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1 **PERFORMANCE OF A FIELD-SCALE BIOLOGICAL PERMEABLE REACTIVE**
2 **BARRIER FOR IN-SITU REMEDIATION OF NITRATE-CONTAMINATED**
3 **GROUNDWATER**

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21 **Abstract**

23 We report the performance of a field-scale permeable reactive barrier (PRB) for the biological
24 treatment of nitrate-contaminated groundwater. The reactive material of the PRB consisted of a
25 mixture of gravel and mulch as a carbon source for denitrifying bacteria. The PRB was
26 equipped with a delivery system that allowed injecting NO₃⁻ at controlled rates from the surface
27 directly into the up-gradient layer of the PRB. This way, NO₃⁻ concentration entering the PRB

28 was varied (from 1 to 530 mg/L) with the purpose of evaluating the ultimate efficiency of the
29 PRB under different NO_3^- loadings. The PRB was successful at removing NO_3^- from
30 groundwater at inlet concentrations up to 280 mg/L (with NO_3^- removal percentages $\geq 97\%$).
31 Monitoring of groundwater at different depths within the PRB provided evidence that NO_3^-
32 underwent denitrification preferably at the deepest part of the PRB, where more favourable
33 reducing conditions were achieved. Among the shortcomings of the PRB were the fluctuations
34 of groundwater fluxes caused by intense rainfalls during the study period, although they
35 generally did not pose concern for the denitrification capacity of the PRB. Emission fluxes of
36 gases (CO_2 , CH_4 and N_2O) from the PRB to the atmosphere were also measured. The results are
37 finally compared with the few others reported existing PRBs for nitrate-contaminated
38 groundwater worldwide.

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40 **Keywords:** Denitrification, Groundwater contamination, Nitrate, In-situ remediation,
41 Permeable reactive barrier

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45 1. INTRODUCTION

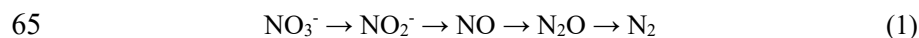
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47 Nitrate (NO_3^-) contamination of groundwater has become an environmental and public
48 health issue worldwide (Fazal et al., 2003; Rivett et al., 2018). It generally originates from
49 anthropogenic sources, mainly from intensive application of fertilisers and animal manure, from
50 landfill leachates and septic tanks leakages (Della Rocca et al., 2007; Stuart and Lapworth,
51 2016). NO_3^- easily percolates into groundwater, through which it can be discharged into surface
52 waterbodies (streams, rivers, lakes) adversely affecting ecosystems (e.g. causing eutrophication)
53 (Addy et al., 2016; Rivett et al., 2018). NO_3^- concentration exceeding the nominal limit of 50
54 mg/L for drinking water set by the World Health Organization have been recorded in numerous
55 aquifers worldwide (Rivett et al., 2008; Huang et al., 2015). Excessive NO_3^- ingestion from

56 polluted drinking waters can induce methemoglobinemia, hypertension, cancers and a number
57 of currently inconclusive health repercussions (Della Rocca et al., 2007).

58 Remediation of groundwater contaminated by NO_3^- is a matter of active research.
59 Among the available remediation approaches, biological denitrification appears to be the most
60 effective and desirable one (Della Rocca et al., 2007). Denitrification is defined as the
61 dissimilatory biological reduction of NO_3^- to nitrogen gas (N_2) through a multistep process, in
62 which NO_3^- is sequentially converted into nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O)
63 and, finally, harmless nitrogen gas (N_2) as shown in the following equation:

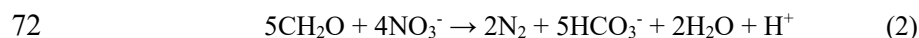
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67 Microbial nitrate reduction is accomplished by the oxidation under anaerobic conditions
68 of either an organic compound (by heterotrophic bacteria) or an inorganic compound (by
69 autotrophic bacteria). Heterotrophic denitrification, on which most of the denitrification-based
70 treatments rely, can be described by the following overall reaction:

71



73

74 where CH_2O represents a generic organic compound. In subsurface environments, the lack of
75 readily available organic carbon has often been reported as the most common hindrance to
76 denitrification (Jahangir et al., 2012). This limitation explains why, until recently, the use of
77 denitrifying bacteria for groundwater treatment has traditionally been reserved to ex-situ
78 treatments in bioreactors. However, latterly attention has focused on the supply of an external
79 organic substrate in the aquifer itself (in-situ treatment).

80 One option of applying an organic substrate into the aquifer is through a permeable
81 reactive barrier (PRB). A PRB consists in placing a reactive material across the flow path of
82 contaminated groundwater so that the contaminants can be transformed as groundwater flows
83 through the reactive material (Scherer et al., 2000; Kalin, 2004). The selection of the reactive

84 material is crucial: it must be chemically effective to eliminate the target contaminant(s) and
85 must maintain an adequate permeability to ensure flow through the PRB. In a heterotrophic
86 denitrification PRB, the reactive material consists of an organic substrate to stimulate
87 denitrifying activity. PRBs are designed to be passive treatment systems in the sense that, once
88 installed, groundwater typically flows through the reactive zone under its natural hydraulic
89 gradient, and thereby energy input is not needed.

90 Most of the PRBs currently installed worldwide are based on abiotic processes, and
91 only a small number on biotic processes, mostly for the bioremediation of groundwater
92 contaminated by acid mine drainage (Benner et al., 2002; Gibert et al. 2013), hydrocarbons
93 (McGovern et al., 2002; Gibert et al., 2007) and, as it is the case of the present study, nitrate
94 (Robertson et al., 2008). With regard to the latter case, there is considerable laboratory-based
95 research on promoting denitrification by the addition of organic substrates (Della Rocca et al.,
96 2006; Su and Puls, 2006; Huang et al., 2015; Li et al., 2017). Nevertheless, most of these studies
97 have been performed with configurations (e.g. batch, column and tank tests) and under
98 controlled operational conditions (e.g. constant water composition, constant flow rate, constant
99 temperature, homogeneous reactive materials, biostimulation of denitrifying bacteria) that differ
100 from those in field-scale PRBs, where site weather, geochemistry and hydrology can all
101 fluctuate.

102 Hence, while lab-studies undoubtedly provide useful information and contribute to a
103 better understanding of denitrification in carbon-amended porous media, their results cannot
104 automatically nor reliably be extrapolated to field-scale PRBs. As highlighted by other
105 researchers (Addy et al., 2016), further research is required, as it is only through accumulated
106 experience at field-scale that such a technology can be successfully applied and tailored to site-
107 specific conditions.

