Contamination of groundwater resources by a variety of anthropogenic pollutants from both point and non-point sources represents a key global environmental problem. In soil, organic carbon is needed as an energy source for heterotrophic denitrification but the potential for denitrification is limited due to carbon availability beneath the water table in the saturated zone. Research has suggested that groundwater denitrification is limited due to low organic C contents of sub-soils and aquifer media. In-situ treatment systems such as subsurface permeable reactive barriers, comprising a treatment zone of non hazardous carbon reactive materials that degrade or immobilize contaminants such as nitrates, as groundwater flows through, may be used to attenuate the movement of nutrients in agricultural settings. Some available solid carbon materials may cause clogging with subsequent bypass flow of groundwater contaminants around or through the barrier due to low hydraulic conductivity. A number of potentially suitable carbonaceous materials are identified for permeable reactive barriers in Ireland.
INTRODUCTION

The Water Framework Directive (WFD) (EC, 2000) rationalizes and updates existing European water legislation and provides for water management on the basis of River Basin Districts. To meet the objectives of the WFD the agricultural sector aims to maintain the “high status” of waters where it exists, to prevent any deterioration in the existing status of waters and to achieve at least “good status” in relation to a waterbody by 2015.

The WFD requires that a groundwater body does not cause an associated surface water body to fail in achieving their environmental targets nor cause any significant damage to dependent terrestrial ecosystems (Dahl et al., 2007). The WFD will bring about major changes in the regulation and management of Europe’s water resources and must include the planning and implementation of efficient and cost-effective measures to protect groundwaters and surface waters. Current mitigation strategies are two fold:

Strategy 1 – Reduction of nutrient loss

Traditionally, agricultural wastes are disposed of by land spreading. In land spreading, the recharge rate, the time of year of application, the hydraulic conductivity of the soil, the depth of soil to the water table and/or bedrock, and the concentration of nutrients and suspended sediment in the wastewater (soiled water and any discharge containing nutrients) are some of the defining parameters that determine nitrate (NO$_3^-$) movement through the soil to the water table. The recommended maximum rate of application is 5 mm per hour and the quantity applied should not exceed 50 m$^3$ per hectare per application (ADAS, 1985). Infiltration depth of irrigated water and rainfall may be calculated when the annual effective drainage, number of effective drainage days, effective porosity, annual precipitation and the landspreading hydraulic load are known. These data may then be combined with water table data to estimate if excess nutrients recharge to groundwater within a specific time frame.

The Nitrates Directive, 91/676/EEC (EEC, 1991) and rising costs are now forcing better utilization of nutrients in slurry. Current research in Ireland and the U.K. is focusing on improving N recovery from slurry by examining the effect of spreading timing and by comparing splashplate, trailing shoe or trailing hose slurry application methods. The average efficacy of these methods varies, and differs when grassland or arable land application are considered (Smith and Misselbrook, 2000; Misselbrook et al., 2002). Present research in Ireland follows similar patterns (Ryan, 2005). Low percentages of slurry landspread in spring coupled with application methods (splashplate) give rise to higher gaseous ammonia losses. Ammonia (NH$_3$) emissions with respect to suitable alternatives (trailing shoe) and subsequent N uptake by the sward are being investigated in Irish grasslands (Lalor, 2007). Farm management strategies aimed at prevention of nutrient loss to water have recently been reviewed overlaying land management pressures, agro-meteorology and pathways to identify areas in Ireland where nutrient loss could be of concern (Schulte, 2006). Risk of diffuse nutrient loss to water was identified where a pressure and a transport vector occur at a given location and time, which changes depending on scale.

