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7 AUTHORS: M.M.R. Jahangira, P. Johnston, M.I. Khalil, K.G. Richards

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15 **Linking hydrogeochemistry to nitrate abundance in groundwater**
16 **in agricultural settings in Ireland**
17

18 M.M.R. JAHANGIR^{1, 2}, P. JOHNSTON², M.I. KHALIL³, K.G. RICHARDS^{1, 4}

19

20 ¹Teagasc Environment Research Centre, Johnstown Castle, Co. Wexford, Ireland

21 ²Department of Civil, Structural and Environmental Engineering, Trinity College Dublin,

22 Ireland; ³Environmental Protection Agency, Co. Wexford, Ireland; ⁴Corresponding Author*

23

24

25

26

27 *Teagasc Environment Research Centre

28 Johnstown Castle

29 Co. Wexford

30 Ireland

31 Tel: +353 (0) 53 9171200

32 E-mail: jahangim@tcd.ie

33

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40 **Abstract**

41 Nitrate (NO_3^- -N) contamination of groundwater and associated surface waters is an
42 increasingly important global issue with multiple impacts on terrestrial, aquatic and
43 atmospheric environments. Investigation of the distribution of hydrogeochemical variables
44 and their connection with the occurrence of NO_3^- -N provides better insights into the
45 prediction of the environmental risk associated with nitrogen use within agricultural systems.
46 The research objective was to evaluate the effect of hydrogeological setting on agriculturally
47 derived groundwater NO_3^- -N occurrence. Piezometers (n=36) were installed at three depths
48 across four contrasting agricultural research sites. Groundwater was sampled monthly for
49 chemistry and dissolved gases, between February 2009 and January 2011. Mean groundwater
50 NO_3^- -N ranged 0.7 to 14.6 mg L⁻¹, with site and groundwater depth being statistically
51 significant (p<0.001). Unsaturated zone thickness and saturated hydraulic conductivity (K_{sat})
52 were significantly correlated with dissolved oxygen (DO) and redox potential (Eh) across
53 sites. Groundwater NO_3^- -N occurrence was significantly negatively related to DOC and
54 methane and positively related with Eh and K_{sat} . Reduction of NO_3^- -N started at Eh potentials
55 <150 mV while significant nitrate reduction occurred <100 mV. Indications of heterotrophic
56 and autotrophic denitrification were observed through elevated dissolved organic carbon
57 (DOC) and oxidation of metal bound sulphur, as indicated by sulphate (SO_4^{2-}). Land
58 application of waste water created denitrification hot spots due to high DOC losses.
59 Hydrogeological settings significantly influenced groundwater nitrate occurrence and
60 suggested denitrification as the main control.

61

62 Key words: K_{sat} , Dissolved Organic C, Dissolved Oxygen, redox-potential, SO_4^{2-} , nitrate
63 retention

64 **1. Introduction**

65 At the global scale, fertilizer production, fossil fuel combustion and the widespread
66 cultivation of leguminous crops now cause more atmospheric N₂ to be fixed into chemically
67 and biologically reactive forms than all natural processes on land combined and at regional
68 scale, the transformations are even more dramatic (Townsend and Davidson, 2006). The high
69 rates of N deposition result in nitrogen (N) saturation in agricultural land causing high nitrate
70 delivery to groundwater which is a widespread problem in agricultural areas in Europe, North
71 America and East Asia. Groundwater nitrate contamination is a global environmental and
72 health concerns (Rivett et al., 2007) due mainly to its potential connection to the deterioration
73 of air quality related to particulate matter and ground level ozone (Townsend et al., 2003),
74 acidification of lakes and streams (Driscoll et al., 2001), eutrophication, hypoxia and algal
75 bloom (Rabalais, 2002; Mason, 2002); and methaemoglobinaemia (WHO, 2004).
76 Groundwater is an important water resource in the Republic of Ireland and accounts for up to
77 15% of total water supplied by local authorities and about 25% of all water supplies (Daly,
78 1993) where nitrate is one of the common contaminants (EPA, 2008).

79 Nitrate concentration in groundwater, however, do not necessarily remain constant and is a
80 function of several physical and biogeochemical processes e.g. dispersion, denitrification,
81 microbial assimilation, immobilization, DNRA and anammox (Burgin and Hamilton, 2007)
82 which are functions of local hydrogeochemistry. Of the biogeochemical processes,
83 denitrification is the principal process which converts the reactive N to dinitrogen gas (Rivett
84 et al., 2008). The organisms that contribute to denitrification are ubiquitous in surface water,
85 soil and groundwater (Beauchamp et al., 1989); they are found at great depths in aquifers e.g.
86 nearly 300m below ground (Francis et al., 1989). Therefore, nitrate reduction should mainly
87 be controlled by hydrologic and geochemical factors. Denitrifiers are facultative anaerobic

88 heterotrophs (obtain C and energy from oxidation of organic compounds e.g. organic C) and
89 autotrophs (obtain energy from oxidation of inorganic compounds e.g. reduced S or Fe).
90 Multiple electron donors can contribute to nitrate reduction by denitrification (Rivett et al.,
91 2008; Böhlke, 2002). Therefore, investigation into the distributions of electron donors and
92 hydrogeochemistry can give insights into the abundances of nitrate in groundwater and
93 subsequent delivery to the surface waters. Denitrification is principally an anaerobic process
94 which starts at an oxygen level 4 mg L⁻¹ (Böhlke and Denver, 1995); 2-3 mg L⁻¹ (Tang and
95 Sakura, 2005) but requires more consensus (Buss et al., 2005). The redox chemistry is an
96 important phenomenon that can be used as an indication of environment favourable for
97 denitrification (Buss et al., 2005). Controls of local hydrology (water table fluctuations and
98 water flow rates), hydrochemistry and hydrogeology on nitrate distribution are therefore
99 important to improving agricultural N management. Thayalakumaran et al. (2008) measured
100 0.1 to 14.4 mg N L⁻¹, 5.9 to 7.6 pH, 4 to 82 mg L⁻¹ DOC, 0.1 to 6 mg L⁻¹ DO, 0 to 235 mV Eh,
101 0 to 361 mg L⁻¹ Fe(II) in groundwater at Burdekin floodplain in Australia. Mean DOC
102 concentration in groundwater ranged 1 to 5 mg L⁻¹ (Starr and Gillham, 1993; Mohamed et al.,
103 2003). Beller et al. (2004) measured NO₃⁻-N between 9.5 and 22 mg L⁻¹ with DO <1 to 10 mg
104 L⁻¹ and DOC 0.3 to 1.7 mg L⁻¹, being monitored in groundwater at California.

