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30 distance from a dirty water point pollution source. Tobit regression, using a
31 background concentration threshold of $2.6 \text{ mg NO}_3\text{-N L}^{-1}$ showed, when assessed
32 individually in a step wise procedure, K_{sat} was significantly related to groundwater
33 $\text{NO}_3\text{-N}$ concentration. Distance of the point dirty water pollution source becomes
34 significant when included with K_{sat} in the model. The model relationships show areas
35 with higher K_{sat} values have less time for denitrification to occur, whereas lower K_{sat}
36 values allow denitrification to occur. Areas with higher permeability transport greater
37 $\text{NO}_3\text{-N}$ fluxes to ground and surface waters. When the distribution of Cl^- was
38 examined by the model, K_{sat} and ground elevation had the most explanatory power but
39 K_{sat} was not significant pointing to dilution having an effect. Areas with low NO_3
40 concentration and unaffected Cl^- concentration points to denitrification, low NO_3
41 concentration and low Cl^- chloride concentration points to dilution and combining
42 these findings allows areas of denitrification and dilution to be inferred. The effect of
43 denitrification is further supported as mean groundwater $\text{NO}_3\text{-N}$ was significantly
44 ($P < 0.05$) related to groundwater N_2/Ar ratio, redox potential (Eh), dissolved O_2 and
45 N_2 and was close to being significant with N_2O ($P = 0.08$). Calculating contaminant
46 mass flux across more than one control plane is a useful tool to monitor natural
47 attenuation. This tool allows the identification of hot spot areas where intervention
48 other than natural attenuation may be needed to protect receptors.

49

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

52

53 **1. INTRODUCTION**

54 Delineation of an elevated nitrate ($\text{NO}_3\text{-N}$) plume in shallow groundwater is difficult
55 as $\text{NO}_3\text{-N}$ concentration differences may be prevalent over short distances. As a result
56 of high denitrification capacity, $\text{NO}_3\text{-N}$ concentration may be low at the centroid of
57 the plume. Contaminated groundwater in aquifers with low hydraulic conductivity
58 (K_{sat}) may represent a long-term threat to groundwater due to long travel times from
59 source to receptor. A shallow watertable allows reduction of nitrate through
60 denitrification before recharge reaches deeper groundwater (Boland *et al.*, 2002). The
61 thickness and permeability of subsoil can control groundwater vulnerability (Lee,
62 1999). In such shallow groundwater sites reduction of $\text{NO}_3\text{-N}$ through denitrification
63 may provide the basis for remediation. Monitored natural attenuation is a valid
64 method in sites with low permeability and high denitrification capacity, leading to a
65 low vulnerability status. In such scenarios surface water and not deeper groundwater
66 may be a potential receptor for $\text{NO}_3\text{-N}$ pollution.

67

68 In spite of efficient nutrient management practices, agricultural activities, such as
69 application methods and storage, are probably the most significant anthropogenic
70 sources of $\text{NO}_3\text{-N}$ contamination in groundwater (Oyarzun *et al.*, 2007). Current
71 agricultural practices (application methods, application rates and storage) while
72 achieving high nutrient efficiency and nutrient management cannot avoid some
73 nutrient losses to surface and groundwater. Contamination of shallow groundwater
74 (<30 m bgl) with $\text{NO}_3\text{-N}$ has been documented in a large number of studies (C. D. A.
75 McLay *et al.*, 2001; Harter *et al.*, 2002; Bohlke *et al.*, 2007; Babiker *et al.*, 2004). To
76 relate different forms of landuse to different shallow groundwater $\text{NO}_3\text{-N}$
77 concentrations spatially, a variety of statistical techniques, such as multivariate cluster
78 analysis (Hussain *et al.*, 2008; Ismail *et al.*, 1995; Yidana *et al.*, 2008), Tobit and

79 logistic regression using mean nutrient data (Gardner and Vogel., 2005; Kaown et al.,
80 2007), weights of evidence modelling techniques (Masetti et al., 2008), and ordinary
81 kriging methods (Hu *et al.*, 2005), have been used. Other tools, such as regression
82 models based on conceptual models, link shallow groundwater NO₃-N concentration
83 with inventories such as landuse and cattle density (Boumans *et al.*, 2008). Other
84 techniques are employed when both spatial and temporal relationships are considered
85 such as the vulnerability of an aquifer to nitrate pollution through the use of
86 DRASTIC and GLEAMS models (Almasri, 2008; Leone et al., 2007). Spatial and
87 temporal correlations of surface and groundwater were described using t-test analysis
88 to show that surface and groundwater management should be integrated (Kannel et
89 al., 2008). Agri-environmental indicators (AEIs) provide information on
90 environmental as well as agronomic performance, which allows them to serve as
91 analytical instruments in research and provide thresholds for legislation purposes
92 Langeveld et al. (2007) investigated AEIs used in various studies: nitrogen use
93 efficiency, nitrogen surplus, groundwater nitrate concentration and residual nitrogen
94 soil concentration, to explain nitrogen management. Results indicated an integrated
95 approach at an appropriate scale should be tested, not forgetting that indicators are
96 simplifications if complex and variable processes.

97

98 The land surface around a well which contributes to the water quality at that well may
99 be calculated from: aquifer discharge ($\text{m}^3 \text{ day}^{-1}$), aquifer thickness (m) and effective
100 Darcian velocity (m day^{-1}). This circular buffer zone contributes direct recharge to a
101 specific monitoring point, such as a borehole or piezometer (Kolpin, 1997). The
102 circular shape is assumed to be homogenous according to its physical properties. If
103 groundwater flow direction is known, any pollution sources down-gradient of the

104 monitoring point may be discounted. The size of the buffer zone is an important
105 factor and many studies have used different buffer zone radii: (Eckhardt *et al.*, 1995) -
106 800 m; (Kolpin, 1997) - 200 to 2000 m; (Barringer *et al.*, 1990) – 250 m to 1000 m,
107 (McLay *et al.*, 2001)- 500 m and (Kaown *et al.*, 2007) – 73 to 223 m. A mean
108 diameter is often taken where a large range occurs. In an area with a common landuse
109 nutrient management within this area will be an important factor as well as identifying
110 potential point sources in this zone.

