 | Middle Control Plane Nodes | 0.0018 | -     | 0.0011 | 0.0001 | 0.0010 | 0.0004 |
|                                 | Bottom Control Plane Nodes | 0.00074 | 0.00001 | 0.0003 | 0.0000 | 0.0004 | 0.0001 |

<table>
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<tr>
<th>Piezometer</th>
<th>Plot Position</th>
<th>Elevation (mAOD)</th>
<th>Total depth (m bgl)</th>
<th>Mean NO$_3$-N (mg L$^{-1}$)</th>
<th>Stdev±</th>
<th>Mean NO$_2$-N (mg L$^{-1}$)</th>
<th>Stdev±</th>
<th>Mean Cl $^-$ (mg L$^{-1}$)</th>
<th>Stdev±</th>
<th>Mean NH$_4$-N (mg L$^{-1}$)</th>
<th>Stdev±</th>
<th>Mean NO$_3$-N/Cl$^-$ ratio</th>
<th>Stdev±</th>
<th>K$_{sat}$ (m day$^{-1}$)</th>
<th>Mean Watertable Elevation (mAOD)</th>
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</tr>
<tr>
<td>9 4 Bottom</td>
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<td>1.3</td>
<td>0.01</td>
<td>0.0</td>
<td>9.9</td>
<td>0.16</td>
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<td>0.02</td>
<td>0.012</td>
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<td>0.0</td>
<td>41.4</td>
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<tr>
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<td>5.7</td>
<td>2.7</td>
<td>0.00</td>
<td>0.0</td>
<td>21.9</td>
<td>0.06</td>
<td>0.2</td>
<td>0.08</td>
<td>0.24</td>
<td>0.01</td>
<td>70.3</td>
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<tr>
<td>12 5 Bottom</td>
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<td>8.7</td>
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<td>32.5</td>
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<td>0.07</td>
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<td>0.09</td>
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<td>0.016</td>
<td>71.0</td>
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<td>15 6 Bottom</td>
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<td>3.6</td>
<td>2.7</td>
<td>0.02</td>
<td>0.0</td>
<td>33.9</td>
<td>0.23</td>
<td>0.4</td>
<td>0.08</td>
<td>0.10</td>
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<td>16 6 Middle</td>
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<td>0.04</td>
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<td>24.5</td>
<td>0.14</td>
<td>0.2</td>
<td>0.11</td>
<td>0.19</td>
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<tr>
<td>17 6 Top</td>
<td>71.1</td>
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<td>9.3</td>
<td>2.0</td>
<td>0.04</td>
<td>0.1</td>
<td>23.2</td>
<td>0.12</td>
<td>0.5</td>
<td>0.13</td>
<td>0.41</td>
<td>0.012</td>
<td>70.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Details of the stepwise procedure used to select the explanatory variables of importance in the relationship between mean groundwater NO$_3$-N concentration and hydrogeological factors. Model containing $K_{sat}$ and distance from point source is chosen as the final model.