Strategy 2 - Remediaion and control

Strategy 2 acknowledges that nutrient losses exist now and will exist in the future, associated with historical contamination, accidental losses or non-compliance with codes of practice, and seeks to use pre-treatment and in situ remediation techniques to satisfy the requirements of the WFD. A solution that seeks remediation of nitrate while controlling P losses at pre-treatment and in situ phases is needed.
In Ireland, groundwater is under increasing risk from “diffuse” (agriculture) and “point” sources (manure and silage storage) and septic tank systems. The safe disposal of on-site wastewater is essential for the protection of groundwater. The accumulation of excess soil P in catchments under intensive animal production has been linked to increases in dissolved P concentrations in rivers and streams draining these catchments (Boesch et al., 2001; Tunney, 1990). Concentrations of dissolved and particulate P are related to discharge rates, land surface slope and suspended soil material and discharge rate, respectively (Djodjic et al., 2000). Overland flow and associated soil erosion lead to P losses from soil to water. The sorption capacity and desorption dynamics were examined in Irish grassland soils (Daly et al., 2001). P sorption capacities correlate negatively with organic matter indicating that a high percentage of organic matter may inhibit P sorption from solution to soil. High organic matter soils have low P sorption capacities and poor P reserves compared to mineral soils at similar Morgan’s extractable P levels. Such soils are vulnerable to P loss where further P amendment exceeds crop needs. Kronvang et al. (2005) examined the effects and uncertainties of targeted mitigation measures in European agricultural areas where P loss is commonplace indicating soil tillage changes, treatment of soils near ditches and streams with amendments, introduction of buffer strips to retain P, and restoration of land area to allow P deposition and water filtration from tile drains as options. Also emphasized are the times taken for water quality improvement and the up-scaling of such measures to catchment scale. As soil has a negative electrostatic charge, nitrate is not retained electrostatically and travels relatively quickly through the soil, leading to increased potential for groundwater contamination (Abu-Ashor et al., 1994; Kung et al., 2000). Nitrate leaching leads to nutrient loss to groundwater and is dependent on the hydraulic loading rate on the irrigated plot, soil water content and soil type (Ryan, 1998).

**IRISH WATERWAYS AND DRINKING WATER**

Recent assessments of Irish waterways indicate that a significant fraction of rivers, lakes, estuaries and coastal waters will require improvements if they are to meet “good ecological status”. Water bodies identified as probably requiring improvement include: 56% of groundwater bodies, 35% of river water bodies, 20% of lake water bodies, 23% of transitional water bodies and 15% of coastal water bodies (EPA, 2004). Local Authorities, group water schemes and private abstractions make up the drinking water distribution in Ireland. 81% of drinking water is sourced from surface water (rivers, lakes and reservoirs), 13% is sourced from groundwater and 6% from springs (EPA, 2005). The main threat to surface and groundwater drinking supplies is bacteria and contamination by organic matter and poor maintenance of large and small-scale wastewater treatment systems (EPA, 2004a). Studies of low-yielding wells have also shown that, although nitrate contamination is not widespread, surface waters in Carlow, Cork, Kerry, Louth and Waterford may be susceptible to eutrophication as a result of nitrate leaching through groundwater (Thorn and Coxon, 1991; Lee et al., 1994; Stapleton, 1996; Lucey et al., 1999; EPA, 2003). McGarrigle et al. (2002) reported drinking water breaches in 15 counties (Carlow, Cavan, Cork, Galway, Kerry, Kildare, Kilkenny, Laois, Louth, Meath, Offaly, Tipperary, Waterford, Wexford and Wicklow). However, overall compliance of nitrate for public water supplies and group water schemes in 2003 was 96.1% (EPA, 2003).

**INCIDENTAL NUTRIENT LOSS**

Integrated water resource management incorporates stakeholder participation. This could involve the farmer becoming actively involved in efficient, low maintenance and cost effective
mitigation measures to reduce N and P losses. A decision support system developed for site specific scenarios should help the farmer and water resource manager to locate an environmental technology on a farm.