105 Process-based understanding of the factors controlling the abundances of nitrate and of
106 their distributions over space and time is crucial for quantifying the effects of human activity
107 on the N cycle and for managing and mitigating the severe environmental consequences
108 associated with N pollution (Boyer et al., 2006) and will provide an important tool for
109 agricultural N management in sustainable agricultural and environmental contexts. The
110 objective of the research was to evaluate the effect of hydrogeological setting on
111 agriculturally derived groundwater NO₃⁻-N occurrence. The research hypothesis was that

112 hydrogeological settings would 1. influence groundwater physiochemical properties and 2.
113 physico-chemical properties would affect groundwater nitrate occurrence.

114

115 **2. Materials and Methods**

116 2.1 Study sites

117 The investigation was carried out in three vertical depths of groundwater to target samples in
118 subsoil, bedrock-interface and bedrock in four agricultural catchments in Southeast Ireland
119 namely: Johnstown castle, (JC); Solohead, (SH); Oak Park, (OP) and Dairy Gold, (DG). An
120 overview of land use, soil type and bedrock geology was summarised in Table 1. Locations
121 of the study sites within Ireland with the soil drainage status are shown in Figure 1.

122

123 2.2 Monitoring well establishment

124 Thirty specifically designed multilevel piezometers (5 cm ID and 2-6 m screen length) were
125 installed along groundwater flow paths in three depths viz. 4-6, 10-12 and 18-30 m bgl
126 representing respectively subsoil, bedrock-interface and bedrock in JC, SH, OP and 6 single
127 piezometers in only bedrock (30-50 m bgl; 6 m screen section) in DG. Well development was
128 carried out by pumping the wells for several times over the next two months after installation
129 until water was clear using a centrifugal pump (Model MP1, Grundfos, Fresno, CA, USA).
130 Well integrity was checked for each borehole by injecting 5 L water to increase static water
131 level by 1 m in one well and measuring the changes in water levels in other two wells around
132 using electronic transducer (Diver, Eijkelkamp, The Netherland) and found intact.

133

134 2.3 Groundwater sampling

135 Groundwater sampling was carried out monthly from Feb, 2009 to Jan, 2011 using a bladder
136 pump (Geotech Environmental Equipment, Inc., USA) following USEPA Region I Low
137 Stress Purging and Sampling Procedures (USEPA, July 30, 1996) for analysing dissolved
138 gases and hydrochemistry. Groundwater pH, temperature, turbidity, DO, electrical
139 conductivity and oxidation reduction potential (Eh) were measured on site using In Situ
140 Multiparameter Probe (In Situ Inc. USA). Triplicate samples were collected through Teflon
141 made water outlet tube (ID 0.6 cm) at a rate of 100 ml min⁻¹ so that withstanding of pressure
142 does not cause any ebullition of dissolved gases. To analyse dissolved CO₂ and CH₄, water
143 samples were collected into 160 ml serum bottle after overflowing of approximately 150 ml
144 water and immediately sealed with butyl rubber septa and aluminium crimp caps
145 (WHEATON, USA), dipped into water in cool box and stored at 4 °C and analysed within
146 one week. Due to low flow pumping no visible air bubble was observed in water samples.
147 The preliminary experimentation on collecting samples in pre-evacuated and without
148 evacuated exetainers and serum bottles showed no significant differences for dissolved gases.

149

150 2.4 Analysis of dissolved CO₂ and CH₄

151 To determine the dissolved CO₂ and CH₄ concentrations, samples were degassed using high
152 purity He (BOC, Linde Group, Germany) (He: water 1:3; v/v). The headspace volume was
153 augmented to 40 ml by an additional injection of 40 ml of He and simultaneous replacement
154 of 40 ml water through the rubber septum of sealed serum bottle using plastic syringe. The
155 needle was connected to Cu tube (which was connected to the gas cylinder) with a 2- way
156 valve. The samples were shaken in mechanical shaker for 5 min at 400 rpm and left standing
157 for 30 min. After equilibration, headspace gas sample was extracted into 15 ml exetainer
158 (Labco, Wycombe, UK) with an additional injection of 15 ml He using PVC syringe. The

159 CO₂ and CH₄ was analysed in auto sampler gas chromatograph (CP-3800, Varian, Inc. USA)
160 equipped with TCD and FID, respectively using Ar as carrier gas. Calculation of CO₂ and
161 CH₄ was carried out using Henry's Law with the solubility co-efficients of the gases at
162 ambient groundwater temperature.

163

164 2.6 Hydrologic properties

165 Daily weather data were collected from the local weather station situated at the close
166 proximity of each site. The modified Penman-Monteith equation (Allen et al., 1998) was used
167 to process the potential evapotranspiration (PET), subsequently the hybrid model for
168 computing soil moisture deficit (SMD) described by Schulte et al. (2005) was used to obtain
169 the actual evapotranspiration (AET). Effective rainfall (ER) was calculated by subtracting
170 daily AET from daily rainfall (P) assuming no overland flow. Thickness of the unsaturated
171 zone was measured by measuring the changes in groundwater table (GWT) depth below the
172 ground level (bgl). The GWT changes were measured continuously for 30 minute interval
173 over the experimental period using electronic transducer (Eijkelkamp, The Netherlands).
174 Water table depth was compensated with the atmospheric pressure measured using a
175 Barodiver (Eijkelkamp, The Netherlands). Monthly measurement of GWT was also carried
176 out manually by electronic dipper every month before the commencement of sampling.
177 Rainfall data were collected for all sites from the local stations. Saturated hydraulic
178 conductivity (K_{sat}) was estimated by slug test using Bouwer and Rice (1976) method.