111

112 Both qualitative and quantitative methods need to be applied to investigate
113 contaminant concentration patterns and to calculate contaminant mass flux.
114 Contaminant flux can prove that natural attenuation occurs on a site but does not
115 differentiate between dilution and denitrification. Contaminant mass flux across a
116 transect of wells, known as a control plane, has been used to quantify the contaminant
117 load leaving a system (Basu *et al.*, 2006; Bockelmann *et al.*, 2001; Bockelmann *et al.*,
118 2003; Brusseau *et al.*, 2007; Campbell *et al.*, 2006; Duncan *et al.*, 2007; Hatfield *et al.*,
119 2004; Kubert *et al.*, 2006). This method allows a quantifiable load of NO₃-N leaving a
120 system to be calculated, rather than focusing on a point where shallow groundwater
121 exceeds target or legislative concentration limits such as 11.3 mg NO₃-N l⁻¹.

122

123 Traditional source treatment assessment has focused on the pollution source zone,
124 partial mass removal and the calculation of the source strength (contaminant mass
125 discharge and mass flux). Contaminant plume properties are a combination of source
126 strength, assimilative capacity (differential mass discharge with distance along a
127 plume) and time. This procedure is based on the assumption that source treatment
128 results in a contaminant mass reduction in the source zone. It gives an incomplete

129 view of potential impacts and there is uncertainty regarding the plume response to
130 partial mass removal (source treatment). Risk reduction is, therefore, uncertain and
131 the associated costs are difficult to ascertain (Jarsjö *et al.*, 2005). The source strength
132 is calculated from groundwater samples, taken at specified time intervals, and the
133 water flow velocity calculated for each well. These data are then inputted into
134 predictive models and the down-gradient concentration in a sentinel well is predicted.
135 The sentinel well is positioned along a compliance plane down-gradient of the control
136 plane and up-gradient of a potential receptor. For the calculation of contaminant mass
137 flux, a number of screened wells along a control plane, which transect the entire
138 contamination plume perpendicular to groundwater flow direction downstream of the
139 pollutant source, are used, as opposed to the standard central line cross section parallel
140 to groundwater flow direction of the plume (Bockelmann *et al.*, 2003). Longitudinal
141 cross sections may over- or underestimate the contaminant mass flux value and this
142 method requires a larger number of piezometers. The contaminant mass flux is then
143 measured directly from the contaminant flow and concentration in the monitoring
144 piezometers. The source strength is interpolated and then inputted into a model for the
145 prediction of down-gradient contaminant concentrations. Natural attenuation rates
146 (dilution and denitrification) may be achieved by the use of two control planes: a
147 control plane to calculate contaminant mass flux (influent) and a compliance plane
148 down-gradient (Kao *et al.*, 2001). Flux-averaged concentrations along the compliance
149 plane must adhere to specified water quality targets.

150 The aim of this study was to investigate the factors contributing to the occurrence of
151 elevated NO₃-N concentration in shallow groundwater (<10 m) on a section of a beef
152 farm in SE Ireland. A statistical framework, combining mean geochemical and
153 physical data (saturated hydraulic conductivity (K_{sat}) measurements, ground elevation

154 (m Above Ordnance Datum), elevation of groundwater sampling (screen opening
155 interval) (m AOD) and distance from point pollution source (m)) from a grid of 17
156 piezometers over a 2 year period, was used to identify factors affecting the occurrence
157 of NO₃-N concentration on site.

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

164

165 **1.1 INTRODUCTION TO THE STUDY SITE**

166

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

170 The field site is bound to the north by an elevated 3.2 ha grassland sandhill area (71-
171 75 m above ordnance datum (AOD), slope 5%), to the northwest by a 2.8 ha grassland
172 site (71-72 m AOD, slope 2%, and on all other sides by agro-forestry. The dirty water
173 point source was located in this sandhill area. Possible receptors on site are a narrow
174 contour stream and the larger Kildavin River boarding the site (Figure 2). The sandhill
175 and northwest areas are up-gradient and hydrologically connected through shallow
176 flow lines to the 4.2 ha study site approximately 200 m away. Groundwater head
177 contours show groundwater flow direction is towards the six isolated plots (Figure 2).

178

179 Two shallow, unlined trapezoidal drains, excavated to a depth of 1 m, with bases
180 ranging from 71.08 m AOD to 70.2 m AOD and 71.10 m AOD to 70.30 m AOD,
181 respectively, were constructed along the northern edge of the plots. This prevents
182 runoff from entering the plots from the elevated up-gradient area. Runoff from the
183 point source flowed directly into these drains. The plots were also isolated laterally to
184 1 m bgl to prevent cross flows from one plot to the other.

185

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

197

198 Topsoil samples (0 to 0.4 m) contained 22 ± 3.7 % coarse sand, 26 ± 3.6 % fine sand,
199 34 ± 5.1 % silt and 18 ± 2 % clay and subsoil samples (0.4 to 1.0 m) contained $18 \pm$
200 5.3 %, 22 ± 4.2 %, 34 ± 4.5 % and 25 ± 4 %, respectively (Diamond, 1988). Clay
201 content increases with depth on site as sand decreases. Silt content remains the same.
202 Textural changes are not due to pedological processes but to small scale sorting of
203 glacial till. It is this transition between sand and clay that governs K_{sat} heterogeneity at

204 depth. Subsoils with a high percentage of fines (clay and silt) are classed as having
205 low permeability, poorly sorted subsoils are assigned as having moderate permeability
206 and well sorted coarse grained subsoils (glaciofluvial sand and gravel) have high
207 permeability (Swartz *et al.*, 1999).