Contaminant species of concern include solvents, fuel hydrocarbons, heavy metals, pesticides, nitrate, and radionuclides. Nitrate has been identified as the most common contaminant identified in groundwater (Freeze and Cherry, 1979) and poses significant global problems (Smith et al., 1990) and is not only a reflection of local physical hydrogeological considerations but also the inherent properties of the contaminants (diffusion, dispersion, retardation) (McNab, 2006). Translocation of nitrate below the rooting zone is one of the major agriculture derived pollutants leaching to groundwater from point (storage and irrigation) and non point sources (urine patches and fertilizers), which makes them unavailable or ineffective for their original use. Agricultural discharges originating from a single, identifiable source, such as a soiled water irrigator, leaking tank, or storage facility are point sources. Soiled water, which is not properly treated or managed, can be a major cause of point source pollution (Dunne et al., 2004). This can lead to a reduction in dissolved oxygen (DO) levels in surface waters and the subsequent damage to sensitive aquatic organisms (salmonid). Pollution that does not originate from a single source, or point, is non point source pollution (diffuse source) (Pierzynski, 2005). The amount of nitrate leached is spatially specific within and between farms and is soil and stocking rate dependent (McLaren and Cameron, 1996). In soil, organic carbon is needed as an energy source for heterotrophic denitrification (Beauchamp et al., 1989; Groffman, 1994), and various indexes of organic matter availability for denitrification have been studied in agricultural and forest soils (Stanford et al., 1975; Burford and Bremner, 1975; Davidson et al., 1987; Bijay-Singh et al., 1988). The shortage of usable organic carbon is cited as a limitation for denitrification in groundwater environments (Wilhelm et al., 1994). The potential for denitrification is limited beneath the water table in subsurface riparian sediments (Ambus and Lowrance, 1991; Lowrance, 1992; Groffman et al., 1992). Research has suggested that ground water denitrification is limited due to low organic C contents of subsoils (Lowrance, 1992; McCarty and Bremner, 1992; Starr and Gillham, 1993; Groffman et al., 1996). Low denitrification potentials between 0.2 and 2.5 mg N kg\(^{-1}\) day\(^{-1}\) were obtained in glacial till under low O\(_2\) and natural C concentrations (Castle, 2004). Incubation and lysimeter studies of denitrification rates in agricultural soils of 2.09 \(\pm\) 0.01 (Brown Earth) and 4.34 \(\pm\) 0.10 (Gley) \(\mu g\) L g day\(^{-1}\) were increased fivefold by amendment of woodchip in gley soil groups (ratio 5:2 g) (Sullivan, 2007). Natural processes cannot be expected to remove the large quantity of nitrate now potentially present in many aquifers. Water treatment processes that stimulate artificial denitrification by the injection of the required nutrients are under development, and may offer a simple and inexpensive method of nitrate removal (Hiscock, 1991). For groundwater remediation and increased denitrification above natural attenuation levels a suitable emplaced carbon amendment in isolation or mixed with soil is needed, placed where contamination migration occurs in the subsurface.

Implementation of current water quality legislation (Nitrates Directive) requires separation of animal waste and water, thereby reducing the nutrient content of soiled water. As the nutrient value of this product is low, volumes, high related storage costs and landspreading are high, an alternative solution is to remediate and recycle this product for yard washing using in-situ remediation technologies such as biofilm reactors coupled with amendments for P sequestration. The farmer would then utilize a lower percentage of mains water. However for incidental nutrient losses to groundwater an alternative technology which treats groundwater in situ must be considered.
The objective of this paper is to identify possible solid carbon reactive media types and sources, which could be used to enhance in situ groundwater denitrification in Ireland as reactive media in a permeable reactive barrier.

**PERMEABLE REACTIVE BARRIER (PRB)**

To meet the requirements of the Nitrates Directive, 91/676/EEC (EEC, 1991a), groundwater and surface water remediation technologies are required to capture nutrient loss where nutrient management and other agricultural management practices fail. An integrated approach is needed to address multiple simultaneous challenges of N and P loss to water. Therefore, in situ and pre-treatment of farmyard manures should integrate N remediation and P control. A low biofilm technology to achieve organic C, N and SS removal, coupled with P sequestration media such as low value ochre (acid mine waste product with site specific P retention capacity), are viable options for soiled water recycling. Low-cost, low-management remediation technologies, such as PRBs and willows, have good potential in Ireland because they can be implemented at farm level (Fenton, submitted).