179

180 2.7 Hydrogeochemistry

181 Groundwater non-metallic ions e. g., total oxidised N, NO₂⁻, NH₄⁺, and Cl⁻ and reduced
182 metals e.g., Mn²⁺, Fe²⁺ and S²⁻ were analyzed by Aquakem 600 Discrete Analyser (Aquakem

183 600A, 01621 Vantaa, Finland). SO_4^{2-} concentration was measured by turbimetric method
184 (Askew and Smith, 2005a). DOC was analysed using Total Organic Carbon Analyser (TOC-
185 V cph/cpn; Shimadzu Corporation, Kyoto, Japan) and total N and total phosphate were
186 analysed using persulfate method (Askew and Smith, 2005b).

187

188 2.8 Statistical analysis

189 Analysis of data was performed using the Mixed Procedure (SAS, 2009). As most of the
190 variables showed an approximately lognormal distribution, log transformations were used
191 with appropriate re-scaling so that residual checks indicated that the assumptions of the
192 analyses were not violated. Pre-specified hypotheses of influential variables were tested by
193 regression modelling for NO_3^- -N. Sequential addition of the variables to the model was
194 performed where the size of the F statistic gives an indication of their relative contribution to
195 the full model. Structural factors like depth and sampling dates were tested. Covariance
196 models were included to account for correlations (Pearson's correlation co-efficient) in the
197 data (e.g. across sampling date). For each hydrologic and geochemical parameter effects
198 of location and depth were examined along with their interactions (2-way ANOVA). In case
199 significant differences were found, Tukey Kramer HSD multiple comparison test were used
200 to distinguish differences between individual site and depth.

201

202 **3. Results**

203 3.1 Hydrology

204 Each of the study sites had different hydrologic regimes with respect to the amount of rainfall
205 recorded over the two years. Total rainfall was significantly higher on all sites in 2009 than
206 2010 (Figure 2) creating a marked contrast in unsaturated zone water content and its delivery

207 to GWT. Despite the two contrasting years of rainfall, mean rainfall was within the range of
208 mean Irish rainfall (800-1400 mm). Both the PET and AET were similar between the study
209 sites within each year (Figure 2). However, ER differed between sites, being highest at JC
210 and lowest at OP (Figure 2) reflecting differences in annual rainfall (2009: 537-836 mm;
211 2010: 241-385 mm). Thickness of unsaturated zone, expressed by the depth between ground
212 surface and GWT, was significantly different between sites and depths (ANOVA; $p < 0.001$)
213 showing mean values of 2.3, 1.7, 4.5 and 29 m bgl in JC, SH, OP and DG, respectively
214 (Table 2). In each site, it showed the same pattern of fluctuations over time and was deepest
215 during July- September and shallowest during November-January (Figure 3). Thickness of
216 unsaturated zone showed moderate to high temporal variability in all sites with mean
217 coefficients of variation ranged from 52-57, 38-116, 20-57 and 14% respectively in JC, SH,
218 OP and DG.

219 The weighted mean values of K_{sat} were 2.3×10^{-2} , 2.2×10^{-2} , 1.5×10^{-1} and 2.6×10^{-1} m d^{-1} ,
220 respectively in JC, SH, OP and DG. The K_{sat} in subsoil was significantly higher in OP than
221 JC and SH ($p < 0.049$ and 0.03) whereas the later two were similar (Table 2). At interface zone
222 it was also significantly higher in OP than JC and SH. In bedrock, K_{sat} was significantly
223 higher in OP and DG ($p < 0.001$) than JC and SH but when compared between OP and DG, it
224 was higher in DG ($p < 0.05$). Considering inter depths differences, no significant difference
225 was observed between depths except SH where subsoil showed lower K_{sat} value than
226 interface ($p < 0.01$) and bedrock ($p < 0.01$). Spatial variability of groundwater hydraulic
227 conductivity was remarkably higher showing mean coefficients of variation of 65-123, 22-
228 126, 44-51 and 42%, respectively in JC, SH, OP and DG. The GWT is deeper where K_{sat}
229 value is higher (Pearson's correlation co-efficient; $r = 0.69$; $p = 0.001$).

230

231 3.2 Hydrogeochemistry

232 Groundwater temperature was approximately similar across sites and depths with very low
233 spatial and temporal variability. It ranged from 11.1-11.3, 10.9-11.0, 10.4-10.6 and 10.0 °C
234 respectively in JC, SH, OP and DG with corresponding mean values of 11.2, 11.0 and 10.5
235 and 10.0 °C. Temperature in subsoil and at interface changed over time but in bedrock it is
236 quite stable. Groundwater pH was neutral to alkaline (mean pH 6.8 - 7.9) in all depths and
237 sites (Table 2) except the OP site which had significantly higher pH (mean pH 7.4-10.4;
238 $p < 0.001$) than other sites. The pH did not vary significantly between depths except OP where
239 it was lower in subsoil and bedrock than interface (ANOVA; $p < 0.001$). The pH showed very
240 low temporal variability with mean coefficients of variation across depths ranged from 4-7, 4-
241 5, 5-23 and 4% respectively in JC, SH, OP and DG sites. DOC concentration in groundwater
242 did not differ between sites and depths ($p > 0.05$). Mean DOC across depths were 2.3-4.0, 1.1-
243 1.6, 0.6-1.1 and 0.9 mg L⁻¹, respectively in JC, SH, OP and DG. Despite a numerically higher
244 mean value in JC, it was similar across sites because DOC in 3 wells in JC (i.e. JC2A, JC2B
245 and JC2C) was unusually higher (8.81-15.60 mg L⁻¹). Land around these wells has a long
246 history of being irrigated with waste water (farm yard washings). It showed moderate
247 temporal variability with highest during December to January and lowest during August to
248 September. During this period DOC consumption was low at low temperature coupled with
249 high water saturation resulting in high DOC transport to groundwater. Temporal variability of
250 DOC was remarkably higher with mean coefficients of variation of 147-159, 75-91, 54-99
251 and 56%, respectively in JC, SH, OP and DG. Dissolved CO₂ concentration varied
252 significantly between sites ($p < 0.001$) and decreased significantly with increasing depths
253 ($p < 0.001$). Mean CO₂ concentrations were 35.5, 27.6, 11.6, and 33.1 mg C L⁻¹, respectively
254 in JC, SH, OP and DG and showed large spatial variability in each site (Table 2). Dissolved

255 CH₄ production was observed in 35% wells in JC and 60% wells in SH but in OP and DG it
256 was very low (Table 2) showing the mean values of 246.5, 29.9, 5.0, and 1.3 µg C L⁻¹. SO₄²⁻
257 concentrations in groundwater were similar in all depths across sites (p>0.05) except in
258 subsoil where it was significantly higher in OP than other sites. SO₄²⁻ concentrations had
259 moderate temporal variability with consistently higher values during July to September and
260 lower during December to February showing mean coefficient of variations of 40-57, 32-76,
261 13-23 and 33%, respectively in JC, SH, OP and DG. The CV values were comparatively
262 higher in JC and SH sites because there were couple of wells which have comparatively
263 higher SO₄²⁻ concentrations e.g. JC1A, JC29, JC30, JC31, JC2A, JC2B, JC2C, JC3A, JC3B;
264 SH1A, SH2B, SH2C, SH3A, SH3B and SH3C (Table 2).