208

209 In 2005, the first groundwater samples were taken. (The study site was instrumented
210 with piezometers in 2003.) Initially, 30% of all shallow groundwater samples (< 5 m)
211 exceeded NO₃-N drinking water quality targets (11.3 mg NO₃-N l⁻¹). The present
212 model is only applicable to shallow flow lines of the same groundwater age
213 connecting the pollution source to the 1 m screen intervals in all 17 piezometers.
214 (Fenton *et al.*, 2008) investigated the source of pollution and proposed the use of a
215 continuous shallow denitrification trench to intercept contaminated shallow
216 groundwater. A stationary beef dirty water irrigation system, operated on the sandhill
217 for decades until 2004, and was identified as a pollution point source (Figure 2). This
218 small area has been treated uniformly over a long period of time, before and after
219 implementation of the irrigation system. Currently, the site is cut for silage twice a
220 year and is being used to monitor natural attenuation of the elevated groundwater
221 NO₃-N plume migration, position and concentration on site.

222

223 **2. MATERIALS AND METHODS**

224 **2.1 NUTRIENT MANAGEMENT**

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

229

230 **2.2 MONITORING ON SITE**

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

239

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

251

252 Surface water features, such as streams, drains and lagoons, were also levelled on the
253 same date. The maps were used to construct groundwater maps and elucidate

254 groundwater flow direction. A topographic base map with a field boundary overlay
255 was generated using ArcGIS™ and merged with well location and groundwater head
256 input files. 2-dimensional groundwater data models were generated using GW-
257 Contour 1.0 software (Waterloo Hydrogeologic, Canada).

258

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

265

266 **2.3 WATER BALANCE**

267 A water balance of the site was used to calculate the travel time from surface level to
268 the watertable in the six isolated plots. Daily weather data, recorded at the Johnstown
269 Castle Weather Station, were used to calculate daily soil moisture deficit (SMD) using
270 a Hybrid model for Irish grasslands. Potential evapotranspiration, ET_0 (mm day⁻¹),
271 was calculated using the FAO Penman-Montieth equation (Allen *et al.*, 1998):

272

$$273 \quad ET_0 = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)} \quad (1)$$

274

275 where R_n is the net radiation at the crop surface (m⁻² day⁻¹), T is the air temperature at
276 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
277 saturation and the actual vapour pressure curves (kPa °C⁻¹), and γ is the psychrometric

278 constant ($\text{kPa } ^\circ\text{C}^{-1}$). ET_0 was then converted to actual evapotranspiration (Ae) using an
 279 Aslyng scale recalibrated for Irish conditions (Schulte *et al.*, 2005). Effective rainfall
 280 was calculated by subtracting daily actual evapotranspiration from daily rainfall
 281 (assuming no overland flow losses due to the high infiltration capacity of the soil on
 282 this site). Higher K_{sat} zones were found in the topsoil, even in the poorly drained plot.
 283 SMD on day one (January 1st, 2006 and 2007) was set to zero and effective drainage
 284 was estimated for each subsequent day. Modelling the effective drainage enables the
 285 infiltration depth of water to be calculated at specific hydraulic loads where the soil
 286 effective porosity is known. This infiltration depth may be compared to watertable
 287 data to investigate if recharge to groundwater in that particular year affects water
 288 quality.

289

290 **2.4 HYDRAULIC CONDUCTIVITY DETERMINATION**

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

$$299 \quad K_{sat} = \frac{r_c^2 \ln\left(\frac{R_e}{r_w}\right)}{2d} \frac{1}{t} \ln \frac{h_0}{h_i} \quad (2)$$

300 where r_c is radius of the unscreened part of the well where the head is rising, r_w is the
 301 horizontal distance from the well centre to the undisturbed aquifer, R_e is the radial

302 distance over which the difference in head, h_o , is dissipated in the flow system of the
 303 aquifer, d is the length of the well screen, h_o is the head in the well before the start of
 304 the test and h_t is the head in the well at time $t > t_o$.

305

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

$$307 \quad \ln \frac{R_e}{r_w} = \left[\frac{1.1}{\ln\left(\frac{b}{r_w}\right)} + \frac{A + B \ln\left[\frac{(D-b)}{r_w}\right]^{-1}}{\frac{d}{r_w}} \right] \quad (3)$$

308 where b is the distance from the watertable height to the bottom of the well, D is the
 309 distance from the watertable to the impermeable zone, and A and B are dimensionless
 310 parameters, which are function of d/r_w . If $D \gg b$, the effective upper limit of $\ln [(D-$
 311 $b)/r_w]$ may be set to 6. A spatial K_{sat} map was developed in ArcGIS™ and merged
 312 with well location and groundwater head input files. b is measured by an electronic
 313 dipper before commencement of the slug test.

314

315 **2.4.1 DISCHARGE AND DARCIAN VELOCITY**

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

$$318 \quad Q = -K_{sat} A \frac{dh}{dx} \quad (4)$$

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

321

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

$$323 \quad v = -K_{sat} \frac{1}{n} \frac{dh}{dx} \quad (5)$$

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

326

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

$$328 \quad T = K_{sat} b \quad (6)$$

329

330 **2.4.2 BUFFER ZONE DIAMETER AND CONTAMINANT MASS FLUX**

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

$$335 \quad D = \frac{Q}{bv} \quad (7)$$

336 where Q is calculated using equation 4, b is the aquifer thickness as used in equation
337 6 and v is calculated using equation 5. The central piezometer in each plot was taken
338 as the centre of the buffer area. In areas where groundwater flow direction is known
339 the buffer zone method over estimates the groundwater contribution down hydraulic
340 gradient, while underestimating the area of contribution up hydraulic gradient, which
341 should extend to a groundwater divide. When groundwater flow direction is known
342 the buffer zone becomes a true zone of contribution (ZOC). This is then defined as the
343 area surrounding the piezometer that encompasses all areas or features that supply
344 groundwater recharge to the piezometer up hydraulic gradient to the groundwater
345 divide. In this case the groundwater divide is represented by the brow of the sandhill.
346 Over a period of time, determined by effective Darcian velocity, groundwater within
347 the ZOC will flow past the piezometer monitoring point and thus will affect the

348 hydrochemistry at that point. In this study land use management within the entire
349 ZOC, was assessed.