Nitrate although mobile may not be affected by biodegradation reactions in the plume under aerobic shallow groundwater conditions, but may be attenuated in anaerobic groundwater zones where additional carbon sources are available. An emerging environmental technology in Ireland is the PRB, which is defined as ‘an engineered treatment zone of reactive media that is placed subsurface and designed to intercept a contaminant plume, provide a flow path through the reactive media and transform the contaminants into an environmentally acceptable form to attain remediation concentration goals downgradient of the barrier’ (Carey et al., 2002). An in-situ PRB, installed perpendicular to groundwater flow direction, which intercepts a migrating groundwater contaminant plume is a viable groundwater nitrate remediation technology (Nyer, 1998). PRBs have a low energy demand and are cost effective (Manz and Quinn, 1997; Mitchell, 1997) and are therefore potentially viable options for agricultural scenarios. Each site will have specific conditions unique to it but a methodology based on site and groundwater characterization can successfully calculate the dimensions and orientation of the barrier (Fenton, submitted). PRBs suitable for nitrate remediation from a point source on a farm are continuous (Pierzynski, 2005) (remediation of the entire width of the plume) or gate and funnel barriers (bio-curtain) where the barrier is placed across an opening in an impermeable subsoil wall that intercepts the plume (Starr, 1994).

**SOLID CARBON AMENDMENTS**

In Ireland total roundwood production for 2006 was estimated at 3,154,000 m$^3$. This figure breaks down into three distinct categories: sawlog (large diameter wood) (2,176,000 m$^3$), pulpwood (smaller diameter wood) (820,000 m$^3$) and stakewood (158,000 m$^3$). Within the sawlog category, sawmill residues generated amount to 1,079,000 m$^3$. This may be further divided into bark (218,000 m$^3$), sawdust (215,000 m$^3$) and woodchip 646,000 m$^3$ (Knaggs, 2007). However, these materials are presently used in panelboard mills (woodchip - 600,000 m$^3$ and sawdust - 105,000 m$^3$), or used as a fuel (sawdust - 60,000 m$^3$). Another 50,000 m$^3$ of sawdust and 46,000 m$^3$ of woodchip are exported.

Thinning of a plantation provides more room for the development of more economically viable sawlog wood. A portion of woodchips could be set aside from these thinnings together with crown, branches, unsaleable assortments or undersized trees not used for fuel could potentially provide a low cost carbonaceous reactive media. The longevity of a PRB based on denitrification rate (0.7
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to 32 mg L N day\(^{-1}\)) and amount of the initial carbon mass utilized (2% to 3%) by heterotrophic denitrification over a 6 year period has been investigated. Results give the PRB a lifetime of at least a decade without renewal of reactive media (Robertson, 2000).

Willows (Salix spp.) are also gaining in popularity in Ireland and elsewhere for the treatment of domestic and agricultural wastewater (Rosenqvist and Dawson, 2005; Börjesson and Berndes, 2006). A long growing season and a high nutrient retention capacity make them ideal for wastewater treatment (Dimitriou and Aronsson, 2004). Short Rotation Coppice (SRC) involves the cultivation of Willow or Poplar, which are grown in plantations at approximately 15 thousand trees per hectare. The stems are harvested at regular intervals every 2-3 years whereupon the remaining stumps re-grow new multiple stems (coppice). The harvested stems are chipped to become bio fuel mainly for heat and occasionally for electricity generation or may also provide a source of woodchip for reactive media.

A variety of cellulose based waste materials have been studied at laboratory and field scale. Many experiments have investigated nitrate removal using sawdust or woodchip and have achieved different nitrate removal rates (Table 1). The build up of microbial biomass on the reactive media at higher nitrate concentrations can result in clogging (Fahner, 2002). Shallow groundwater migrating to drains with baseflow concentration of total nitrogen (TN) typically of 2.0 - 3.0 mg l\(^{-1}\) and total phosphorous (TP) typically of 0.2 - 0.3 mg l\(^{-1}\) coupled with urban storm water drainage with TN and TP concentrations of 6.3 mg l\(^{-1}\) and 0.7 mg l\(^{-1}\) respectively was intercepted with a PRB containing solid carbon reactive material. Sawdust and woodchip were investigated as reactive materials but woodchip was chosen for its higher durability over time and ability to mimic aquifer permeability (Horn et al., 2006). When using sawdust as a reactive material in the field the permeability of the material may change during construction. After barrier construction saturated hydraulic conductivities of 0.48 m day\(^{-1}\) and 65.4 m day\(^{-1}\) were measured in a PRB sawdust wall and aquifer respectively causing groundwater flow to bypass the reactive wall (Schipper, 2004). A porous reactive media layer comprising wood particles (woodchip) with very high hydraulic