265

266 3.3 Groundwater redox chemistry

267 The DO concentration showed very contrasting results across depths and sites (Table 2).
268 Mean DO values were similar in JC and SH in all depths but were significantly higher in OP
269 (7.1 mg L⁻¹) than JC (2.5 mg L⁻¹) and SH (1.0 mg L⁻¹) in subsoil. In bedrock, it was
270 significantly higher in DG (8.7 mg L⁻¹) than in JC (1.5 mg L⁻¹), SH (1.3 mg L⁻¹) and OP (4.8
271 mg L⁻¹) (ANOVA; p<0.001). Very interestingly, DO at interface was similar across sites.
272 However, DO did not differ significantly with depths in individual site. Comparatively higher
273 DO was measured from November to January and lower from July to September regardless
274 of sites and depths. The DO equilibrated with recharge water and transported to groundwater
275 resulting in a high concentration during winter. In addition, in winter groundwater flow rate
276 was higher than summer due to water saturation which might have reduced the residence time
277 and enhanced the accumulation of DO in groundwater. The mean coefficients of variations
278 were 74-127, 62-113, 49-62 and 28%, respectively in JC, SH, OP and DG sites.

279 Mean Eh was significantly different between sites ($p < 0.001$) and depths ($p < 0.01$) and ranged
280 from 51-107, 42-92, 120-160 and 176 mV respectively in JC, SH, OP and DG regardless of
281 depths. There were some wells in JC (JC2B, JC2C, JC33, and JC34) and SH (SH2A, SH2B,
282 SH3A, and SH3B) where Eh ranged from -1 to -72 mV. Mean coefficients of variation in
283 each site were medium to high which ranged from 68-217, 83-250, 42-76 and 40%
284 respectively in JC, SH, OP and DG sites. The Eh increased with the increase in K_{sat} values
285 and thickness of unsaturated zone (normalized with ratio of depth below water table to depth
286 bgl) (Figure 4).

287 Fe^{2+} concentration was significantly higher in JC and SH than OP and DG ($p < 0.001$) with the
288 mean values of 30.7, 26.0, 1.2 and 10.4 $\mu g L^{-1}$, respectively in JC, SH, OP and DG. It showed
289 similar concentration across depths ($p > 0.05$). High temporal variability of Fe^{2+} was observed
290 in all sites with coefficients of variation of 218, 111, 98 and 201%, respectively in JC, SH,
291 OP and DG. Mn^{2+} concentration showed similar phenomenon to Fe^{2+} with significant
292 differences between sites ($p < 0.05$) but similar concentrations between depths. Mean Mn^{2+}
293 concentration was 301, 130, 3 and 5 $\mu g L^{-1}$, respectively in JC, SH, OP and DG with
294 coefficients of variation of 167, 106, 198 and 178%. Reduced S (S^{2-}) concentration was
295 similar across sites and depths ($p < 0.05$) with the mean values of 0.24, 0.19, 0.20 and 0.14 μg
296 L^{-1} . Clearly, its concentrations as well as spatial variability were lower than reduced Fe^{2+} and
297 Mn^{2+} concentrations and variabilities (Table 2). The mean coefficients of variation were 116,
298 126, 118 and 125%, respectively in JC, SH, OP and DG. The Eh showed negative correlation
299 with Fe^{2+} and Mn^{2+} and DO concentrations but quadratic relation with S^{2-} (Figure 5). It was
300 also inversely correlated with the DOC concentrations ($r = -0.334$; $p < 0.023$). Very
301 interestingly, Fe^{2+} and Mn^{2+} started to increase in groundwater while Eh drops below 150 mV

302 and reached maximum levels while Eh drops below 100 mV. S^{2-} decreased with the increase
303 in Fe^{2+} and Mn^{2+} concentrations in some of the wells in JC and SH sites.

304

305 3.4 Groundwater N dynamics

306 Groundwater mean NO_3^- -N distributions in different depths across sites were shown in Table
307 2. Mean NO_3^- -N concentrations were 3.7, 0.7, 11.0, and 14.6 mg N L⁻¹, respectively at JC,
308 SH, OP and DG which were significantly different between sites (ANOVA; $p < 0.001$) and
309 depths ($p < 0.01$). Moderate temporal variability of NO_3^- -N concentrations were observed
310 across sites and depths (Table 2) showing consistently higher NO_3^- -N concentrations during
311 December to February and lower during August to October (Figure 6). Due to lack of
312 recharge in summer, soil aeration can increase nitrate content which is flushed to
313 groundwater in winter with recharge as an advective transport. In addition recharge increases
314 DO concentration in groundwater in winter at a low temperature. Mean coefficients of
315 variation over time were 62-86, 103-149, 10-31 and 42% respectively in JC, SH, OP and DG
316 sites. In few wells at JC (JC2B, JC2C, JC33, JC34) in interface and bedrock but most of the
317 wells in SH in all depths it was close to detection limit (0.02 mg L⁻¹).

318 Very trace level of NO_2^- in JC and OP was detected with respectively 0.01-0.06 and 0.02-
319 0.38 mg N L⁻¹ but in SH and DG most of the sampling times it was close to detection limit.
320 OP site showed significantly higher NO_2^- concentrations than JC ($p < 0.001$). Though NH_4^+
321 concentration was detected in all sites and depths, it was significantly higher in JC than SH,
322 OP and DG ($p < 0.001$). Few wells in JC e.g. JC2B, JC2C, JC32, JC33 and OP2B, it was
323 remarkably higher than other wells ranging from 0.05 - 0.22 mg N L⁻¹ (Table 2). The
324 coefficient of variations over time in individual sites were 257-324, 372-424, 139-301 and
325 600% respectively in JC, SH, OP and DG sites.

