

Performance of a field-scale biological permeable reactive barrier for in-situ remediation of nitrate-contaminated groundwater.

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1	PERFORMANCE OF A FIELD-SCALE BIOLOGICAL PERMEABLE REACTIVE
2	BARRIER FOR IN-SITU REMEDIATOIN OF NITRATE-CONTAMINATED
3	GROUNDWATER
4	
5	
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21	Abstract
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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 NO₃⁻ loadings. The PRB was successful at removing NO₃⁻ from 30 groundwater at inlet concentrations up to 280 mg/L (with NO₃⁻ removal percentages \geq 97%). 31 Monitoring of groundwater at different depths within the PRB provided evidence that NO₃⁻ 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. 39 40 Keywords: Denitrification, Groundwater contamination, Nitrate, In-situ remediation, 41 Permeable reactive barrier 42 43 44 45 **1. INTRODUCTION** 46 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). NO₃⁻ 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 NO₃⁻ ingestion from polluted drinking waters can induce methemoglobinemia, hypertension, cancers and a number
of currently inconclusive health repercussions (Della Rocca et al., 2007).

Remediation of groundwater contaminated by NO_3^- is a matter of active research. Among the available remediation approaches, biological denitrification appears to be the most effective and desirable one (Della Rocca et al., 2007). Denitrification is defined as the dissimilatory biological reduction of NO_3^- to nitrogen gas (N₂) through a multistep process, in which NO_3^- is sequentially converted into nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O) and, finally, harmless nitrogen gas (N_2) as shown in the following equation:

64

$$65 \qquad NO_3^- \to NO_2^- \to NO \to N_2O \to N_2 \qquad (1)$$

66

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

72
$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 5HCO_3^- + 2H_2O + H^+$$
 (2)

73

where CH₂O represents a generic organic compound. In subsurface environments, the lack of readily available organic carbon has often been reported as the most common hindrance to denitrification (Jahangir et al., 2012). This limitation explains why, until recently, the use of denitrifying bacteria for groundwater treatment has traditionally been reserved to ex-situ treatments in bioreactors. However, latterly attention has focused on the supply of an external organic substrate in the aquifer itself (in-situ treatment).

One option of applying an organic substrate into the aquifer is through a permeable reactive barrier (PRB). A PRB consists in placing a reactive material across the flow path of contaminated groundwater so that the contaminants can be transformed as groundwater flows through the reactive material (Scherer et al., 2000; Kalin, 2004). The selection of the reactive material is crucial: it must be chemically effective to eliminate the target contaminant(s) and must maintain an adequate permeability to ensure flow through the PRB. In a heterotrophic denitrification PRB, the reactive material consists of an organic substrate to stimulate denitrifying activity. PRBs are designed to be passive treatment systems in the sense that, once installed, groundwater typically flows through the reactive zone under its natural hydraulic 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.

Hence, while lab-studies undoubtedly provide useful information and contribute to a better understanding of denitrification in carbon-amended porous media, their results cannot automatically nor reliably be extrapolated to field-scale PRBs. As highlighted by other researchers (Addy et al., 2016), further research is required, as it is only through accumulated experience at field-scale that such a technology can be successfully applied and tailored to sitespecific 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 NO₃⁻ 111 to be injected into the aquifer directly upgradient of the PRB, providing an opportunity to 112 evaluate the NO₃⁻ removal efficiency of the PRB under increasing NO₃⁻ 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. 115 116 117 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%.