<table>
<thead>
<tr>
<th>Study</th>
<th>Experiment type</th>
<th>Nitrate input mg l(^{-1})</th>
<th>Media</th>
<th>Residence time days</th>
<th>Nitrate removal rate mg L N day(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fahner, 2002</td>
<td>Field</td>
<td>63</td>
<td>Sawdust (30%)</td>
<td>3.5 - 7</td>
<td>15</td>
</tr>
<tr>
<td>Fahner, 2002</td>
<td>Column (low nitrate)</td>
<td>12</td>
<td>Sawdust (30%)</td>
<td>0.5 - 7</td>
<td>7.1</td>
</tr>
<tr>
<td>Fahner, 2002</td>
<td>Column (High nitrate)</td>
<td>40</td>
<td>Sawdust (30%)</td>
<td>1.5 - 7</td>
<td>9.5</td>
</tr>
<tr>
<td>Vogan, 1993</td>
<td>Column</td>
<td>70</td>
<td>Sawdust (10 – 20%)</td>
<td>1</td>
<td>2.8 – 6.5</td>
</tr>
<tr>
<td>Carmichael, 1994</td>
<td>Column</td>
<td>50 - 87</td>
<td>Wood Chip (100%)</td>
<td>1.6</td>
<td>14</td>
</tr>
<tr>
<td>Schipper and Vojvodic-Vukovic, 1998, 2000 , 2001</td>
<td>Laboratory microcosm</td>
<td>16</td>
<td>Sawdust (30%)</td>
<td>n/a</td>
<td>3.6</td>
</tr>
<tr>
<td>Robertson et al., 2000</td>
<td>Field</td>
<td>1.2 - 57</td>
<td>Sawdust (15 – 20%)</td>
<td>13 – 30</td>
<td>0.7 – 2.6</td>
</tr>
<tr>
<td>Robertson et al., 2000</td>
<td>Field</td>
<td>4.8</td>
<td>Woodchip (100%)</td>
<td>3 - 7</td>
<td>4 - 32</td>
</tr>
</tbody>
</table>

Table 1. Woodchip and sawdust denitrification rate and retention times for different studies.

Adapted from Fahner, 2002.
conductivity (approximately 865 m day\(^{-1}\)) was used to successfully treat nitrate in a shallow sand-and-gravel aquifer in southern Ontario. Nitrate concentrations of 1.3 to 14 mg l\(^{-1}\) in the aquifer were attenuated to <0.5 mg l\(^{-1}\) in the reactive layer. The use of highly permeable reactive media allowed emplacement of the barrier at shallow levels and at depths not consistent with plume dimension leading to lower costs (Robertson, 2005). The carbon source (tree bark, wood chips and leaf compost) must be cost effective and stable in the subsurface (Blowes, 1994). A laboratory study examined the use of various wood materials as a carbon source in horizontal flow filters to denitrify nitrate from a synthetic wastewater. The filter materials were: sawdust (*Pinus radiata*), sawdust and soil, sawdust and sand, and medium-chip woodchippings and sand. Two influent concentrations of nitrate, 200 mg N L\(^{-1}\) and 60 mg L\(^{-1}\), loaded at 2.9 to 19.4 mg nitrate kg\(^{-1}\) mixture, were used. The horizontal flow filter with a woodchip/sand mixture and an influent nitrate concentration of 60 mg N L\(^{-1}\), which operated over the study duration of 166 days, performed best, yielding a 97% reduction in nitrate at steady-state conditions (Healy, 2006). Kim et al., 2003 investigated column and bio retention systems containing a variety of reactive media including solid carbon material (alfalfa, newspaper, leaf mulch compost, sawdust, wheat straw, woodchips and elemental sulphur) as potential electron donors. Plexiglas columns (40 cm long by 6.4 cm inner diameter) were packed with sand (based on 2 mg l\(^{-1}\) influent synthetic storm-water nitrate concentration) with sieved sawdust and sand and woodchip and sand to < 2mm. Columns were operated for 35 to 40 days at 2.2 ml min\(^{-1}\) at 22\(^\circ\)C. Both sawdust and woodchip columns achieved 95% nitrate removal. Four different C sources were investigated in anaerobic batch experiments with 1:1 soil reactive media mix respectively: (i) wood chips (predominately *Quercus* spp.) approximately 3 to 10 cm in length, (ii) wood chips saturated with soybean oil (48% oil by weight), (iii) dried cornstalks collected after harvest, and (iv) paper fibers from corrugated cardboard. All of the C substrates stimulated denitrification with cornstalks supporting the greatest denitrification, followed by cardboard fibers, wood chips with oil, and wood chips alone. When results are averaged over the 180 day study period, rates of denitrification ranged from 0.427 g N kg\(^{-1}\) substrate d\(^{-1}\) for the ground cornstalks to 0.066 g N kg\(^{-1}\) substrate d\(^{-1}\) for the wood chips (Greenan, 2006).