350

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

$$359 \quad w = \sum_{i=1}^{i=n} C_i q_i A_i \quad (8)$$

360 where w is total mass flux across a control plane ($\text{g m}^3 \text{ day}^{-1}$), C_i concentration of
361 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
362 of i th plot (m^2). Within the plots, three control planes were assigned using the top (3,
363 5, 8, 11, 14, 17), middle (2, 7, 10, 13) and bottom (1, 4, 6, 9, 12 and 15 form the
364 compliance control plane) piezometers (Figure 2). The contaminant mass flux passing
365 through each control plane was calculated and the natural attenuation process
366 assessed.

367

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

$$371 \quad \text{Efficiency} = \frac{N_{IN} - N_{OUT}}{N_{IN}} * 100\% \quad (9)$$

372 where N_{IN} is the up-gradient $\text{NO}_3\text{-N}$ contaminant mass flux and N_{OUT} is the down
373 gradient contaminant mass flux.

374

375 **2.5 TOBIT REGRESSION**

376 The effects on groundwater $\text{NO}_3\text{-N}$ concentration of K_{sat} (m day^{-1}), elevation, screen
377 opening elevation and distance from pollution source were assessed using a Tobit
378 regression model (Tobin, 1958). The $\text{NO}_3\text{-N}$ concentration was left censored using a
379 background concentration threshold of 2.6 mg L^{-1} . Model selection was performed
380 using a forward selection stepwise procedure. Due to the grid layout of the
381 piezometers, residuals could not be assumed to be independent and their spatial
382 dependence was modeled using an anisotropic power covariance structure. The
383 anisotropic power correlation model depends on two parameters: one that represents
384 the correlation between piezometers in the direction of rows and the other that
385 represents the correlation in the direction of columns. Models were fitted using the
386 MIXED procedure (SAS, 2003). To separate the effect of groundwater $\text{NO}_3\text{-N}$
387 denitrification from dilution, groundwater $\text{NO}_3\text{-N}$ retention is studied by evaluating
388 concurrently groundwater $\text{NO}_3\text{-N}$ and Cl^- concentration (Altman et al., 1995). To
389 investigate the effect of dilution on the study area Cl^- was also inputted into the
390 model. Cl^- is considered a conservative tracer.

391

392 **2.6 DENITRIFICATION**

393 Denitrification is considered the most important reaction for NO_3^- remediation in
394 aquifers. The process of denitrification occurs in O_2 depleted layers with available
395 electron donors and in agricultural environments with N nutrient losses considerable
396 NO_3^- reduction is possible. To investigate further if denitrification is a viable pathway

397 for NO_3^- reduction some additional water quality measurements were taken on a
398 random date. Physio-chemical parameters- pH, redox potential (Eh (mV)),
399 conductivity (cond ($\mu\text{S cm}^{-1}$)), temperature (temp ($^{\circ}\text{C}$)) and rugged dissolved oxygen
400 (RDO ($\mu\text{g L}^{-1}$)) were measured in the field using a multi parameter Troll 9500 probe
401 (In-situ, Colorado, U.S.A) with a flow through cell.

402 To elucidate the locations of potential denitrification during groundwater sampling
403 based on dissolved N_2 and the N_2/Ar ratio, three water samples were taken from each
404 piezometer mid way within the screened interval using a 50 ml syringe and gas
405 impermeable tubing. Samples were transferred from the syringe to a 12 ml
406 Exetainer® (Labco Ltd, UK) and sealed to avoid any air entrapment with a butyl
407 rubber septum. Samples were then placed under water in an ice box, transported to
408 laboratory and kept in a cold room at 4°C prior to analysis. Dissolved N_2 , O_2 and Ar
409 were analyzed using a Membrane Inlet Mass Spectrometry (MIMS) at the temperature
410 measured (11°C) during groundwater sampling (Kana et al. 1994). For N_2O
411 concentration, three additional samples were taken in glass bottles for degassing.
412 Eighty ml collected water was injected into a pre-evacuated 160 ml serum bottle
413 followed by 80 ml pure helium. The bottles were shaken for 5 minutes and then 15 ml
414 equilibrated gas in the headspace was collected using an air-tight syringe and
415 transferred into a 12 ml Exetainer for the analysis of dissolved N_2O using a gas
416 chromatography (GC; Varian 3800, USA) equipped with electron capture detector.
417 The concentration of dissolved N_2O was calculated by using the Henry's law constant,
418 the concentration of the gas in the head space, the bottle volume, and the temperature
419 of the sample but the lowest 14°C was taken due to limitation in gas solubility
420 coefficient to calculate Henry's law constant (Hudson, 2004).

421 **3 RESULTS**

422 **3.1 NUTRIENT MANAGEMENT**

423 In 2006 as in previous years after the point source was removed, the sandhill area, the
424 northwest area and the isolated plots received the same N application (Table 1). What
425 about previous years e.g. before 2003-2005. Comment here. These areas were cut for
426 first cut silage at the end of May and for second cut silage in July but they were not
427 grazed by cattle for the duration of this study. Half of the fertiliser N was applied as
428 urea in late-February and April and the remaining N was applied in June and August
429 as calcium ammonium nitrate (CAN). Loss of N to the environment from urea would
430 tend to be atmospheric ammonia (NH_3) losses as urea tends to be immobile and is
431 retained in the soil by cation exchange capacity (CEC). Whereas N applied as CAN is
432 already partially nitrified and would be susceptible to leaching and denitrification.