108 The aim of this study was to evaluate the ultimate performance of a denitrification PRB,
109 the first of its kind in Europe, over a period of 11 months. An aspect that made this PRB unique
110 is that it was equipped with an injection system that allowed controlled concentrations of NO_3^-
111 to be injected into the aquifer directly upgradient of the PRB, providing an opportunity to

112 evaluate the NO_3^- removal efficiency of the PRB under increasing NO_3^- loadings. From a
113 broader perspective, and given the scarce data within this field, the objective of this study was
114 to contribute to a better understanding of these systems and aid design of future PRBs.

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117 **2. MATERIALS AND METHODS**

118

119 **2.1. Site characterization**

120

121 The site is located on the eastern edge of Ballymena (Northern Ireland), within the
122 relatively flat flood plain of the River Braid. It was used in the past for agricultural purposes
123 until 1998, when the Ballymena Borough Council purchased the site for the Millenium Ecos
124 Centre used to study the local environment.

125 A total of 21 boreholes, aligned in transects approximately perpendicular to the Braid
126 River, were drilled in the study area to provide the site geologic lithology and to allow the
127 installation of piezometers for monitoring the groundwater hydrology and quality (Figure 1). An
128 additional number of 8 boreholes were drilled beyond the study area to yield information on the
129 lithology of the whole site (data not shown). The intrusive works revealed a shallow aquifer
130 over much of the site, which presented a lithology consisting of an upper layer of silt and clay
131 (generally to 1.5 m below ground level), underlain by a coarse layer (primarily gravel and sand
132 with some silt) ranging in thickness approx. 1.5 to 3 m below ground level, underlain in turn by
133 a stiff boulder clay (subglacial till) that acts as an aquitard beneath the aquifer due to its low
134 permeability. Measurements of groundwater levels showed that groundwater flows in a
135 southwesterly direction, with groundwater flow lines converging to the river (Figure 1). The
136 mean hydraulic conductivity of the aquifer, based on slug tests, is 2 m/d, and the mean hydraulic
137 gradient is 0.53%.

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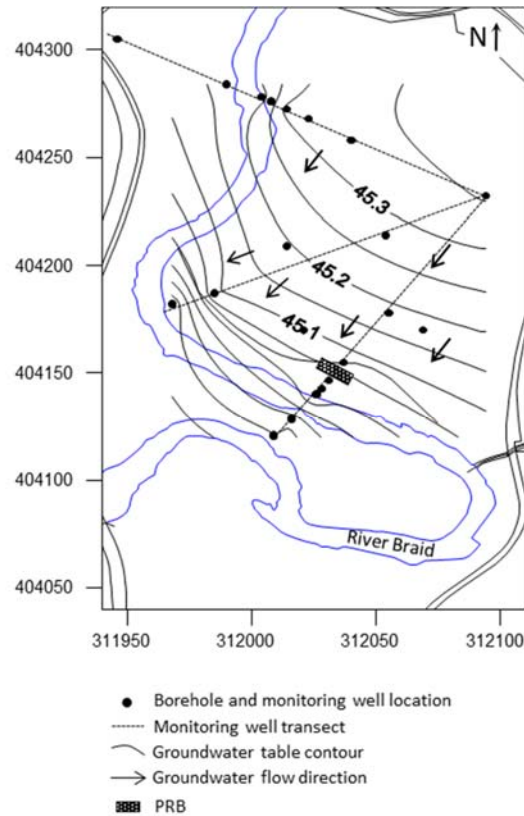


Figure 1: Map view of the site showing the monitoring well locations and the groundwater flow direction. Dash area corresponds to the denitrification PRB.

Soil and groundwater analysis demonstrated that there were no early indications of any pollution of the aquifer at the site and that N-species were clearly not of regulatory concern (Table 1).

	units	Concentration
pH		6.8 ± 0.5
ORP	mV	21 ± 63
DO	mg/L	<1
Cond.	$\mu\text{S}/\text{cm}$	270 ± 112
NO_3^-	mg/L	4.5 ± 3.5
NO_2^-	mg/L	1.4 ± 0.8
NH_4^+	mg/L	0.5 ± 0.3
TOC	mg/L	2.7 ± 0.9
Na^+	mg/L	14 ± 2
K^+	mg/L	3 ± 2
Ca^{2+}	mg/L	40 ± 8
Mg^{2+}	mg/L	12 ± 4
Cl^-	mg/L	14 ± 1
SO_4^{2-}	mg/L	8 ± 7
Alk (as CaCO_3)	mg/L	178 ± 62

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Table 1: Composition of the groundwater at the Ecos site

179

180 The site was chosen as there was NO_3^- contamination at the site, and therefore the
 181 ability for the PRB to naturally exhibit denitrifying potential, and under increasing loads of
 182 NO_3^- in groundwater was ideal for this study. Therefore the proposed PRB was designed to
 183 incorporate a controlled delivery system of NO_3^- to test its denitrification performance at
 184 different NO_3^- loading rates.

185

186 2.2. Design of the PRB

187

188 The design of the PRB was performed according to established guidelines (Gavaskar et
 189 al., 1999; Obiri-Nyarco et al., 2014). Briefly, site characterisation allowed setting the location,
 190 configuration, orientation and dimensions (width and depth) of the PRB in order to successfully
 191 intercept the contaminated plume, while laboratory experiments allowed selecting the most
 192 suitable components of the PRB and, with the denitrification kinetics data, determining the
 193 required thickness of the PRB to ensure a targeted removal of NO_3^- . Among the substrates

194 evaluated in this laboratory study, mulch consisting of hardwood with small amounts of leaves
195 supplied by the local company M. Large Tree Services Ltd (Newtownabbey, Northern Ireland)
196 was the top performing substrate, attaining an overall NO_3^- removal mostly via denitrification of
197 >96% in both batch and column systems (Gibert et al. 2008).

198 The PRB was designed as a continuous trench perpendicular to the groundwater flow
199 direction and parallel to the Braid River approximately 13 m from the riverbank (Figure 1). The
200 vertical position of the PRB was selected in order to be keyed into the underlying clay and to
201 intercept the groundwater in the shallow aquifer. The dimensions were 20 m long, 1.7 m deep
202 and 1.8 m thick, and it was positioned 1.5 to 3.2 below the ground level. The excavated trench
203 was backfilled using gabion technology with a mixture of 50% (v/v) mulch and gravel (approx.
204 5-10 mm size) previously homogenised (porosity of the mixture approx. 0.30) identical to that
205 used in the laboratory experiments (Gibert et al., 2008). Mulch was added as the organic
206 substrate to promote denitrification, while gravel was added to ensure a high permeability
207 within the PRB. Denitrifying bacteria are ubiquitous in groundwater (Rivett et al., 2008), and
208 their proliferation within the PRB was expected under the assumption that mulch would provide
209 a long-term source of carbon and energy.

210 Two adjacent layers of gravel of 0.75 m thick were placed upgradient and downgradient
211 of the reactive zone to provide a highly permeable zone that facilitated uniform flow of
212 groundwater through the PRB (Figure 2). It is in the upgradient layer of gravel where NO_3^- was
213 injected. On completion of backfilling, the top of the PRB was covered with excavated material
214 and compacted to limit oxygen diffusion and flow of infiltrating water into the barrier.