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Include all variables individually in model</th>
<th>Step 3</th>
<th>Add other variables to model containing $K_{sat}$ and distance from point source (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect</td>
<td>$F(1,11) \quad \text{P-value}$</td>
<td>Effect</td>
<td>$F(1,9) \quad \text{P-value}$</td>
</tr>
<tr>
<td>$K_{sat}$ (m day$^{-1}$)</td>
<td>24.55</td>
<td>0.0004</td>
<td>$K_{sat}$ (m day$^{-1}$)</td>
</tr>
<tr>
<td>Elevation (m AOD)</td>
<td>10.23</td>
<td>0.0085</td>
<td>Distance from point source (m)</td>
</tr>
<tr>
<td>Distance from point source (m)</td>
<td>0.6</td>
<td>0.4562</td>
<td>Elevation (m AOD)</td>
</tr>
<tr>
<td>Screen depth (m AOD)</td>
<td>1.28</td>
<td>0.2826</td>
<td></td>
</tr>
<tr>
<td>Result of step 1</td>
<td>K chosen as most important</td>
<td>Result of step 2</td>
<td>Other variables not significant in a model that contains $K_{sat}$ and distance from point source</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step 2</th>
<th>Add other variables to model containing $K_{sat}$</th>
<th>Result of step 3</th>
<th>Other variables not significant in a model that contains $K_{sat}$ and distance from point source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect</td>
<td>$F(1,10) \quad \text{P-value}$</td>
<td>Effect</td>
<td>$F(1,9) \quad \text{P-value}$</td>
</tr>
<tr>
<td>$K_{sat}$ (m day$^{-1}$)</td>
<td>13.05</td>
<td>0.0048</td>
<td>$K_{sat}$ (m day$^{-1}$)</td>
</tr>
<tr>
<td>Elevation (m AOD)</td>
<td>1.75</td>
<td>0.2156</td>
<td>Distance from point source (m)</td>
</tr>
<tr>
<td>$K_{sat}$ (m day$^{-1}$)</td>
<td>78.85</td>
<td>&lt;0.0001</td>
<td>Screen depth (m AOD)</td>
</tr>
<tr>
<td>Distance from point source (m)</td>
<td>19.1</td>
<td>0.0014</td>
<td></td>
</tr>
<tr>
<td>$K_{sat}$ (m day$^{-1}$)</td>
<td>33.75</td>
<td>0.0002</td>
<td>Screen depth (m AOD)</td>
</tr>
<tr>
<td>Screen depth (m AOD)</td>
<td>1.47</td>
<td>0.2526</td>
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</tr>
<tr>
<td>Result of Step 2</td>
<td>Distance is significant when $K_{sat}$ is already in the model</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Estimated model coefficients for final NO$_3$-N model but also for Cl$^-$ from the regression.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Coefficient</th>
<th>Standard Error</th>
<th>Degrees of Freedom (DF)</th>
<th>t-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3$-N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
<td>-13.7328</td>
<td>3.6584</td>
<td>0</td>
<td>-3.75</td>
<td>&lt;0.001</td>
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<tr>
<td>K</td>
<td>960.98</td>
<td>108.22</td>
<td>10</td>
<td>8.88</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Distance</td>
<td>0.0506</td>
<td>0.01158</td>
<td>10</td>
<td>4.37</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect</th>
<th>Coefficient</th>
<th>Standard Error</th>
<th>Degrees of Freedom</th>
<th>t-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
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<td>62.22</td>
<td>0</td>
<td>3.41</td>
<td>0.1854</td>
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<tr>
<td>K</td>
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<td>390.49</td>
<td>12</td>
<td>1.40</td>
<td>0.1854</td>
</tr>
<tr>
<td>Elevation</td>
<td>-2.73</td>
<td>0.9294</td>
<td>12</td>
<td>-2.94</td>
<td>0.0123</td>
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</table>
Table 6. Percentage variation explained by different factors

<table>
<thead>
<tr>
<th>Fixed</th>
<th>Degrees of freedom</th>
<th>SS</th>
<th>% variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{sa}$ (m day$^{-1}$)</td>
<td>1</td>
<td>63.72</td>
<td>55.5</td>
</tr>
<tr>
<td>Distance from point source (m)</td>
<td>1</td>
<td>15.52</td>
<td>13.3</td>
</tr>
<tr>
<td>Screen depth (m AOD)</td>
<td>1</td>
<td>5.48</td>
<td>4.8</td>
</tr>
<tr>
<td>Elevation (m AOD)</td>
<td>1</td>
<td>0.62</td>
<td>0.5</td>
</tr>
<tr>
<td>Random</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row</td>
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<td>7.95</td>
<td>6.9</td>
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<tr>
<td>Column</td>
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<td>3.7</td>
</tr>
<tr>
<td>Residual</td>
<td>5</td>
<td>17.58</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Total 114.90
Table 7. Relationships between dissolved groundwater gases, redox potential (Eh) and average NO$_3$-N. Each parameter is regressed in turn against average NO$_3$-N. The spatial structure on the variance covariance matrix is as described for the stepwise regression.

| Parameter       | Estimate | Standard Error | T value | P>|t| | AIC |
|-----------------|----------|----------------|---------|---|---|-----|
| N$_2$/Ar ratio  | -1.33    | 0.544          | -2.45   | 0.029 | 81 |
| Redox potential (Eh) | 0.040 | 0.013          | 3.17    | 0.0073 | 86.4 |
| N$_2$O          | 0.2247   | 0.1182         | 1.9     | 0.0798 | 87 |
| RDO             | 0.0012   | 0.0003         | 3.58    | 0.0034 | 91.4 |
| O$_2$           | 0.0011   | 0.0004         | 2.48    | 0.0275 | 95 |
| N$_2$           | -0.0012  | 0.001          | -2.17   | 0.0493 | 95.5 |