433

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

441

442 In June 2007, in addition to fertilizer application (Table 1), the sandhill and northwest
443 area received 118 kg N ha^{-1} as cattle slurry. The sandhill area was N-deficient by
444 approximately 24 kg N ha^{-1} for first cut silage in May. With addition of CAN and
445 slurry in June, there was an N-surplus of approximately 70 kg N ha^{-1} after second cut

446 silage. In July and August 2007, there was a large increase in effective drainage. With
447 the time lag between second cut silage and the final application of CAN in the middle
448 of August, there was just enough N available for grass recovery. The same was true
449 for the northwest site but there was a surplus after first cut silage in May.

450

451 **3.2 WATER BALANCE**

452 A water balance for the site showed total precipitation of 992.6 mm and 889.1 mm for
453 2006 and 2007, respectively. For the two years, the Hybrid model calculated 483 mm
454 and 335 mm drainage through the root zone in a process known as effective drainage.
455 It was assumed that all of this direct recharge reached the watertable as the rainfall
456 intensity is generally lower than the soil infiltration capacity. Model output showed
457 effective drainage occurred on 87 and 74 days, giving an average recharge rate of 5.5
458 and 4.5 mm day⁻¹, respectively. Cumulative drainage for both years is presented in
459 Figure 3. The mean soil total porosity was 32.2±4.9%. The average pore velocity was
460 estimated to be 17.3 and 14.1 mm day⁻¹, giving an approximate mean travel depth of
461 1.5 and 1.04 m in a moderately-drained soil for 2006 and 2007. The mean watertable
462 depth for 2006- 2008 on site was 2.2 m bgl. This is the unsaturated zone vertical
463 travel time (approx 2 years) achievable due to effective drainage, representative of
464 drainage during the winter period. Lateral migration of the nutrients is with
465 groundwater flow direction under the experimental plots.

466

467 Accumulative effective drainage shows differential recharge each year and seasonal
468 differences in recharge led to differential NO₃-N dilutions over time. Both years had
469 wet winters but 2006 had a dry summer period (Figure 3). Slurry was only spread in
470 times of dry weather. This contributed to higher mean site NO₃-N concentrations for

471 sampling events in early 2006. The dry summer of 2006 halted significant recharge
472 and NO₃-N concentrations reached steady state. As effective drainage increases,
473 overall mean NO₃ concentration on site increases.

474

475 Each piezometer followed the same pattern for mean NO₃-N concentration, with some
476 piezometers falling below the 11.3 mg L⁻¹ threshold for drinking water quality within
477 1 year. There was no increase in the shallow groundwater NO₃-N concentration, after
478 the slurry application in June 2007 due to a combination of slow groundwater
479 transport (K_{sat} ranges from 0.001 – 0.016 m day⁻¹ with subsequent travel distance of
480 2.9 and 4.5 m yr⁻¹) (Table 2) and gaseous losses of NH₃.

481

482 **3.3 BUFFER ZONE AND CONTAMINANT MASS FLUX**

483 Buffer zone diameter for plots 1-6, using equation 7, was 193, 178, 195, 195, 148 and
484 120 m respectively. A mean area of 2.4 ha for the ZOC was calculated. The buffer
485 zones can extend beyond the isolated study site to the groundwater divide in the
486 sandhill area. Therefore, land management and recharge in the entire ZOC area can
487 contribute to shallow groundwater NO₃-N contamination within the study site. The
488 historical stationary dirty water point source pollution occurred within this ZOC.

489 The contaminant mass fluxes calculated for three control planes are presented in Table
490 2. Influent contaminant mass flux through the upper control plane cells ranged from
491 0.0008 to 0.0016 g N m³ day⁻¹ and the contaminant mass fluxes leaving the site at the
492 compliance plane ranged from 0.00001 to 0.0007 g N m³ day⁻¹. Total contaminant
493 mass flux on a plot basis was as follows: Plot 3>1>5>4>6. Total contaminant mass
494 flux decreased from the top plane to the central plane to the compliance plane
495 demonstrating natural attenuation. Using equation 9, a 42 % contaminant mass flux

496 reduction efficiency was calculated from the influent control plane to the central
497 plane. From the central plane to the compliance plane a 64 % reduction occurred. Plot
498 3 contributed the greatest contaminant mass flux. The load transfer from the influent
499 control plane to the central control plane showed a reduction of 33.6 %, with a
500 subsequent reduction of 69.5 % at the compliance control plane. Plot 4 showed a 96 %
501 reduction in contaminant mass flux from the influent control plane and the central
502 control plane. Plot 1 doubled its contaminant mass flux from the influent control plane
503 to the central control plane, but then decreased by 51.2 % downgradient at the
504 compliance control plane. The upper, middle and lower control planes are 18%, 44%
505 and 76% below the compliance control plane threshold (11.3 mg l⁻¹ with present flux)
506 respectively.

507

508 **4 TOBIT REGRESSION**

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

516

517 When assessed individually, K_{sat} ($p=0.0004$) had significant impacts on NO₃-N
518 concentrations. However, K_{sat} ($p=<0.001$) and distance from point source ($p=0.0014$)
519 are significant when K is already in the model. The stepwise procedure selected the
520 K_{sat} and distance from point source as having more explanatory power than when

521 other parameters are inputted into the model. The final model contains only K_{sat} and
522 distance from point source. The final model is presented in Figure 4.

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

527

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

537

538 **4.1 DILUTION AND DENITRIFICATION DIFFERENTIATION**

539 In some locations the Cl^- concentration is representative of natural background levels
540 (NBL). In Ireland groundwater has a median NBL of 18 mg L^{-1} . Some points
541 therefore were not included in the regression process. Plots 1, 2, 4, 5 and 6 have the
542 highest ratio in the top of the plots nearest the source but standard deviation shows
543 some change over time (Table 3).