138



	units	Concentration
pН		6.8 ± 0.5
ORP	mV	21 ± 63
DO	mg/L	<1
Cond.	µS/cm	270 ± 112
NO ₃ ⁻	mg/L	4.5 ± 3.5
NO ₂ ⁻	mg/L	1.4 ± 0.8
$\mathrm{NH_4}^+$	mg/L	0.5 ± 0.3
TOC	mg/L	2.7 ± 0.9
Na^+	mg/L	14 ± 2
\mathbf{K}^+	mg/L	3 ± 2
Ca ²⁺	mg/L	40 ± 8
Mg^{2+}	mg/L	12 ± 4
Cl	mg/L	14 ± 1
SO4 ²⁻	mg/L	8 ± 7
Alk (as CaCO ₃)	mg/L	178 ± 62

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**

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The design of the PRB was performed according to established guidelines (Gavaskar et al., 1999; Obiri-Nyarco et al., 2014). Briefly, site characterisation allowed setting the location, configuration, orientation and dimensions (width and depth) of the PRB in order to successfully intercept the contaminated plume, while laboratory experiments allowed selecting the most suitable components of the PRB and, with the denitrification kinetics data, determining the required thickness of the PRB to ensure a targeted removal of NO₃⁻. Among the substrates evaluated in this laboratory study, mulch consisting of hardwood with small amounts of leaves supplied by the local company M. Large Tree Services Ltd (Newtownabbey, Northern Ireland) was the top performing substrate, attaining an overall NO_3^- removal mostly via denitrification of >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.

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

The NO_3^{-1} delivery system consisted of two elevated 230 L tanks (with 1.5 meters of hydraulic head) connected to a drip irrigation system through which site groundwater with variable concentrations of NO_3^{-1} was continuously injected into the upgradient gravel layer, ultimately through the reactive zone. The injection was accomplished by a row of 22 drip emitters situated along the upgradient gravel layer. The close spacing between the drip emitters was to provide a uniform front of NO_3^{-1} flowing towards the barrier. This delivery system allowed a precise control of the NO_3^{-1} loading rate injected into the aquifer by selecting the NO_3^{-1} 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).



Figure 2: Conceptual scheme of the PRB; a) isometric view of the PRB showing the delivery system of NO₃⁻ and the position of the monitoring wells within the PRB, b) aerial view of the PRB showing the monitoring well network.

260 **2.3. Monitoring wells network**



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.

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- 273 2.4. Hydraulic PRB validation
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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.

2.5. NO_3^- delivery plan



A stepwise increase of NO₃⁻ concentration in barrels was planned in order to investigate the PRB performance at various NO₃⁻ loading rates. Before proceeding with any increment of NO₃ loading rate, action and regulatory oversight was agreed with the Environment Agency of Northern Ireland. The delivery plan carried out during the study is presented in Figure 3. NO₃⁻ was first spiked into the aquifer with a concentration of NO_3^- in the barrels of 500 mg/L (before dilution by the groundwater flowing through the PRB) for 157 days. The PRB immediately demonstrated the denitrifying ability was effective at removing all NO₃⁻ from groundwater during this first phase, and NO_3^- concentration in the barrels was increased to 5,000 mg/L until day 206, when it was further increased to 10,000 mg/L for the following 49 days. Given that NO_3 removal was maintained >97%, it was decided to further increase NO_3 concentration in barrels to 20000 mg/L until day 340.







[NO₃⁻] in barrels (mg/L)

318 Figure 3: NO_3^- delivery plan during the operation of the PRB and dates of sampling events

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Groundwater sampling

O Gas sampling

time (days)

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 NO_3^- 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 NO_3^- and K^+ were injected together into the PRB in the form of KNO₃ (ratio 1:1). Any observed 331 decrease of NO_3^- concentration as compared to K^+ concentration would be indicative of NO_3^- 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
$$DNF = \frac{\frac{[NO_{3}]_{out}}{[NO_{3}]_{in}}}{[NO_{3}]_{in}} / [K^{+}]_{in}}$$

336

where subindexes "in" and "out" refer to inlet and outlet of the PRB, respectively. A DNF approaching 0 was indicative of total NO_3^- removal, whereas a DNF tending to 1 was indicative of no removal at all (and that any observed decrease in NO_3^- 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.

Groundwater analysis comprised the determination of pH, nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), dissolved organic carbon (DOC) and major cations and anions (K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻). After collection, samples were immediately stored at 4°C and shipped to an ISO17025 accredited laboratory under the United Kingdom Schemes (UKAS) (Alcontrol Laboratories) for analysis within 48 hours in order to avoid any post sampling microbial degradation. A total of nine campaigns were carried out for groundwater analysis, as shown in Figure 3.