215 The NO_3^- delivery system consisted of two elevated 230 L tanks (with 1.5 meters of
216 hydraulic head) connected to a drip irrigation system through which site groundwater with
217 variable concentrations of NO_3^- was continuously injected into the upgradient gravel layer,
218 ultimately through the reactive zone. The injection was accomplished by a row of 22 drip
219 emitters situated along the upgradient gravel layer. The close spacing between the drip emitters
220 was to provide a uniform front of NO_3^- flowing towards the barrier. This delivery system
221 allowed a precise control of the NO_3^- loading rate injected into the aquifer by selecting the NO_3^-

222 concentration within the barrels and controlling the injection rate at ca. 0.1 L/min (refilling of
 223 barrels approximately every 3 days). A scheme of the drip irrigation system is shown in Figure
 224 2. By using values of groundwater flow rates and injection rates, the expected dilution factor for
 225 NO_3^- once injected into the upgradient gravel layer was quantified at approx. 10 (this value was
 226 later validated by a tracer test).

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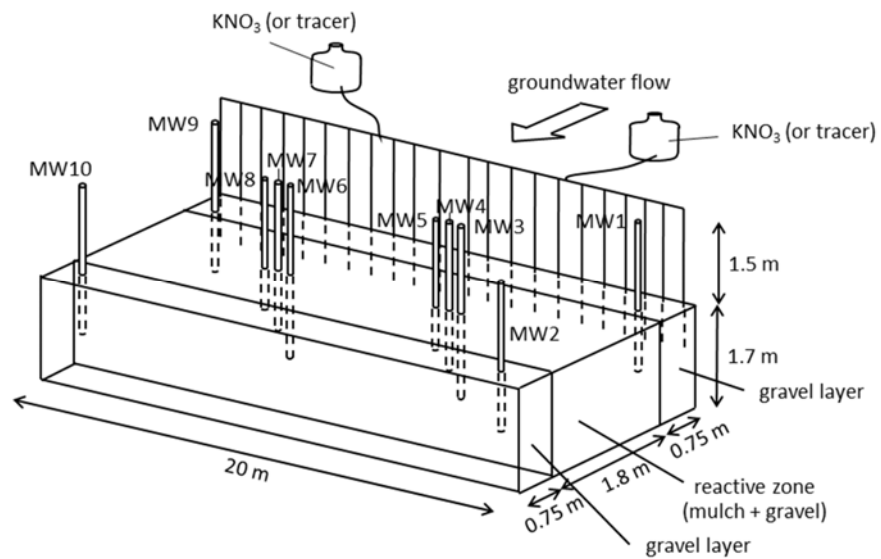
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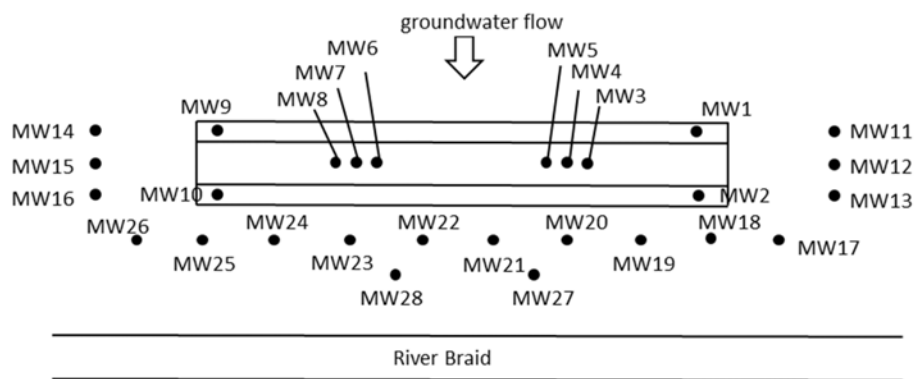
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a) isometric view of the PRB



b) aerial view of the PRB



256 Figure 2: Conceptual scheme of the PRB; a) isometric view of the PRB showing the delivery

257 system of NO_3^- and the position of the monitoring wells within the PRB, b) aerial view of the

258 PRB showing the monitoring well network.

259

260 **2.3. Monitoring wells network**

261

262 A monitoring network consisting of 28 wells was installed within and around the PRB
263 to evaluate its performance. Unless otherwise stated the wells were completed in the Gravel
264 Aquifer at 2.5 m below ground level. As shown in Figure 2, two monitoring wells were installed
265 in the upgradient gravel layer (to monitor the groundwater entering the barrier) and two more in
266 the downgradient gravel layer (to monitor treated groundwater). Two additional sets of
267 monitoring wells were emplaced to monitor groundwater inside the barrier. Both consisted of
268 three nested piezometers with a 0.5 m slotted screen each, terminated at depths of 2.0, 2.5 and
269 3.0 m below ground. Six wells were installed at either side of the PRB and the remaining twelve
270 wells were placed between the PRB and the River Braid (Figure 2b) to assure that water
271 entering the river was satisfying regulatory requirements placed on the research programme.

272

273 **2.4. Hydraulic PRB validation**

274

275 A NaCl tracer test was conducted soon after the installation of the PRB and before any
276 NO_3^- delivery in order to validate the flow through the PRB and the dilution factor estimated
277 from the initial hydrogeological survey. For that purpose, a solution of Cl^- (1621 mg/L as
278 measured) was injected from the barrels into the upgradient gravel layer. Monitoring carried
279 out during the 8 week period of the tracer test showed that: 1) no Cl^- was measured at either side
280 of the PRB (MW11 to MW16), proving that groundwater flow direction was perpendicular to
281 the PRB and that no by-pass flow occurred around the PRB, 2) the maximum measured Cl^-
282 concentration in wells in the upgradient gravel layer and within the PRB was 150 mg/L,
283 indicating a dilution factor of 10.8 (which was in close agreement with the dilution factor of 10
284 estimated from the design based on hydrogeological modelling), and 3) the time needed for the
285 Cl^- to travel from the upgradient to downgradient layers (residence time within the PRB) was 14
286 days. All these findings confirmed the design parameters were reflected in the PRB operation as
287 built.

288

289 2.5. NO₃⁻ delivery plan

290

291 The calculated dilution factor (10.8) was used to select NO₃⁻ concentration in the barrels
292 that, after dilution, would provide a desired concentration of NO₃⁻ entering the PRB.