544

545 The model was run a second time to explain Cl⁻ occurrence using the same parameters
546 as before. Here K_{sat} and ground elevation have the greatest explanatory power but K_{sat}
547 is not significant. As shown previously, NO₃-N occurrence in the same piezometers
548 was explained by K_{sat} and distance from the dirty water point pollution source
549 pollution, while both being significant. Due to the fact that K_{sat} influences NO₃-N
550 occurrence but not Cl⁻ occurrence denitrification can be inferred. But distances from
551 the dirty water source and ground elevation are linked due to the nature of the sloped
552 site and therefore dilution is a factor for Cl⁻ occurrence. In general on site:

- 553 • Low NO₃ concentration and unaffected Cl⁻ concentration points to
554 denitrification (Figure 5a)
- 555 • Low NO₃ concentration and low Cl⁻chloride concentration points to dilution
556 (Figure 5b)
- 557 • Over lying Figure 6a and 6b allows areas of denitrification and dilution to be
558 inferred (Figure 5c)

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

563

564 To further elucidate the effect of groundwater denitrification on NO₃-N occurrence on
565 the site, dissolved gases and physiochemical properties of groundwater collected on a
566 random date were determined and related to the mean groundwater NO₃-N
567 concentration during the study. Average groundwater NO₃-N was significantly
568 ($P<0.05$) related to groundwater N₂/Ar ratio, redox potential (Eh), dissolved O₂ and
569 N₂ and was close to being significant with dissolved N₂O concentration ($P=0.08$)

570 (Table 7). Based on the AIC score N_2/Ar ratio and redox potential (Eh) were the best
571 fitting models of groundwater NO_3-N occurrence. The higher ratio of N_2/Ar directly
572 indicates that denitrification is occurring on the site (Figure 5d) and that lower redox
573 potentials and dissolved oxygen are related to lower groundwater NO_3-N occurrence
574 (Table 7).

575

576 **5 DISCUSSION**

577 Documented nutrient management of the study site, while contributing to the elevated
578 NO_3-N concentration in shallow groundwater, could not solely account for NO_3-N
579 distribution on site. Surplus nutrients calculated for 2007 in the sandhill area had not
580 yet reached the shallow groundwater under the plots due to slow travel times. Historic
581 dirty water irrigation occurred on the sandhill site for decades prior to this study with
582 excessive hydraulic loads leading to elevated infiltration on the sandhill.

583

584 Vertical unsaturated zone travel time was not within a single drainage season.

585 Saturated shallow groundwater and contamination plume migration time was from
586 2.92 to 4.50 $m\ yr^{-1}$ underneath the plots. The travel time from the sandhill (source) to
587 the plots approximately 200 m away was much quicker due to the sand.

588 Dilution of the groundwater NO_3-N concentrations by recharge to the shallow
589 watertable occurred in both study years. A two-layered conceptual model of the site
590 emerged, where higher NO_3-N concentrations existed in the shallower, high K_{sat}
591 subsurface.

592

593 The model describes the relationship between mean groundwater NO_3-N
594 concentration and the explanatory variables K_{sat} and distance of the piezometers from

595 the point pollution source. To account for bias due to the distance of each piezometer
596 within the grid pattern from the pollution source, the spatial dependence of residuals
597 was modelled using an anisotropic power covariance structure. Higher K_{sat} zones in
598 the subsurface allow faster migration of contaminated groundwater, resulting in
599 shorter retention time. The shorter retention time in the high K_{sat} zone decreases the
600 opportunity for denitrification to occur. Lateral flow in higher K_{sat} layers may result
601 in surface water pollution. The opposite is true of lower K_{sat} zones, where a longer
602 retention time is available for denitrification to occur. This is why low $\text{NO}_3\text{-N}$
603 concentrations may be present at the plume centroid. In elevated areas, the watertable
604 mirrors topography and has a greater hydraulic gradient and higher K_{sat} values.
605
606 Groundwater $\text{NO}_3\text{-N}$ occurrence was statistically related to topsoil denitrifying
607 enzyme activity, topsoil inorganic N content, depth to water table and a stronger
608 relationship was observed with vadose zone permeability (McLay et al., 2001). The
609 effect of vadose zone permeability on groundwater $\text{NO}_3\text{-N}$ distribution was
610 recognised by (Vellidis *et al.*, 1996) who observed low N leaching associated with low
611 subsoil permeability and (Hansen *et al.*, 1996) observed high N leaching with high
612 subsoil permeability. (Richards *et al.*, 2005) observed lower groundwater $\text{NO}_3\text{-N}$
613 occurrence in deeper wells with clay soils with no cropland nearby but they could not
614 separate the effect of K_{sat} from landuse or well depth. In Ireland (Ryan *et al.*, 1996)
615 also highlighted the importance of soil type and permeability with lower $\text{NO}_3\text{-N}$
616 losses from soil with the percentage fines (silt and clay) >75% estimated mean
617 subsoil travel times of 0.01 m day^{-1} on a site with elevated groundwater $\text{NO}_3\text{-N}$
618 concentrations. The unsaturated vadose zone transport of $\text{NO}_3\text{-N}$ is clearly influenced
619 by the permeability and thus longer residence time in lower permeability subsoil

620 favouring NO₃-N reduction through denitrification. The strong relationship observed
621 in this work also clearly identifies the importance of the saturated subsoil zone in
622 favouring NO₃-N reduction by denitrification in low subsoil permeable zones. Also
623 importance is the exact location of the point pollution source. The strong correlations
624 between mean groundwater NO₃-N and denitrification end products (N₂O and N₂) and
625 physiochemical properties favouring denitrification (dissolved O₂ and Eh) further
626 supports that denitrification is the dominant process controlling groundwater NO₃-N
627 occurrence and transport on the study site. The relationship between subsoil/aquifer
628 K_{sat} and denitrification requires further investigation.