354 The Kone analyser was used for the analysis of NO_3^- and NO_2^- (APHA Method 4500H) (AWWA/APHA, 1999), NH4⁺ (BS 6068: Part 2.11:1984) (BSI, 1984), SO4²⁻ (APHA Method 355 356 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) while Ca²⁺ and Mg²⁺ by ICP-MS according to APHA Method 3125B (AWWA/APHA, 1999). 360 361 The limits of detection for these analytes (in mg/L) were 0.3 (NO₃⁻), 0.05 (NO₂⁻), 0.2 (NH₄⁺), 3 (SO4²⁻), 1 (Cl⁻), 2 (DOC), 0.2 (K⁺ and Na⁺), 0.1 (Ca²⁺ and Mg²⁺). 362

363

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

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In a denitrification system, NO_3^- is ideally converted totally to N_2 according to reaction (1). However, incomplete denitrification may result in the accumulation of intermediate species, e.g. NO and N₂O. Moreover, degradation of organic matter in anaerobic conditions (either by denitrifying bacteria or other bacteria also present in the system) can lead to the accumulation of carbon dioxide (CO₂) and methane (CH₄). These gases, together with N₂O are known to be potent greenhouse gases of major environmental concern, and in this case by the regulator on site. In fact, N₂O and CH₄ 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 m^2 and the created headspace volume 0.0115 m^3 . 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 (Gasmet DX 4030).

382 To further elucidate the generation of CO_2 , CH_4 and N_2O 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.

CO₂, CH₄ and N₂O measurements were performed during the period when the highest
 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

395

396 3.1. Denitrification performance of the PRB

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Figure 4 shows the performance of the PRB in removing NO₃⁻ from groundwater.
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 NO₃⁻ with a DNF ≤ 0.03

401 or, equivalently, at removal percentage $\geq 97\%$. This meant that $[NO_3^-]/[K^+]$ 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).



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 NO₃⁻ load:

First, the study period saw increasing severity of weather in Northern Ireland, resulting in near monthly flooding of the field by the River Braid and strong perturbations to the groundwater flow regime. This led to measured dilution factors in the upgradient gravel layer (mostly between 10 and 70) higher than that estimated during the tracer test (quantified at 10.8). 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 NO₃⁻ 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 $[NO_3^{-1}]/[K^+]$ 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.

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

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

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476 Figure 5: Evolution of DOC in groundwater within the PRB at different depths (MW3 to477 MW5).

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

486

$$488 \qquad 2CH_2O + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+ \qquad (4)$$

$$489 \qquad \qquad 2CH_2O + H_2O \rightarrow CH_4 + HCO_3^- + H^+ \tag{5}$$

490

491 The observed increases in K^+ -normalised molar ratio $[HCO_3^-]/[K^+]$ (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 CO₂, CH₄ and N₂O (see 498 below), indicating that eq. 3-5 were taking place.

Competition for CH₂O between denitrifiers, aerobic degraders, methanogens and sulphate-reducers should not be seen necessarily detrimental for denitrification to proceed, as it is known that denitrifiers do not degrade complex polymeric carbon found in organic substrates but depend on a consortium of miroorganisms to release more labile, simple organic compounds (Schipper and Vojvodić-Vuković, 1998; Schipper and Vojvodić-Vuković, 2001). The synergies in such a consortium was beyond the scope of this study, but it is likely that the co-occurrence of reactions 2-5 helped denitrification to progress.

No change of the level of NO₃⁻ in the river water between upstream and downstream of the PRB was observed throughout the study. At all times, NO₃⁻ in the River Braid water ranged between 11 and 16 mg/L, and these measured concentrations were always higher than concentrations measured in any of the monitoring wells between the PRB and the River Braid.