293 A stepwise increase of NO₃⁻ concentration in barrels was planned in order to investigate
294 the PRB performance at various NO₃⁻ loading rates. Before proceeding with any increment of
295 NO₃⁻ loading rate, action and regulatory oversight was agreed with the Environment Agency of
296 Northern Ireland. The delivery plan carried out during the study is presented in Figure 3. NO₃⁻
297 was first spiked into the aquifer with a concentration of NO₃⁻ in the barrels of 500 mg/L (before
298 dilution by the groundwater flowing through the PRB) for 157 days. The PRB immediately
299 demonstrated the denitrifying ability was effective at removing all NO₃⁻ from groundwater
300 during this first phase, and NO₃⁻ concentration in the barrels was increased to 5,000 mg/L until
301 day 206, when it was further increased to 10,000 mg/L for the following 49 days. Given that
302 NO₃⁻ removal was maintained >97%, it was decided to further increase NO₃⁻ concentration in
303 barrels to 20000 mg/L until day 340.

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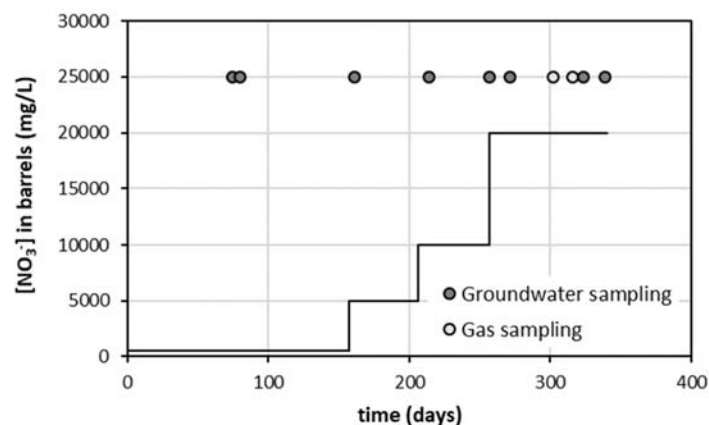
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318 Figure 3: NO₃⁻ delivery plan during the operation of the PRB and dates of sampling events

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321 **2.6. Denitrification quantification**

322

323 We recognized that dilution within the PRB may occur due to changes in flow rates
324 and/or direction of groundwater (caused by e.g. rainfall episodes), and these could bias the
325 interpretation of results. The choice of the nitrate source (KNO₃) allowed the concentration of
326 NO₃⁻ to be normalized with respect to the conservative K⁺ ion. K⁺ was used for the following
327 reasons: (1) it was found to behave conservatively within the mulch/gravel media (not suffering
328 from lateral mechanisms e.g. adsorption) in lab-tests, (2) it presented very low background
329 concentrations in the site groundwater, and (3) it is easy to detect at low concentration. Hence,
330 NO₃⁻ and K⁺ were injected together into the PRB in the form of KNO₃ (ratio 1:1). Any observed
331 decrease of NO₃⁻ concentration as compared to K⁺ concentration would be indicative of NO₃⁻
332 removal due to processes other than simple dilution (e.g. through denitrification).

333 A denitrification factor (DNF) was thus defined as follows:

334

$$335 \text{ DNF} = \frac{[\text{NO}_3^-]_{\text{out}} / [\text{K}^+]_{\text{out}}}{[\text{NO}_3^-]_{\text{in}} / [\text{K}^+]_{\text{in}}}$$

336

337 where subindexes “in” and “out” refer to inlet and outlet of the PRB, respectively. A DNF
338 approaching 0 was indicative of total NO₃⁻ removal, whereas a DNF tending to 1 was indicative
339 of no removal at all (and that any observed decrease in NO₃⁻ concentration was due to dilution).

340

341 **2.7. Groundwater sampling and chemical analysis**

342

343 Groundwater was collected from monitoring wells for chemical analysis. Each well was
344 purged using a submersible pump (whales minipurger, flowrate 10 l/min) for about 1 minute

345 prior to sampling (representing over 5 well volumes). River water from upstream and
346 downstream of the PRB was also sampled using the same submersible pump.

347 Groundwater analysis comprised the determination of pH, nitrate (NO_3^-), nitrite (NO_2^-),
348 ammonium (NH_4^+), dissolved organic carbon (DOC) and major cations and anions (K^+ , Na^+ ,
349 Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}). After collection, samples were immediately stored at 4°C and shipped to
350 an ISO17025 accredited laboratory under the United Kingdom Schemes (UKAS) (Alcontrol
351 Laboratories) for analysis within 48 hours in order to avoid any post sampling microbial
352 degradation. A total of nine campaigns were carried out for groundwater analysis, as shown in
353 Figure 3.

354 The Kone analyser was used for the analysis of NO_3^- and NO_2^- (APHA Method 4500H)
355 (AWWA/APHA, 1999), NH_4^+ (BS 6068: Part 2.11:1984) (BSI, 1984), SO_4^{2-} (APHA Method
356 4500E) (AWWA/APHA, 1999) and Cl^- (modified US EPA Method 325.1 & 325.2) (USEPA,
357 1983). pH was analysed using a GLpH pHmeter (BS 1377 Method) (BSI, 1984). DOC was
358 analysed by combustion according to APHA Method 5310 (AWWA/APHA, 1999). Cations Na^+
359 and K^+ were analysed by ICP-OES according to APHA Method 3111 (AWWA/APHA, 1999)
360 while Ca^{2+} and Mg^{2+} by ICP-MS according to APHA Method 3125B (AWWA/APHA, 1999).
361 The limits of detection for these analytes (in mg/L) were 0.3 (NO_3^-), 0.05 (NO_2^-), 0.2 (NH_4^+), 3
362 (SO_4^{2-}), 1 (Cl^-), 2 (DOC), 0.2 (K^+ and Na^+), 0.1 (Ca^{2+} and Mg^{2+}).

363

364 **2.8. Gases sampling and chemical analysis**

365

366 In a denitrification system, NO_3^- is ideally converted totally to N_2 according to reaction
367 (1). However, incomplete denitrification may result in the accumulation of intermediate species,
368 e.g. NO and N_2O . Moreover, degradation of organic matter in anaerobic conditions (either by
369 denitrifying bacteria or other bacteria also present in the system) can lead to the accumulation of
370 carbon dioxide (CO_2) and methane (CH_4). These gases, together with N_2O are known to be
371 potent greenhouse gases of major environmental concern, and in this case by the regulator on
372 site. In fact, N_2O and CH_4 exhibit a global warming potential for a 100-year time horizon 298

373 and 25 times greater, respectively, than that of CO₂ (IPCC, 2007). In subsurface systems, gases
374 can be emitted via upward diffusion from groundwater through the unsaturated zone to the
375 atmosphere (Jurado et al., 2017). For this reason, emissions of CO₂, CH₄ and N₂O were
376 measured using the closed chamber method (Hensen et al., 2012). The chamber consisted of a
377 plastic box (31x31 cm) inserted into the soil above the PRB to a depth of 5 cm. The enclosure
378 surface area was 0.0961 m² and the created headspace volume 0.0115 m³. Gas from the
379 headspace of the chamber was pumped continuously through PTFE tubing connected to the
380 chamber for a 70-min collection period and contents of CO₂, CH₄ and N₂O were analysed using
381 a portable MCERTS accredited FTIR multiparameter gas analyser (Gasmeter DX 4030).