629

630 In Ireland, groundwater protection is based on the mapping of vulnerability zones for
631 the protection of groundwater source (wells and springs) and the groundwater
632 resource. Irish aquifers are deemed to have low attenuation potential due to there
633 fractured and karstified nature and thus they are mainly protected by the overlying
634 glacial tills. Vulnerability zones are ranked in four classes from extreme to low
635 vulnerability based primarily on the thickness and lithology/permeability of the
636 Quaternary subsoil deposits (Daly *et al.*, 1988). Vulnerability decreases with
637 increasing thickness and decreasing permeability of subsoil. The definition of
638 groundwater in Ireland often excludes the shallow groundwater in subsoils (with the
639 exception of sand and gravel aquifers) as it is not valued as a potential source of water
640 for human consumption. Although not sufficient for consumption shallow subsoil
641 groundwater is environmentally important as it contributes to through flow and drain
642 flow to surface waters bypassing any potential for abatement when transported
643 through deeper aquifers.

644

645 Groundwater protection in Ireland for subsoil permeability is not routinely measured
646 in Irish subsoils, (Fitzsimons *et al.*, 2006) classified Irish till permeability as being
647 highly permeable $K_{sat}=10 \text{ m day}^{-1}$, moderately permeable when $K_{sat} = 0.004$ to 0.009
648 m day^{-1} and low permeability (clay content >13%) when $K_{sat}= 0.0004$ to 0.0009 m
649 day^{-1} . Mean plot K_{sat} values on site range from $0.008 - 0.01 \text{ m day}^{-1}$. This suggests
650 further classification may be needed from moderate to highly permeable classes.

651

652 Contaminant mass flux calculations show that the load of $\text{NO}_3\text{-N}$ passing through
653 parallel control planes perpendicular to groundwater flow was uneven across the site.
654 A 96 % reduction in contaminant mass flux occurred across the control planes in Plot
655 3. This leads to groundwater $\text{NO}_3\text{-N}$ loads of acceptable quality leaving the site.

656 Natural attenuation occurred down-gradient in all plots except Plot 1.

657

658 In this study subsoil permeability and distance from point source pollution have been
659 clearly identified as significant factors in determining the occurrence of $\text{NO}_3\text{-N}$ in
660 groundwater. The subsoil on the study classified as moderate permeability and this
661 study highlights the need to further subdivide this category for risk assessment of
662 $\text{NO}_3\text{-N}$ occurrence in groundwater and transport to surface waters via through flow or
663 artificial drainage. Furthermore as subsoil K_{sat} is incorporated in the contaminant mass
664 flux calculation, particular hot spot locations may be identified, which contribute
665 significantly more contaminant flux per unit area to potential down-gradient receptors.
666 The identification of hot spots of groundwater contaminants may be used to target
667 areas for locating an environmental remediation technology to reduce contaminant
668 fluxes to sensitive receptors.

669

670 **6 CONCLUSION**

671 K_{sat} and distance from point source are important when assessing the spatial
672 distribution of NO_3-N in shallow groundwater. Within subsoils classified as
673 moderately permeable subsoil saturated hydraulic conductivity was significantly
674 related to groundwater NO_3-N occurrence and slight differences in permeability
675 greatly influenced the concentrations on site. Groundwater denitrification is likely to
676 be the dominant process influencing groundwater NO_3-N occurrence and transport at
677 this site. Calculating contaminant mass flux across more than one control plane is a
678 useful tool to monitor natural attenuation. This tool allows the identification of hot
679 spot areas where intervention other than natural attenuation may be needed to protect
680 receptors.

681

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867 **LIST OF FIGURES**

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870 **Figure 1.** Field site and northwest and elevated sandhill locations.

871

872 **Figure 2.** Field site and elevated sandhill. Groundwater flow map. Sandhill
873 groundwater head contours are based on watertable data from 3 wells drilled in this
874 area. Wells 1, 4, 6, 9, 12 and 15 form the compliance control plane. Wells 3, 5, 8, 11,
875 14, and 17 form the first control plane. Wells 2, 7, 10, 13 and 16 form the
876 intermediate control plane.

877

878 **Figure 3.** Calculated cumulative effective drainage (mm) from 2006 to 2007.

879 **Figure 4.** Predictions of NO₃-N from fitted model.

880

881 **Figure 5** Spatial distribution across the six plots (x axis) of groundwater a) Mean

882 NO₃-N concentration b) Mean Cl⁻ concentration c) mean NO₃/Cl⁻ ratio and d) N₂/Ar

883 ratio on a random date.

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Table 1. Nutrient management of the sandhill, northwest and field site for 2006 and 2007.

Year	Location	Area (ha)	Month	N fertiliser application rate (kg N ha ⁻¹)	Nitrogen fertiliser type
2006	Sandhill	3.2	Feb	28.5	Urea†
			April	124.1	Urea
			June	102.1	CAN†
			Aug	51.1	CAN
	Northwest	2.8	Feb	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	Plots	4.2	Feb	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	83.7	CAN
2007	Sandhill	3.2	March	56.9	Urea
			April	71.2	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	Northwest	2.8	March	56.9	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	Plots	4.2	March	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	83.7	CAN

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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

Parameters	Plot Number					
	1	2	3	4	5	6
Area (ha)	0.78	0.75	1.01	0.94	0.41	0.41
Width of plot (m)	50	50	55	55	30	30
Mean effective velocity v (m day ⁻¹)	0.011	0.006	0.012	0.013	0.012	0.008
Hydraulic conductivity K (m day ⁻¹)	0.009	0.0083	0.0117	0.0117	0.0123	0.008
Transmissivity T (m ² day ⁻¹)	0.07	0.07	0.09	0.09	0.1	0.06
Mean hydraulic head (Top) (m AOD)	67.13	68.65	70.13	69.92	69.53	69.3
Mean hydraulic head (Bottom) (m AOD)	63.31	66.21	66.8	66.4	66.5	66.28
Mean Travel Distance in 1 year	3.92	2.31	4.44	4.70	4.25	2.76
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Q	m ³ 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
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Contaminant Mass Flux	g m ³ 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 3. Selected piezometer parameters from 2005 – 2008.