326 3.5 Environmental processes controlling the abundances of NO_3^- -N

327 The pattern of changes in chloride concentrations were approximately consistent over time
328 showing the coefficients of variation of 16, 28, 32, and 43% in JC, SH, OP and DG whereas
329 nitrate concentrations showed moderate to high temporal changes. In addition, the change in
330 Cl^- /nitrate ratio over time was remarkably higher which showed higher amplitude of
331 fluctuations during June to September. The Cl^- /nitrate ratio showed remarkable fluctuations
332 over time suggesting natural nitrate attenuation (Figure 7). Plots between NO_3^- -N vs.
333 groundwater hydrogeochemical properties revealed that NO_3^- -N concentrations showed
334 strong positive relation with the depths of unsaturated (normalized with the ratio of depth
335 below GWT to depth bgl) and K_{sat} (Figure 8a and b). Furthermore, NO_3^- -N concentrations
336 were positively correlated with DO and Eh (Figure 9a and b) which are the indicators of
337 groundwater higher aerobiocity. Conversely, NO_3^- -N concentrations showed strong negative
338 correlations with NH_4^+ and CH_4 concentrations (Pearson's correlation co-efficient; $r=-0.59$,
339 $p<0.05$, $r=-0.62$, $p<0.05$, respectively), being an indicator of groundwater anaerobiocity.
340 Decrease in NO_3^- -N concentrations were observed with increased with Fe^{2+} and Mn^{2+}
341 concentrations in groundwater ($r=-0.59$, $p<0.05$; $r=0.52$, $p<0.05$, respectively). Nitrate
342 concentrations decreased with increase in SO_4^{2-} concentrations in JC and SH but in OP and
343 DG it showed inverse relation. In addition, SO_4^{2-} concentrations increased in groundwater
344 with corresponding decrease in S^{2-} ions ($r=0.35$; $p<0.032$).

345 Multiple linear regressions following the stepwise method based on the changes in F-values
346 revealed a good fit model where $\log\text{DOC}$, $\log\text{Eh}$, and $\log\text{CH}_4$ and $\text{Log}K_{sat}$ showed significant
347 impact on the predicted NO_3^- -N concentrations which could explain 74% of the variances of
348 groundwater ambient NO_3^- -N concentrations.

349 $\log \text{NO}_3^- \text{-N} = -0.964 - 1.245 \log \text{DOC} + 0.865 \log \text{Eh} - 0.342 \log \text{CH}_4 + 0.156 \log K_{sat}$ ($R^2=0.74$;
350 $p<0.001$; $n=36$) (1)

351 where $\text{NO}_3^- \text{-N}$, DOC , CH_4 concentrations are in mg L^{-1} ; Eh is in mV and K_{sat} is in m d^{-1} . The
352 model sequentially included the variables with their relative contributions as shown by F
353 values of 78.22, 50.76, 37.69, and 21.46, respectively for $\log \text{DOC}$, $\log \text{Eh}$, $\log \text{CH}_4$, and
354 $\log K_{sat}$.

355

356 **4. Discussion**

357 4.1 Hydrology vs. nitrate abundances

358 GWT fluctuations reflect the pattern of rainwater recharge and drainage to and from
359 groundwater which has significant implication on groundwater hydrochemistry. It shows the
360 change in the depth of unsaturated zone overlying the saturated zone over the sampling
361 period. Recharge generally begins in July and builds up GWT up to shallowest level in
362 November. Fenton et al. (2009b) estimated vertical travel time in Irish aquifers from 0.017 m
363 d^{-1} in poorly productive aquifer to 0.083 m d^{-1} in sand and gravel aquifer irrespective of
364 depth of unsaturated zone and effective porosity. Saturated hydraulic conductivity data
365 showed that water can flow 0.8 m at low permeability sites to 8 m at high permeability sites
366 per month. In DG and OP, deeper unsaturated zone with correspondingly higher K_{sat} values
367 revealed higher solute transport potential i.e. higher vulnerability than JC and SH (Figure 2a
368 and b). Higher $\text{NO}_3^- \text{-N}$ concentrations are consistent with higher K_{sat} (approximately >0.05 m
369 d^{-1}) values suggesting that groundwater travel time is inversely related to groundwater $\text{NO}_3^- \text{-N}$
370 reduction. Because, higher K_{sat} is resulted from the numerous larger as well connected
371 pores which enriched groundwater with DO that equilibrated with infiltrating water which in
372 turn consume DOC and produce CO_2 . However, DOC input was not sufficient in

373 groundwater to significantly consume DO. As a consequence of free draining conditions, DO
374 concentrations dramatically increased in groundwater which ultimately affected the overall
375 biogeochemical N transformations in groundwater. Therefore, the shorter is the travel time
376 the higher is the vulnerability of groundwater to nitrate pollution. Sediments with coarse
377 sands allow faster leaching through larger as well as better connected pores (Goss et al.,
378 1998) which shows higher groundwater vulnerability (NRA, 1995) than clayey soils.
379 Conversely, shallow unsaturated zone in JC and SH corresponded to lower permeability but
380 higher nitrate residence time and hence higher nitrate removal capacity than DG and OP.
381 Similar K_{sat} values (0.007 - 0.016 m d⁻¹) in subsoil (1.5 - 4.5 m) were reported by Fenton et
382 al. (2009a) in JC site. However, in SH the distinctly lower K_{sat} values in subsoil than
383 interface and bedrock is due to the presence of densed clay that is intermixed with gravels.
384 Higher spatial structure of GWT depths and K_{sat} values revealed higher heterogeneity in the
385 subsurface hydraulic regimes across sites. In addition, slower permeability increases the
386 potential to build up shallower GWT and can lower unsaturated area. High permeabilities
387 with the correspondingly high thickness of unsaturated zone are also consistent with the high
388 DO and Eh (Figure 4a and b). The GWT is known to play a regulatory role in the functioning
389 of shallow groundwater ecosystems by supplying organic matter for heterotrophic
390 metabolism (Baker et al., 2000). Therefore, deeper unsaturated with higher K_{sat} are not
391 favourable for nitrate reduction which in turn increases the vulnerability of groundwater to
392 nitrate.