382 To further elucidate the generation of CO₂, CH₄ and N₂O and their potential for upward
383 migration and discharge to the atmosphere, these gases were measured in the headspace of each
384 of the three nested wells at different depths within the PRB. Wells were sealed with gas tight
385 caps prior to and during the measurements to ensure that the headspace of the monitoring wells
386 was not diluted with air. The headspace of the wells was not purged prior to gas analysis in
387 order to measure highest possible concentration. The gas phase of the wells was re-circulated at
388 1 l/min for 2 to 3 hours during measurements (i.e. approximately 2 to 3 times the volume of the
389 headspace). Spectra were continuously recorded at a rate of 1 measurement per minute.

390 CO₂, CH₄ and N₂O measurements were performed during the period when the highest
391 nitrate load was spiked in order to assess highest potential concentration of gases (see Figure 3).

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394 **3. RESULTS AND DISCUSSION**

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396 **3.1. Denitrification performance of the PRB**

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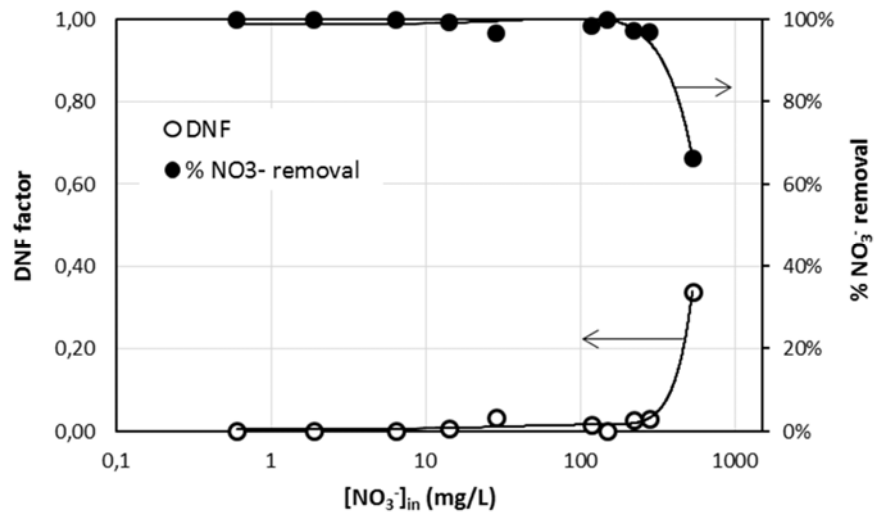
398 Figure 4 shows the performance of the PRB in removing NO₃⁻ from groundwater.

399 During the first 257 days of operation, when NO₃⁻ concentration in feed barrels was 500, 5,000

400 and 10,000 mg/L (see Figure 1), the PRB was successful at removing NO_3^- with a DNF ≤ 0.03
 401 or, equivalently, at removal percentage $\geq 97\%$. This meant that $[\text{NO}_3^-]/[\text{K}^+]$ was lower
 402 downgradient the PRB (MW2 and MW10) than upgradient (MW1 and MW9).

403 However, when NO_3^- concentration in feed barrels was increased to 20,000 mg/L from
 404 day 257 onwards, the DNF declined to 0.34 (NO_3^- removal percentage of 66%), making evident
 405 that the PRB has an ultimate design limit for NO_3^- load (530 mg/L measured in the inlet gravel
 406 layer).

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423 Figure 4: Denitrification factor (DNF) and NO_3^- removal percentage observed in the PRB as a
 424 function of NO_3^- concentration entering the PRB.

425

426 Three observations can be highlighted on the response of the PRB to the increase in the
 427 NO_3^- load:

428 First, the study period saw increasing severity of weather in Northern Ireland, resulting
 429 in near monthly flooding of the field by the River Braid and strong perturbations to the
 430 groundwater flow regime. This led to measured dilution factors in the upgradient gravel layer
 431 (mostly between 10 and 70) higher than that estimated during the tracer test (quantified at 10.8).
 432 Moreover, additional dilution (at factors 1-40) were occasionally observed within the PRB,

433 likely due to lateral groundwater inputs during flooding. These dilutions factors resulted in NO_3^-
434 concentrations in the inlet of the PRB (between 0.6 and 530 mg/L) that were up to 100-fold
435 lower than the expected ones without the additional dilution. Although K^+ -normalized molar
436 ratio $[\text{NO}_3^-]/[\text{K}^+]$ accounted for dilution effects and, thus, findings were not compromised by
437 them, for some campaigns, the low measured concentration of K^+ prevented reliable calculation
438 of DNF.

439 Second, neither NO_2^- nor NH_4^+ were detected in groundwater samples at relevant
440 concentrations (averaged concentrations of 0.5 mg/L and 0.3 mg/L, respectively) throughout the
441 study, suggesting that most NO_3^- removal was due to denitrification and not through other
442 processes such as dissimilatory nitrate reduction to ammonia (DNRA). A possible NO_3^- removal
443 process that cannot be ruled out from the measurements taken alone is N-immobilization in
444 microbial biomass (Calderer et al., 2010). This process has been found of minor importance in
445 other denitrification PRBs (Schipper and Vojvodić-Vuković, 1998).

446 Third, DOC measured in groundwater from within the PRB exhibited a sustained
447 concentration in the range of 4-10 mg/L throughout the study (Figure 5), showing that mulch
448 was providing significantly increased level of DOC to sustain heterotrophic microbial activity.
449 An initial peak of up to 71 mg/L was measured in MW3, likely as a result of washout of organic
450 carbon. Similar high initial releases of DOC have also been observed in other denitrification
451 PRBs filled with natural organic substrates (Robertson and Cherry, 1995; Schipper and
452 Vojvodić-Vuković, 1998; Schmidt and Clark, 2012).

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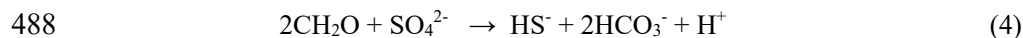
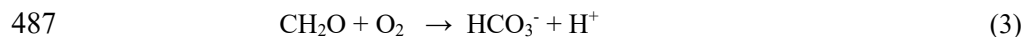
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476 Figure 5: Evolution of DOC in groundwater within the PRB at different depths (MW3 to
477 MW5).