Piezometer	Plot	Position	Elevation (mAOD)	Total depth (m bgl)	Mean NO ₃ -N (mg L ⁻¹)	Stdev±	Mean NO ₂ -N (mg L ⁻¹)	Stdev±	Mean Cl ⁻ (mg L ⁻¹)	Stdev±	Mean NH ₄ -N (mg L ⁻¹)	Stdev±	Mean NO ₃ -N/Cl ⁻ ratio	Stdev±	K _{sat} (m day ⁻¹)	Mean Watertable Elevation (mAOD)
1	1	Bottom	67.8	3.6	6.9	2.7	0.04	0.1	27.1	6.1	0.24	0.3	0.08	0.25	0.007	63.7
2	1	Middle	70.2	4.1	11.6	4.9	0.05	0.2	24.9	7.4	0.25	0.6	0.09	0.48	0.01	66.9
3	1	Top	72.1	4.3	5.6	3.5	0.07	0.1	18.4	4.8	0.34	0.3	0.25	0.30	0.01	67.9
4	2	Bottom	67.6	3.1	1.4	3.5	0.07	0.0	28.8	8.1	1.67	1.1	0.18	0.10	0.001	66.3
5	2	Top	72.0	4.3	11.8	5.7	0.02	0.0	19.0	5.2	0.21	0.5	0.27	0.62	0.015	68.8
6	3	Bottom	68.2	3.5	12.8	3.4	0.09	0.2	32.5	5.5	0.26	0.4	0.09	0.41	0.015	66.6
7	3	Middle	70.0	2.6	7.3	2.6	0.01	0.0	19.0	10.4	0.06	0.1	0.08	0.43	0.01	68.5
8	3	Top	71.7	3.2	11.0	3.4	0.03	0.1	59.0	9.5	0.22	0.4	0.04	0.53	0.01	69.6
9	4	Bottom	67.7	2.7	0.1	1.3	0.01	0.0	9.9	10.6	0.16	0.1	0.06	0.02	0.012	65.1
10	4	Middle	69.5	2.9	0.3	1.5	0.00	0.0	41.4	6.3	0.10	0.1	0.06	0.01	0.013	67.9
11	4	Top	71.8	2.4	5.7	2.7	0.00	0.0	21.9	7.8	0.06	0.2	0.08	0.24	0.01	70.3
12	5	Bottom	67.7	1.5	8.7	2.3	0.01	0.0	32.5	7.2	0.08	0.1	0.07	0.27	0.006	65.6
13	5	Middle	69.4	2.8	9.4	2.7	0.00	0.0	29.1	4.9	0.07	0.1	0.09	0.32	0.015	68.2
14	5	Top	72.0	4.3	12.8	4.1	0.02	0.1	30.2	2.9	0.24	0.4	0.15	0.47	0.016	71.0
15	6	Bottom	67.4	2.9	3.6	2.7	0.02	0.0	33.9	4.1	0.23	0.4	0.08	0.10	0.002	64.0
16	6	Middle	68.4	3.1	5.0	1.7	0.04	0.1	24.5	6.4	0.14	0.2	0.11	0.19	0.01	67.1
17	6	Top	71.1	3.0	9.3	2.0	0.04	0.1	23.2	12.2	0.12	0.5	0.13	0.41	0.012	70.2

Table 4. Details of the stepwise procedure used to select the explanatory variables of importance in the relationship between mean groundwater NO₃-N concentration and hydrogeological factors. Model containing K_{sat} and distance from point source is chosen as the final model.

Step 1	Include all variables individually in model		Step 3	Add other variables to model containing K _{sat} and distance from point source (m)	
Effect	F(1,11)	P-value	Effect	F(1,9)	P-value
K _{sat} (m day ⁻¹)	24.55	0.0004	K _{sat} (m day ⁻¹)	53.5	<0.0001
Elevation (m AOD)	10.23	0.0085	Distance from point source (m)	9.68	0.0125
Distance from point source (m)	0.6	0.4562	Elevation (m AOD)	0.08	0.7884
Screen depth (m AOD)	1.28	0.2826			
Result of step 1	K chosen as most important		K _{sat} (m day ⁻¹)	73.45	<0.0001
			Distance from point source (m)	15.79	0.0032
			Screen depth (m AOD)	1.69	0.2253
Step 2	Add other variables to model containing K		Result of step 3	Other variables not significant in a model that contains K _{sat} and distance from point source	
Effect	F(1,10)	P-value			
K _{sat} (m day ⁻¹)	13.05	0.0048			
Elevation (m AOD)	1.75	0.2156			
K _{sat} (m day ⁻¹)	78.85	<0.0001			
Distance from point source (m)	19.1	0.0014			
K _{sat} (m day ⁻¹)	33.75	0.0002			
Screen depth (m AOD)	1.47	0.2526			
Result of Step 2	Distance is significant when K _{sat} is already in the model				

Table 5. Estimated model coefficients for final NO₃-N model but also for Cl⁻ from the regression.

Effect	Coefficient	Standard Error	Degrees of Freedom (DF)	t-value	P-value
NO ₃ -N					
Intercept	-13.7328	3.6584	0	-3.75	
K	960.98	108.22	10	8.88	<0.001
Distance	0.0506	0.01158	10	4.37	0.0014
Cl ⁻					
Intercept	212.34	62.22	0	3.41	
K	548.59	390.49	12	1.40	0.1854
Elevation	-2.73	0.9294	12	-2.94	0.0123

Table 6. Percentage variation explained by different factors

	Degrees of freedom	SS	% variation
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Fixed			
K_{sat} (m day ⁻¹)	1	63.72	55.5
Distance from point source (m)	1	15.52	13.3
Screen depth (m AOD)	1	5.48	4.8
Elevation (m AOD)	1	0.62	0.5
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Random			
Row	1	7.95	6.9
Column	1	4.26	3.7
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Residual	5	17.58	15.3
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	Total	114.90	
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Table 7. Relationships between dissolved groundwater gases, redox potential (Eh) and average NO₃-N. Each parameter is regressed in turn against average NO₃-N. The spatial structure on the variance covariance matrix is as described for the stepwise regression.

Parameter	Estimate	Standard Error	T value _{13 DF}	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