393

394 4.2 Hydrogeochemistry and the abundances of nitrate

395 Groundwater temperature is relatively stable across all sites as well as within depths in each
396 site and does not response profoundly to the seasonal changes. Though pH was near to

397 neutral across all sites but exceptionally higher pH in OP site was due to the presence of
398 calcareous materials. Thayalakuamaran et al. (2009) reported similar results for groundwater
399 pH in Australia as they noted that groundwater was mostly neutral to alkaline with no
400 obvious spatial and temporal variability.

401 Groundwater DOC concentration was very small in amount in all sites (mean DOC 0.90 mg
402 L⁻¹ in OP to 2.92 mg L⁻¹ in JC) but their similar concentrations in all depths indicates that
403 DOC can leach out from surface soil to deeper groundwater that can affect groundwater
404 biogeochemistry. DOC concentrations in most aquifers are relatively low, typically <5 mg L⁻¹
405 (Rivett et al., 2007). DOC can consume DO and produce CO₂ which can be reduced to CH₄.
406 Substantial CO₂ reduction to CH₄ was observed in approximately 35 and 60% wells in JC and
407 SH which wells are indicating the existence of potential anaerobic environment for nitrate
408 reduction. Though DOC low, dissolved CO₂ and CH₄ concentrations shows that groundwater
409 can be an important storage for C sequestration. Higher spatial variability in DOC
410 concentration indicates the higher variability in water percolation, leaching, land topography,
411 management practices etc. In JC2A, JC2B and JC2C, respectively in subsoil, interface and
412 bedrock unusually high DOC concentrations (8-25 mg L⁻¹) were measured which was
413 accumulated due to waste water irrigation which influenced the DO, Eh and other
414 biogeochemical variables like NO₃⁻-N and SO₄²⁻ concentrations (Table 2). Similar
415 concentrations of DOC to our study sites were reported by Starr and Gillham, (1993),
416 Wassenaar, (1995), Beller et al. (2004) and Mohamed et al. (2003) but higher by
417 Thayalakuamaran et al. (2009). Higher spatial variability of DOC was in line with Von der
418 Heide et al. (2008) who found 68% CV of DOC in shallow groundwater in Germany.

419 Similar concentration of SO₄²⁻ in groundwater across sites and depths could be due to two
420 reasons: firstly sulphide reduction to SO₄²⁻ under limited O₂ (<2 mg L⁻¹) resulting in very low

421 nitrate (electron acceptor) reduction by denitrification and another one is sulphur oxidation
422 due to high O₂ concentration having high nitrate abundance. The spatial and temporal
423 variability of SO₄²⁻ concentrations were similar to NO₃⁻-N concentrations in all sites and
424 depths. High spatial distribution of SO₄²⁻ concentrations in groundwater (CV 86%) were
425 found by Von der Heide et al. (2008). In subsoil in OP higher SO₄²⁻ concentration could be
426 due to pyrite oxidation under higher DO concentration and higher pH. Inversely, higher SO₄²⁻
427 concentrations in few wells in JC and SH (JC1A, JC2B, JC2C, JC3A, JC3B, JC29, JC30,
428 JC31; SH2B, SH2C, SH3B, SH3C) could be due to their highly reduced environment (very
429 low DO and Eh) where S²⁻ oxidation might occurred by NO₃⁻-N reduction due to absence of
430 DO.

431

432 4.3 Groundwater redox chemistry

433 Groundwater DO was 0.3 - 10 mg L⁻¹ across all sites and depths while at JC and SH sites it
434 was <1.5 mg L⁻¹. Similar DO in groundwater was reported by Beller et al. (2004) in a range
435 of unconfined (4 - 10 mg L⁻¹) to confined (<1 - 4 mg L⁻¹) aquifers in California, USA where
436 denitrification is considered as an important process of nitrate reduction in groundwater. In
437 subsoil, lower DO at JC and SH could be due to their shallow GWT, lower amplitude of
438 GWT fluctuation and lower K_{sat} values. Consumption of DO due to microbial
439 transformations of C to CO₂ could be another reason of low DO in groundwater. Similarly,
440 considering differences in DO in bedrock between 4 sites, higher DO at DG site could be due
441 to deeper unsaturated zone and higher K_{sat} values allowing better aeration. DO did not vary
442 with depth at each site probably because of hydrogeological heterogeneity e.g. preferential
443 passage both in vertical and horizontal directions. In some wells, DO was higher in subsoil
444 but in some others it was higher at interface or in bedrock (Table 2) which is supported by

445 their remarkably higher CV values. Lower Eh in JC and SH even negative values in some
446 wells may be due to the lower DO concentrations which indicates a high reduced
447 environment. Higher DO and Eh during winter (Nov-Jan) could be due to prevailing low
448 temperature in this period and inverse conditions were observed during summer. Another
449 reason of higher DO during this period could be due to DO enrichment with recharging water
450 from rainfall. In a recently infiltrated recharge water, groundwater becomes fully oxygenated
451 which requires an indicative concentrations of DOC below which anaerobic conditions may
452 not develop (Rivett et al., 2008). The wells that have reduced environment, Fe^{2+} and Mn^{2+}
453 concentrations start to increase but S^{2-} starts to decrease while groundwater Eh drops below
454 150 mV indicating that the Eh value of 150 mV is the turning point in groundwater when
455 nitrate starts to reduce. Moreover, Fe^{2+} and Mn^{2+} reach their maximum levels in some wells
456 in JC and SH sites when the Eh drops below 100 mV indicating that at ± 100 mV nitrate
457 reduction is high.