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511 **3.2.** Vertical profile of NO₃⁻ within the PRB

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

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		Flux of em	itted gas
		Average	st. dev.
$\rm CO_2$	$mg/(m^2 \cdot h)$	411.09	164.66
CH_4	$mg/(m^2 \cdot h)$	23.05	3.99
N_2O	$mg/(m^2 \cdot h)$	0.40	0.38

560 Table 2: Emissions of generated CO_2 , CH_4 and N_2O from the PRB to the atmosphere measured 561 from the closed chamber tests

562

The generation of CO_2 , CH_4 and N_2O was indicative of heterotrophic processes. CO_2 can be formed from HCO_3^- as a product of reactions (2-5). CH_4 reflected the prevalence of anaerobic conditions (at least in some parts) within the PRB, whereas N_2O was indicative of (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 ($353-732 \text{ mg/(m^2 \cdot h)}$) (Audet et al., 571 2013), constructed wetlands (32-489 $mg/(m^2 \cdot h)$) (Søvik et al., 2006) and undisturbed natural 572 soil (230-557 mg/($m^2 \cdot h$)) (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/($m^2 \cdot h$)) (Whalen, 575 2005; Audet et al., 2013), constructed wetlands $(1-47 \text{ mg/(m^2 \cdot h)})$ (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/($m^2 \cdot h$)) (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 $(0.02-31 \text{ mg/(m^2 \cdot h)})$ (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 (0.4-137 mg/(m²·h)) (Machfert et al., 2002) and constructed wetlands (<0.01-58 mg/(m²·h)) (Søvik 581 582 et al., 2006; Bruun et al., 2017). These values of N₂O have been reported to not represent a significant contribution to the atmosphere compared to the direct emissions from agricultural fields (Hinshaw and Dahlgren, 2016; Jurado et al., 2017). Taking into account the small area of the PRB (compared to other systems such as natural or constructed wetlands) it appears that the measured gas emissions in this study represent a minor contribution of total emissions to the 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). CO_2 , CH_4 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.

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

The opposite trend was exhibited by N_2O . Higher contents were seen in the deepest piezometer while lower contents in the shallowest piezometer. This was consistent with the DNF vertical profile showing that it is in the deepest part where denitrification is favoured. Degassing of N_2O generated in the deepest part to the atmosphere is often hindered by 1) the low N_2O diffusivity through saturated soil (the diffusion coefficient of N_2O 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 CH₄. More measurements should be 616 done to elucidate whether CH₄ differs between monitoring wells at different depths.