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479 The achieved DOC concentration at stabilized conditions was in line with PRB design
480 parameters (gravel to mulch ratio) where calculations showed it should be low enough to avoid
481 both a negative impact on groundwater quality and undesirable processes like DNRA, but high
482 enough to support heterotrophic denitrification activity. We should bear in mind here that other
483 heterotrophic processes consuming DOC may inevitably also take place by other indigenous
484 microorganisms, such as aerobic respiration, sulphate-reduction and methanogenesis, as shown
485 by the following equations, respectively:

486



490

491 The observed increases in K^+ -normalised molar ratio $[\text{HCO}_3^-]/[\text{K}^+]$ (which averaged 15-
492 fold) after the passage of groundwater through the PRB suggested that heterotrophic processes
493 (reactions 2-5) were taking place in the PRB. This was further supported by the observed slight

494 decreases of pH from inlet to outlet monitoring wells (averaged decreases of 0.3 units of pH).
495 The occurrence of sulphate-reduction (reaction 4) in the PRB was evidenced by the observed
496 decrease of K^+ -normalised molar ratio $[SO_4^{2-}]/[K^+]$, which averaged 30%. Finally, analysis of
497 air in the headspace of the monitoring wells showed an enrichment in CO_2 , CH_4 and N_2O (see
498 below), indicating that eq. 3-5 were taking place.

499 Competition for CH_2O between denitrifiers, aerobic degraders, methanogens and
500 sulphate-reducers should not be seen necessarily detrimental for denitrification to proceed, as it
501 is known that denitrifiers do not degrade complex polymeric carbon found in organic substrates
502 but depend on a consortium of microorganisms to release more labile, simple organic compounds
503 (Schipper and Vojvodić-Vuković, 1998; Schipper and Vojvodić-Vuković, 2001). The synergies
504 in such a consortium was beyond the scope of this study, but it is likely that the co-occurrence
505 of reactions 2-5 helped denitrification to progress.

506 No change of the level of NO_3^- in the river water between upstream and downstream of
507 the PRB was observed throughout the study. At all times, NO_3^- in the River Braid water ranged
508 between 11 and 16 mg/L, and these measured concentrations were always higher than
509 concentrations measured in any of the monitoring wells between the PRB and the River Braid.

510

511 **3.2. Vertical profile of NO_3^- within the PRB**

512

513 Figure 6 illustrates NO_3^- vertical profiles inside the PRB at different inlet NO_3^-
514 concentrations. Denitrification activity seemed to depend on the vertical location, as DNF
515 generally declined downward from averaged values of 0.51 at depth -2.0 m to 0.10 at depth -3.0
516 m. The greater NO_3^- removals at the bottom of the PRB can be justified by the fact that the
517 deeper the location the less atmospheric O_2 intrusion and, therefore, the more reducing
518 conditions, which favours denitrification (Jahangir et al., 2012; Coco et al., 2018).

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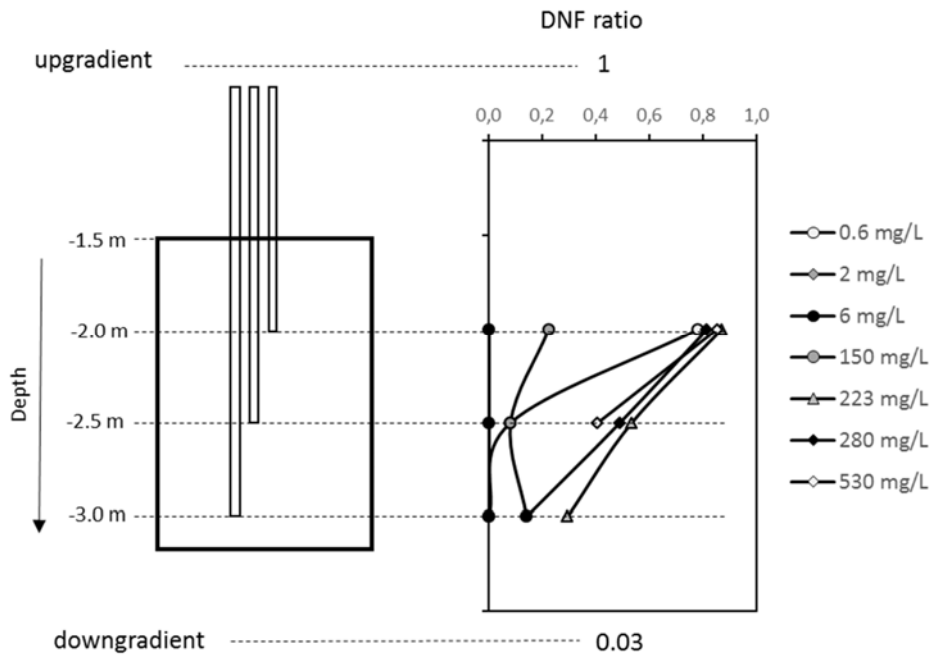


Figure 6: Vertical profiles of DNF within the PRB. Corresponding values for upgradient and downgradient the PRB are also shown

It must be underlined that DNF values shown in Figure 6 correspond to the monitoring wells in half of the PRB flow-distance. The overall NO_3^- removal was higher as groundwater travelled the whole width of the PRB (as shown in Figure 4).

3.3. Gases analysis

Emissions of generated $\text{CO}_{2(g)}$, $\text{CH}_{4(g)}$ and $\text{N}_2\text{O}_{(g)}$ from the PRB to the atmosphere can occur vertically via upward diffusion from groundwater through the unsaturated zone. Averaged emissions of $\text{CO}_{2(g)}$, $\text{CH}_{4(g)}$ and $\text{N}_2\text{O}_{(g)}$ measured from the closed chamber tests were 411.09 $\text{mg}/(\text{m}^2 \cdot \text{h})$, 23.05 $\text{mg}/(\text{m}^2 \cdot \text{h})$ and 0.403 $\text{mg}/(\text{m}^2 \cdot \text{h})$, respectively (Table 2).

558

		Flux of emitted gas	
		Average	st. dev.
CO ₂	mg/(m ² ·h)	411.09	164.66
CH ₄	mg/(m ² ·h)	23.05	3.99
N ₂ O	mg/(m ² ·h)	0.40	0.38

559

560 Table 2: Emissions of generated CO₂, CH₄ and N₂O from the PRB to the atmosphere measured
561 from the closed chamber tests

562

563 The generation of CO₂, CH₄ and N₂O was indicative of heterotrophic processes. CO₂
564 can be formed from HCO₃⁻ as a product of reactions (2-5). CH₄ reflected the prevalence of
565 anaerobic conditions (at least in some parts) within the PRB, whereas N₂O was indicative of
566 (incomplete) denitrification.