Possible sources of solid carbon materials in Ireland may come from a variety of sources (Table 2). Many of these sources which have untreated waste materials are suitable for emplacement as reactive media.

**Thickness of the REACTIVE Trench**

The characteristics of a solid carbon media will determine the thickness of the PRB. Several stages need to be considered for the successful implementation and long term operation of a PRB (Table 3). The thickness and amount of reactive material needed in a PRB are directly related to:

<table>
<thead>
<tr>
<th>Fuel source</th>
<th>Description</th>
<th>Current Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawmill residues</td>
<td>Bark, cut offs, brown and white chip, sawdust and wood shavings</td>
<td>Animal bedding</td>
</tr>
<tr>
<td>Wood Industry residue</td>
<td>Off cuts, sawdust, shavings trimmings</td>
<td>Fuel</td>
</tr>
<tr>
<td>Arboricultural residues</td>
<td>Waste cuttings from parks, gardens and hedgerows</td>
<td>Mulch, Fuel</td>
</tr>
<tr>
<td>Small diameter roundwood</td>
<td>Early thinnings</td>
<td>Fuel</td>
</tr>
<tr>
<td>Forest logging residues</td>
<td>Tops and branches of trees (waste)</td>
<td>Fuel</td>
</tr>
<tr>
<td>Short rotation forestry</td>
<td>Woodchip, pellets</td>
<td>Fuel</td>
</tr>
</tbody>
</table>

Table 2. Possible sources of solid carbon reactive media for use in PRBs in Ireland.
Adapted from Healion, 2007.
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The kinetics of denitrification will depend on carbon and nitrate availability, pH, temperature, soil texture, soil management, tillage, rainfall events, rates of microbial respiration and nitrification, water filled porosity, soil mineral N content, soil type, and redox conditions (Boyer, 2006). The laboratory stage investigates the suitability of the reactive material, the denitrification rate of the available carbon media and the time the plume needs to remain in the reactive media to achieve water quality targets (retention time). Retention or denitrification rates may be calculated in the laboratory by mini lysimeter incubation studies (Sullivan 2007), batch reactor studies (Healy, 2006) or column experiments (Fahner, 2002; Volokita, 1996; Bedessem, 2005). A complete list of parameters and formulae for a column experiment setup together with example experimental values based on an industrial sand column are presented in Table 4.

Following this method, adequate samples at correct intervals (pore volumes) can be taken for breakthrough curve determination. By using CXTFIT (Toride et al., 1995) transport parameters may be estimated by using experimental data from the breakthrough curve (inverse problem) using the convection dispersion equation as the transport model. As nitrate is a conservative tracer no interactions between the (soil and the solute occur) the distribution coefficient \((K_d = 0)\) and the retardation factor \((R = 1)\) have nominal values (van Genuchten and Wierenga, 1986). The retention time \((t)\) needed to achieve water quality targets, is calculated by the following formula:

\[
t = \frac{C_{\text{treated}}}{r} \frac{1}{C_{\text{max}}}
\]

where: \(C_{\text{treated}}\) is the desired concentration downgradient of the PRB after remediation, \(C_{\text{max}}\) is the greatest concentration entering the PRB and \(r\) is the denitrification rate determined from batch,