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

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

652

To our best knowledge, there are only six other PRBs for NO_3^- remediation worldwide as reported in peer-reviewed journals. Four of these are in Canada and USA and two in Australia and New Zealand. This is, thus, the first PRB of this type in Europe. Table 3 presents an inventory of these denitrification PRBs, together with the one reported here, to facilitate comparisons among them. The principles and design of all them are comparable in general 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, NO₃⁻ removal within the PRB was 663 found >70% (with inlet NO₃⁻ inputs ranging between 2-438 mg/L) and the main NO₃⁻ 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 NO₃-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	tr (d)	[NO ₃ ⁻] (mg/L) [DOC] (mg/L)		Hydraulic performance	Reference					
				up-	in the	down-	removal	up-	in the	down-		
				gradient	PRB	gradient	up-down	gradient	PRB	gradient		
Long Point,	L=n.r.	Soil (80%)	10-13	106-283	n.d.	9-111	72-97%	2.9-5.7		4.4-5.6	Difficulties in intercepting	Robertson and Cherry, 1995
Ontario,	D=1.2 m	Sawdust									the contaminated plume,	Robertson et al., 2000; 2008
Canada	T=0.6 m	(20%)									causing dilution with	
											uncontaminated groundwater	
											within the PRB	
Cambridge,	L=35 m	Soil (70%)	"several	22-71	2.7-	<8.8	70-95%				Difficulties in intercepting	Schipper and Vojvodić-
North Island,	D=1.5 m	Sawdust	days"		8.8						the plume, "because the	Vuković, 1998; 2000; 2001.
New Zealand	T=1.5 m	(30%)									majority of the sampled	Long et al., 2011
											groundwater had flowed	
-											beneath the wall".	
Cambridge,	L=40	Soil (80%)	n.r.	93-173	0.9	84-194	$\approx 0\%$	n.d.	n.d.	n.d.	Difficulties in intercepting	Schipper et al., 2004
North Island,	D=3.0 m	Sawdust									the plume, as "most of the	
New Zealand	T=3.0 m	(20%)									groundwater flowed under	
											rather than through the	
-											wall".	
Zorra,	L=8 m	Sediment	13	27-438	31	23	90%	3.5	667	330	None reported	Robertson et al., 2007
Ontario,	D=0.5 m	Wood particle										
Canada	T=4.0 m											
Waquoit Bay,	L=20 m	Woodchips	n.r.	2	<d.1.< td=""><td><d.1.< td=""><td>>99%</td><td>0.7</td><td>1.4</td><td></td><td>None reported</td><td>Hiller et al., 2015</td></d.1.<></td></d.1.<>	<d.1.< td=""><td>>99%</td><td>0.7</td><td>1.4</td><td></td><td>None reported</td><td>Hiller et al., 2015</td></d.1.<>	>99%	0.7	1.4		None reported	Hiller et al., 2015
Falmouth,	D=2.5 m											
Massachussets	T=3.7 m											
(USA)												
Alachua,	L=55 m	Sand (50%)	1.8	27		7	77%	2	34	70	Some "groundwater	Schmidt and Clark, 2012
Florida (USA)	D=1.8 m	Sawdust									bypassing the edge of the	
	T=1.7 m	(50%)									wall"	
Ballymena,	L=20 m	Gravel (50%)	14	0.6-530	<d.1< td=""><td><d.129< td=""><td>66-99%</td><td>1-3</td><td>4-10</td><td>4-7</td><td>Occasional lateral</td><td>This study</td></d.129<></td></d.1<>	<d.129< td=""><td>66-99%</td><td>1-3</td><td>4-10</td><td>4-7</td><td>Occasional lateral</td><td>This study</td></d.129<>	66-99%	1-3	4-10	4-7	Occasional lateral	This study
Northern Ireland,	D=1.7 m	Mulch (50%)	(variable)		182						groundwater inputs resulting	
United Kingdom	T=1.2 m										in dilution within the PRB	

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 .

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- 3

The conclusions of the study can be summarised as follows:

4

• The denitrification PRB was successful at removing NO_3^- from groundwater at inlet concentrations up to 280 mg/L (with NO_3^- removal percentages $\ge 97\%$). When $NO_3^$ concentration was 530 mg/L the NO_3^- removal percentage declined to 66%. To reliably attribute any decrease of NO_3^- concentration to NO_3^- removal, its concentration was normalized with respect to a conservative ion (K⁺) also spiked with NO_3^- (as KNO₃) to account for possible dilution effects.

The marginal levels of NO₂⁻ and NH₄⁺ indicated that NO₃⁻ removal was mainly through
 denitrification and not through other processes such as DNRA.

Monitoring groundwater at different depths within the PRB provided evidence that NO₃ underwent denitrification preferably at the deepest part of the PRB (removals mostly >60%),
 where more favourable reducing conditions were achieved. The higher contents of N₂O_(g)
 measured in the headspace of the deeper monitoring well seemed to confirm this trend.

• The analysis of other dissolved ion species (SO₄²⁻) and gases (CO₂, CH₄) revealed that heterotrophic processes other than denitrification were also active within the PRB. These processes included aerobic respiration, sulphate-reduction and methanogenesis.

• The intense rainfalls during the operation period of the PRB resulted in greater NO₃⁻ dilutions than expected from the initial site hydrogeological characterisation. Although this additional dilution did not pose concern for the denitrification capacity of the PRB, for some campaigns the low concentration of the conservative ion K⁺ prevented reliable calculation of denitrification removal percentage.

• Emission fluxes of CO₂, CH₄ and N₂O were comparable with other ecosystems under 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.
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5	CONFLICTS OF INTEREST
6	
7	The authors declare no conflict of interests.
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9	
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