567 There are no published studies that have examined gases emission from field-scale
568 denitrification PRBs. However, the values obtained in this study compare well with other
569 ecosystems under field conditions. In fact, CO₂ emission fluxes were in the same order of
570 magnitude as those measured in restored riparian wetlands (353-732 mg/(m²·h)) (Audet et al.,
571 2013), constructed wetlands (32-489 mg/(m²·h)) (Søvik et al., 2006) and undisturbed natural
572 soil (230-557 mg/(m²·h)) (Yang et al., 2013), but considerably lower than those measured in
573 some Danish agricultural peatlands (4033-5500 mg/(m²·h)) (Elsgaard et al., 2012). CH₄
574 emission fluxes were also comparable to those measured in wetlands (4-49 mg/(m²·h)) (Whalen,
575 2005; Audet et al., 2013), constructed wetlands (1-47 mg/(m²·h)) (Søvik et al., 2006) and
576 undisturbed natural soil (1-20 mg/(m²·h)) (Yang et al., 2013), and much lower than those
577 measured in landfills (96 g/(m²·h)) (Bruun et al., 2017 and references therein). Finally, N₂O flux
578 values measured for the PRB fell in the lower end of values reported in literature in riparian
579 soils (0.02-31 mg/(m²·h)) (Audet et al., 2013; Audet et al., 2014; Hinshaw and Dahlgren, 2016;
580 Jurado et al., 2017 and references therein), European agricultural and forested ecosystems (0.4-
581 137 mg/(m²·h)) (Machfert et al., 2002) and constructed wetlands (<0.01-58 mg/(m²·h)) (Søvik
582 et al., 2006; Bruun et al., 2017). These values of N₂O have been reported to not represent a

583 significant contribution to the atmosphere compared to the direct emissions from agricultural
584 fields (Hinshaw and Dahlgren, 2016; Jurado et al., 2017). Taking into account the small area of
585 the PRB (compared to other systems such as natural or constructed wetlands) it appears that the
586 measured gas emissions in this study represent a minor contribution of total emissions to the
587 atmosphere.

588 The low CO₂, CH₄ and N₂O emissions do not necessarily imply that the concentrations
589 of these gases in groundwater may not be high. It is well known that gases in groundwater can
590 be over-saturated with respect to the overlying atmosphere (Jurado et al., 2017). CO₂, CH₄ and
591 N₂O concentrations in groundwater were not measured directly in the current study. However,
592 their content was measured in the headspace of the nested monitoring wells within the PRB.
593 Because these wells were filled with groundwater that entered through the screened zone at a
594 different depth, the content of gases in their headspace can be regarded as an indicator for
595 microbial activity being active at different locations in the PRB. It must be bear in mind that
596 these released gases do not diffuse through any soil layer (unlike those analysed in closed
597 chamber tests), and thereby their contents are expected to the be higher than those measured in
598 the closed chamber test.

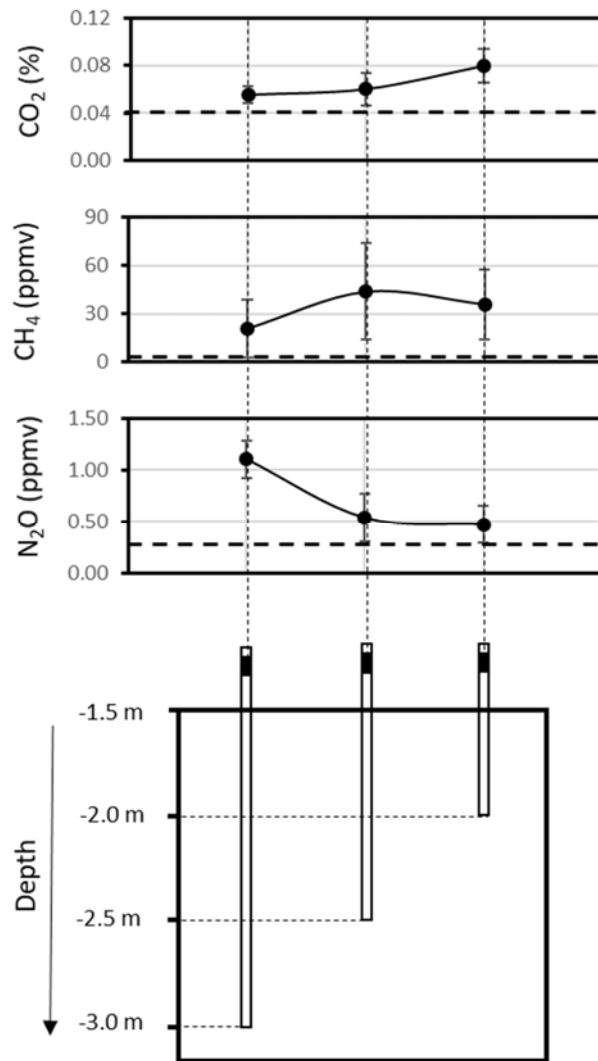
599 Headspace gas within the three nested wells presented contents notably greater (for
600 CH₄), greater (for N₂O) and only slightly greater (for CO₂) than atmospheric background
601 (Figure 7). Contents varied depending on the depth of the monitoring well. CO₂ contents were
602 higher in the headspace of the shallowest piezometer, likely coming from aerobic respiration,
603 favoured in the upper part where diffusion of atmospheric O₂ is not as limited as in deeper parts,
604 and to a lesser extent from denitrification and sulphate-reduction (which require much more
605 reducing conditions) (Stuart and Lapworth, 2016).

606 The opposite trend was exhibited by N₂O. Higher contents were seen in the deepest
607 piezometer while lower contents in the shallowest piezometer. This was consistent with the
608 DNF vertical profile showing that it is in the deepest part where denitrification is favoured.
609 Degassing of N₂O generated in the deepest part to the atmosphere is often hindered by 1) the
610 low N₂O diffusivity through saturated soil (the diffusion coefficient of N₂O in water is around

611 four orders of magnitude smaller than in air), which makes that the larger the water column
612 above a location the lower the amount released to the atmosphere (Heincke and Kaupenjohann,
613 1999) and 2) the microbial reduction of N_2O to N_2 during the slow upward diffusion (Jahangir et
614 al., 2012; Jurado et al., 2017; Cocco et al., 2018).

615 No specific pattern was observed with regard to CH_4 . More measurements should be
616 done to elucidate whether CH_4 differs between monitoring wells at different depths.

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647 Figure 7: Contents of CO_2 , CH_4 and N_2O in the headspace of the nested wells at three different
648 depths within the PRB. The dashed horizontal lines delineate the atmospheric background levels
649 of CO_2 , CH_4 and N_2O .

650

651 **3.4. Comparison against other denitrification PRB**

652

653 To our best knowledge, there are only six other PRBs for NO_3^- remediation worldwide
654 as reported in peer-reviewed journals. Four of these are in Canada and USA and two in
655 Australia and New Zealand. This is, thus, the first PRB of this type in Europe. Table 3 presents
656 an inventory of these denitrification PRBs, together with the one reported here, to facilitate
657 comparisons among them. The principles and design of all them are comparable in general
658 terms. The one reported here is singular in that it is the only one with a NO_3^- delivery system.