458

459 4.4 Groundwater N dynamics

460 Very low NO_3^- -N concentrations in anoxic groundwater has been observed in a number of
461 other studies, and in some case it has been linked to denitrification in the anoxic zones
462 (Robertson et al., 1996; Tesoriero et al., 2000). Therefore, lower NO_3^- -N in JC and SH than in
463 OP and DG indicated that denitrification in groundwater required proper anaerobicity e.g.
464 $\text{DO} < 2.0 \text{ mg L}^{-1}$, $\text{Eh} \pm 150$ and an electron donor like DOC or reduced Fe/S. Conversely, very
465 small amount of NO_3^- -N can be retained probably as N_2O (a potent greenhouse gas) in high
466 $\text{DO} (6.0 - 9.0 \text{ mg L}^{-1})$ and $\text{Eh} (100-250 \text{ mV})$ with available electron donors mainly DOC and
467 sometimes with reduced S and Fe in OP and DG sites. Unusually high pH (mean 7.4 - 8.6) in
468 OP could be another reason of low denitrification because Rust et al. (2000) quoted an

469 acceptable higher limit for pH of 8.3 above which denitrification is arrested. The decrease in
470 NO_3^- -N concentrations with depths indicated that denitrification can take place along
471 groundwater flow paths from its sources to the receptors (Konrad, 2007) and it is not really
472 confined in shallow layer only. Considering temporal pattern, similar pattern of NO_3^- -N
473 removal in riparian groundwater was observed by Maître et al. (2003) who found highest
474 nitrate removal in spring and lowest in winter due to the combination of a high nitrogen input
475 and a low plant uptake. Thayalakuamaran et al. (2009) reported higher NO_3^- -N in
476 groundwater during January and lower during September/October. But the spatial variability
477 is more pronounced than temporal showing that groundwater hydrochemical properties are
478 considerably heterogeneous.

479 NO_2^- -N and NH_4^+ concentrations were almost absent in either of groundwater zones except
480 few wells in OP (OP2A and OP2B) which have considerably higher NO_2^- -N and few wells in
481 JC (JC2B, JC2C, JC33 and JC34) which have considerably higher NH_4^+ during the study
482 period. Temporal changes in NO_2^- -N concentration shows approximately consistent trend
483 with slightly higher in winter across all sites and depths because of higher leaching potential
484 with rainwater or could be due to lower chemical and microbial changes during this period.
485 Relatively constant NO_2^- -N concentrations were also reported by Beller et al. (2004) in
486 denitrifying aquifer in USA. A steady decline in groundwater NO_2^- -N was also reported by
487 Brodie et al. (1984). Spatial variability of NO_2^- -N concentration was rather higher in
488 groundwater than soil and resembles to the higher spatial structure of groundwater
489 biogeochemical variables which implies that groundwater nitrate is not a conservative ion
490 rather it undergoes biogeochemical changes in groundwater while passing through and from
491 landscape to potential receptors. Similar spatial variability of NO_2^- -N in groundwater (CV
492 24%) was reported by Von der Heide et al. (2008).

493

494 4.5 Nitrate reduction processes and factors

495 Neither chloride nor nitrate is affected by chemical processes in groundwater except where
496 nitrate may undergo denitrification (Buss et al., 2005) and an increase in the Cl⁻/nitrate ratio
497 indicates that nitrate removal process e.g., denitrification occurs (Altman and Parizek, 1995;
498 Mengis et al., 1999). Nitrate concentration decreases resulting in the increase in Cl⁻/nitrate
499 ratio potentially suggesting that nitrate reduction is not only a function of dilution but also a
500 process of denitrification. Van Beek et al. (2007) found that the increase in Cl⁻/nitrate ratio in
501 groundwater was due to nitrate removal by denitrification. The deeper GWT increases
502 groundwater DO ($r=0.680$; $p=0.001$) which in turn increase groundwater Eh and hence
503 reduces nitrate retention capacity because, NO₃⁻ reduction follows the DO consumptions
504 (Puckett and Cowdery, 2002; Thayalakuamaran et al., 2009). Positive correlation between
505 NO₃⁻-N and DO and Eh (Figure 9a and b) indicates that low NO₃⁻-N in groundwater with low
506 DO and Eh is due mainly to denitrification because low DO and Eh favour denitrification
507 process (Thayalakuamaran et al., 2009). Therefore, larger K_{sat} with correspondingly deeper
508 GWT have significantly higher groundwater NO₃⁻-N concentrations (Figure 8a and b) which
509 were observed at OP and DG, in particular. At JC and SH sites mean DO (mean 1.7 and 1.4
510 mg L⁻¹) and Eh (71 and 60 mV) indicates the potential of those sites for denitrification to
511 occur. DO concentration <2 mg L⁻¹ and Eh values <250 mV have been reported to be
512 favourable for denitrification (Korom, 1992). Low DO and Eh, and availability of electron
513 donors are used as geochemical indicators to indicate conditions suitable for groundwater
514 denitrification (Thayalakuamaran et al., 2009). Rivett et al. (2008) identified DO and electron
515 donor concentration and availability as the primary factors governing denitrification in
516 groundwater.

517 Ammonium production in groundwater is an indication of the anaerobic conditions which
518 shows significant negative correlation with NO_3^- -N, indicating that NO_3^- -N reduction occurs
519 in groundwater at an anaerobic environment. Negative linear relationships of groundwater
520 NH_4^+ concentration with NO_3^- -N (Pearson's correlation co-efficient; $r=-0.369$; $p=0.032$), DO
521 ($r=-0.322$; $p=0.022$) and Eh ($r=-0.463$; $p=0.003$) imply that both dissimilatory nitrate
522 reduction to ammonium (DNRA) and denitrification take place in groundwater at anaerobic
523 conditions. High ammonium concentrations in few wells coupled with very low NO_3^-
524 concentrations indicating the occurrence of DNRA because low NO_3^- with high NH_4^+
525 suggests the occurrence of DNRA (Thayalakuamaran et al., 2009). Similarly, CH_4 production
526 in groundwater shows the anaerobicity in groundwater which in turn shows significant
527 negative relation with NO_3^- -N. The effect of land-use is difficult to disaggregate in this study
528 as there was only a single arable site. There were no significant difference in the groundwater
529 NO_3^- concentrations observed on the high permeability grassland (DG) and arable sites (OP).
530 However, N input rates with corresponding nitrate concentration in groundwater, being
531 variable at the study sites (Table 1), reflect that biogeochemical processes can be the main
532 driver of nitrate occurrence in groundwater. For instances, at JC and DG sites N input were
533 312 and 298 kg N ha^{-1} but nitrate in groundwater were 3.7 and 14.6 mg N L^{-1} . In addition, at
534 OP site (arable site with spring barley) N input was the lowest (150 kg ha^{-1}) but nitrate
535 concentration in groundwater was very high (11.0 mg N L^{-1}) which can be attributed to
536 higher nitrification due to tillage and subsequent transport to groundwater due to high
537 permeability. Thus hydrogeological setting, over and above N input level, appears to have
538 the dominant control on groundwater NO_3^- -N occurrence.