659 Successes and failures of these PRBs must be evaluated from both chemical and
660 hydraulic points of view. From a chemical point of view, all reported PRBs demonstrate that
661 denitrification can satisfactorily be promoted in the subsurface by means of a natural solid
662 organic substrate (sawdust, woodchips, mulch). In all cases, NO_3^- removal within the PRB was
663 found >70% (with inlet NO_3^- inputs ranging between 2-438 mg/L) and the main NO_3^- removal
664 mechanism was identified to be heterotrophic denitrification, promoted by the release of DOC
665 from the solid natural organic substrate. For two of the PRBs, authors have estimated that, based
666 on the release rate of DOC, the denitrification capacity can be maintained for many decades
667 (Schipper and Vojvodić-Vuković, 2001; Robertson et al., 2008; Long et al., 2011). In some
668 PRBs, denitrification has been confirmed by monitoring denitrification enzyme activity (DEA)
669 (Schipper and Vojvodić-Vuković, 2001; Schipper et al., 2004; Schmidt and Clark, 2012) or by
670 means of microbiological tools (Hiller et al., 2015). Residence time (t_R) within these
671 denitrification PRBs ranges from 1.8-13 days (based on the explicitly reported values), which
672 indicates that denitrification is a faster process than sulphate-reduction, for which t_R required in
673 a PRB is in the order of (at least) 90 days to satisfactorily take place (Benner et al., 2002; Gibert
674 et al., 2011).

675 However, it is from hydrogeological perspective that some of these documented PRB
676 show their flaws. In fact, it is not rare that PRBs suffer from unforeseen changes in groundwater
677 directions and/or improper hydraulic characterization of the site prior to PRB installation, which

678 results in limited capture of the NO_3^- -contaminated plume, diversion and/or partial or total by-
679 pass of the groundwater around the PRB. Fluctuations of groundwater flow rates (with up to 25-
680 fold decreases) or even bypasses around the PRB depending on the season have been reported
681 for four of the six reported denitrifying PRBs (Schipper and Vojvodić-Vuković, 2000; Schipper
682 et al., 2004; Robertson et al., 2008; Schmidt and Clark, 2012). Design flaws on the site
683 characterization with the subsequent loss of hydraulic control have been reported to be the most
684 common cause of PRB failures (Henderson and Demond 2007), especially when climatic
685 conditions can vary considerably over the year and so do the aquifer hydrologic conditions, in
686 particular following heavy and sustained rainfalls.

Location	Dimensions	Composition	t _R (d)	[NO ₃ ⁻] (mg/L)				[DOC] (mg/L)			Hydraulic performance	Reference
				up-gradient	in the PRB	down-gradient	removal up-down	up-gradient	in the PRB	down-gradient		
Long Point, Ontario, Canada	L=n.r. D=1.2 m T=0.6 m	Soil (80%) Sawdust (20%)	10-13	106-283	n.d.	9-111	72-97%	2.9-5.7		4.4-5.6	Difficulties in intercepting the contaminated plume, causing dilution with uncontaminated groundwater within the PRB	Robertson and Cherry, 1995 Robertson et al., 2000; 2008
Cambridge, North Island, New Zealand	L=35 m D=1.5 m T=1.5 m	Soil (70%) Sawdust (30%)	“several days”	22-71	2.7-8.8	<8.8	70-95%				Difficulties in intercepting the plume, “because the majority of the sampled groundwater had flowed beneath the wall”.	Schipper and Vojvodić-Vuković, 1998; 2000; 2001. Long et al., 2011
Cambridge, North Island, New Zealand	L=40 D=3.0 m T=3.0 m	Soil (80%) Sawdust (20%)	n.r.	93-173	0.9	84-194	≈0%	n.d.	n.d.	n.d.	Difficulties in intercepting the plume, as “most of the groundwater flowed under rather than through the wall”.	Schipper et al., 2004
Zorra, Ontario, Canada	L=8 m D=0.5 m T=4.0 m	Sediment Wood particle	13	27-438	31	23	90%	3.5	667	330	None reported	Robertson et al., 2007
Waquoit Bay, Falmouth, Massachussets (USA)	L=20 m D=2.5 m T=3.7 m	Woodchips	n.r.	2	<d.l.	<d.l.	>99%	0.7	1.4		None reported	Hiller et al., 2015
Alachua, Florida (USA)	L=55 m D=1.8 m T=1.7 m	Sand (50%) Sawdust (50%)	1.8	27		7	77%	2	34	70	Some “groundwater bypassing the edge of the wall”	Schmidt and Clark, 2012
Ballymena, Northern Ireland, United Kingdom	L=20 m D=1.7 m T=1.2 m	Gravel (50%) Mulch (50%)	14 (variable)	0.6-530	<d.l.-182	<d.l.-29	66-99%	1-3	4-10	4-7	Occasional lateral groundwater inputs resulting in dilution within the PRB	This study

L= length, D=depth, T=thickness
d.l.: detection limit, n.r.: not reported

Table 3: Compilation of the existing biological PRBs for the treatment of NO₃⁻-contaminated groundwater worldwide .

1 **4. CONCLUSIONS**

2

3 The conclusions of the study can be summarised as follows:

4

5 • The denitrification PRB was successful at removing NO_3^- from groundwater at inlet
6 concentrations up to 280 mg/L (with NO_3^- removal percentages $\geq 97\%$). When NO_3^-
7 concentration was 530 mg/L the NO_3^- removal percentage declined to 66%. To reliably attribute
8 any decrease of NO_3^- concentration to NO_3^- removal, its concentration was normalized with
9 respect to a conservative ion (K^+) also spiked with NO_3^- (as KNO_3) to account for possible
10 dilution effects.

11 • The marginal levels of NO_2^- and NH_4^+ indicated that NO_3^- removal was mainly through
12 denitrification and not through other processes such as DNRA.

13 • Monitoring groundwater at different depths within the PRB provided evidence that NO_3^-
14 underwent denitrification preferably at the deepest part of the PRB (removals mostly $>60\%$),
15 where more favourable reducing conditions were achieved. The higher contents of $\text{N}_2\text{O}_{(g)}$
16 measured in the headspace of the deeper monitoring well seemed to confirm this trend.

17 • The analysis of other dissolved ion species (SO_4^{2-}) and gases (CO_2 , CH_4) revealed that
18 heterotrophic processes other than denitrification were also active within the PRB. These
19 processes included aerobic respiration, sulphate-reduction and methanogenesis.

20 • The intense rainfalls during the operation period of the PRB resulted in greater NO_3^-
21 dilutions than expected from the initial site hydrogeological characterisation. Although this
22 additional dilution did not pose concern for the denitrification capacity of the PRB, for some
23 campaigns the low concentration of the conservative ion K^+ prevented reliable calculation of
24 denitrification removal percentage.

25 • Emission fluxes of CO_2 , CH_4 and N_2O were comparable with other ecosystems under
26 field conditions. Because of the small area covered by the PRB, these fluxes do not represent

1 any significant contribution to greenhouse gases to the atmosphere. Further work is required on
2 this field.

3

4

5 **CONFLICTS OF INTEREST**

6

7 The authors declare no conflict of interests.

8

9

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11

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