539 Contribution of DOC as electron donor in groundwater denitrification seems to be an
540 important electron donor because it showed significant negative relation with NO_3^- -N ($r=-$

541 0.327; $p=0.023$). Denitrification reactions at some sites may be driven by multiple electron
542 donors, for example, where organic carbon, sulphide and iron minerals are coupled (Rivett et
543 al., 2008). However, in all sites the DOC remains relatively consistent over time which
544 indicates that DOC is not completely bioavailable (Siemens et al., 2003) and addition and
545 transformation of bioavailable fractions of DOC in groundwater equates to each other. We
546 observed significantly positive correlation with DOC and CO_2 ($r=0.453$; $p=0.021$). In
547 denitrification process, if organic C is the electron donor, bicarbonate and CO_2 are formed but
548 if reduced S is the electron donor, SO_4^{2-} are formed (Rivett et al., 2008). Furthermore, some
549 other particulate C sources can affect denitrification which are not analysed in present study.
550 Groundwater increased SO_4^{2-} concentrations with decreasing NO_3^- -N concentration could be
551 due to sulphide oxidation where S^{2-} (reduced S or metal bound S) might be an important
552 electron donor (autotrophic denitrification). Postma et al. (1991) identified a sand-and-gravel
553 aquifer containing both organic carbon and pyrite, which both contributed to denitrification;
554 reduction by pyrite was nevertheless the dominant denitrification process as the organic
555 carbon appeared to be poorly bioavailable. Kolle et al. (1985) and Weymann et al. (2010)
556 postulated that high nitrate removal in the autotrophic denitrification zone is most likely
557 caused by practically anoxic conditions and high reactive microcrystalline pyrite components.
558 Therefore, nitrate reduction by iron sulphide or manganese sulphide can release Fe^{2+} and
559 Mn^{2+} ions which were observed in 35% of the wells under study. Numerous researchers have
560 invoked autotrophic denitrification with $\text{Fe}^{2+}/\text{S}^{2-}$ (Bottcher et al., 1990; Tesoriero et al., 2000;
561 Weymann et al., 2010). Oxidation of sulphur therefore, provides a viable alternative electron
562 donor in carbon-limited systems (Moncaster et al., 2000; Broers, 2004).

563 Analysis of groundwater samples for the abundances of denitrifier functional genes in the
564 same wells in our study sites in May and June, 2009 was performed in the Lab of Microbial

565 Ecology, NUI Galway (Data not shown). The denitrification functional genes were present in
566 all sites and depths in similar concentrations ($p>0.05$). The abundance of denitrifying
567 community is generally assumed to be ubiquitous and the denitrifying genes are reported to
568 be widespread in phylogenetically distant organisms (Linne von Berg and Bothe, 1992) but
569 their expressions required favourable environmental conditions.

570

571 **5. Conclusions**

572 Groundwater systems have the potential for the natural nitrate reduction but it shows a large
573 variability between different agricultural sites due mainly to their complex hydrologic (e.g.
574 K_{sat} , changes in groundwater table depth etc.) and hydrogeochemical (redox chemistry i.e.
575 DO and Eh; DOC and other electron donors like reduced Fe and S, nitrate concentration, pH
576 etc.) variabilities. However, more frequent sampling strategies (e.g. daily sampling following
577 recharge and water table fluctuations) will give better insights into the processes-based
578 interpretation of results. Though DOC concentration is not sufficient in groundwater for
579 complete denitrification to occur, multiple electron donors together with DOC (metal bound
580 S or sulphide) are available across all sites under study but hydrogeochemical conditions are
581 restricting the extent of NO_3^- -N reduction. At JC and SH, the hydrochemistry is favourable
582 for denitrification which have low permeability, $<2.5 \text{ mg L}^{-1}$ DO, $\pm 100\text{mV}$ Eh and neutral
583 pH but at OP and DG the conditions were opposite. Hydrochemical results in few wells at JC
584 shows that waste water irrigation practices can create a denitrification 'hot spot' by adding
585 substantial amount of DOC in groundwater causing 100% reduction of delivered nitrate.
586 Hydrogeochemistry data are log-normally distributed and more spatially heterogeneous than
587 temporal changes. The log-transformed K_{sat} , Eh, CH_4 and DOC are the main drivers of the
588 abundances of groundwater nitrate which explain 74% of variances. Hydrogeological settings

589 significantly influenced groundwater nitrate occurrence and suggested denitrification as the
590 main control.

591

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600

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Table 1 Soil type, bedrock geology and drainage conditions of the study sites

Table 2 Mean (\pm SE) of hydrogeochemical properties in different depths of groundwater in four study sites

Figure 1 Location of research sites overlaid on the soil drainage class map of Ireland. Soil drainage map was reclassified from the general soils map of Ireland 1980 by Sean Diamond, Teagasc.

Figure 2 Annual rainfall, potential evapotranspiration (PET), actual evapotranspiration (AET) and effective rainfall (ER) at the study sites during 2009 and 2010

Figure 3 Fluctuations of mean groundwater table (GWT) depth (m, below ground level) over two years (2009-2010) at the study sites

Figure 4 Plots showing relations between DO and (a) depth below GWT/depth bgl (n=36); (b) Eh and K_{sat} (mean \pm SE; n=36)

Figure 5 Plots showing relations between Eh and (a) DO, (b) Fe^{2+} , (c) Mn^{2+} and (d) S^{2-} (n=36)

Figure 6 Temporal changes in groundwater nitrate concentrations over two years (2009-2010) at all study sites

Figure 7 The fluctuations of chloride/nitrate ratios over time at four different sites

Figure 8 Plots showing relations between NO_3^- -N concentrations and (a) K_{sat} values (n=36) (a); (b) ratios of depth below GWT to depth bgl (n=36)

Figure 9 Plots showing relations between NO_3^- -N concentrations and (a) DO and (b) Eh using the mean data during whole study period (n=36)