Table 3. Stages to be undertaken when locating a PRB on a farm site. Selection and reactive media characteristics will determine the thickness of the PRB.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source characterisation</td>
<td>Establishes the type of contaminant and type of pollution on site (point or non point source)</td>
</tr>
<tr>
<td>Site characterisation</td>
<td>Identifies potential receptors</td>
</tr>
<tr>
<td>Hydrogeological characterisation</td>
<td>Allows for the construction of groundwater contour maps, watertable fluctuations data, groundwater quality and plume delineation. Establishes the hydraulic connection between the source and the receptor. This stage calculates the dimensions of the barrier and identifies groundwater flow direction and the orientation of the barrier. It also identifies the water quality targets needed.</td>
</tr>
<tr>
<td>Laboratory study: Reactive material selection and experimentation. Amenability of treatment:</td>
<td>Efficacy of the reactive media to achieve water quality targets. The hydraulic permeability should be high enough to avoid clogging but sufficient to allow for the residence time required. The reactive media required for biologically mediated transformations must also support colonisation by the required bacteria. This stage calculates the thickness of the barrier.</td>
</tr>
<tr>
<td>Locating the barrier</td>
<td>Using data gathered in the site and hydrogeological characterisation.</td>
</tr>
<tr>
<td>Monitoring</td>
<td>Long term multi level monitoring and modelling the flows before, within and after the trench before and after construction. The source and receptor should be especially monitored.</td>
</tr>
<tr>
<td>Construction</td>
<td>The type of trench and the depth of construction will need to be considered. The permeability of the reactive media should not be disturbed. The engineering involved is outlined in Meggyes and Simon, 2000.</td>
</tr>
</tbody>
</table>

· the hydraulic conductivity of the aquifer material and the reactive media

· the retention time needed to achieve water quality targets. This point is determined by the denitrification rate of the reactive material in laboratory experiments.

The kinetics of denitrification will depend on carbon and nitrate availability, pH, temperature, soil texture, soil management, tillage, rainfall events, rates of microbial respiration and nitrification, water filled porosity, soil mineral N content, soil type, and redox conditions (Boyer, 2006). The laboratory stage investigates the suitability of the reactive material, the denitrification rate of the available carbon media and the time the plume needs to remain in the reactive media to achieve water quality targets (retention time). Retention or denitrification rates may be calculated in the laboratory by mini lysimeter incubation studies (Sullivan 2007), batch reactor studies (Healy, 2006) or column experiments (Fahner, 2002; Volokita, 1996; Bedessem, 2005). A complete list of parameters and formulae for a column experiment setup together with example experimental values based on an industrial sand column are presented in Table 4.

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\]

where: \(C_{\text{treated}}\) is the desired concentration downgradient of the PRB after remediation, \(C_{\text{max}}\) is the greatest concentration entering the PRB and \(r\) is the denitrification rate determined from batch,
Table 4. Column experiment setup to obtain a breakthrough curve. Plexiglass or PVC columns should be packed semi wet and flow introduced upwards through the column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻ influent - effluent</td>
<td>10</td>
<td>mg L⁻¹</td>
<td></td>
</tr>
<tr>
<td>Column length (L)</td>
<td>30.5</td>
<td>[cm]</td>
<td></td>
</tr>
<tr>
<td>Diameter (D)</td>
<td>8.9</td>
<td>[cm]</td>
<td></td>
</tr>
<tr>
<td>Volume (Cᵥ)</td>
<td>1897.45</td>
<td>[cm³]</td>
<td></td>
</tr>
<tr>
<td>Cross sectional area (Cᵥ)</td>
<td>62.21</td>
<td>[cm²]</td>
<td></td>
</tr>
<tr>
<td>Mass Air-Dry soil</td>
<td>1961.11</td>
<td>[g]</td>
<td></td>
</tr>
<tr>
<td>Gravimetric Water Content</td>
<td>0.01</td>
<td>[g/g]</td>
<td></td>
</tr>
<tr>
<td>Mass Oven-Dry Soil</td>
<td>1959.41</td>
<td>[g]</td>
<td></td>
</tr>
<tr>
<td>Bulk Density ? b</td>
<td>1.033</td>
<td>[g/cm³]</td>
<td>n = 100(\frac{\rho_w}{\rho_s})</td>
</tr>
<tr>
<td>Particle Density ? s</td>
<td>2.650</td>
<td>[g/cm³]</td>
<td></td>
</tr>
<tr>
<td>Porosity n</td>
<td>61</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Pore Volume (PV)</td>
<td>1158.05</td>
<td>[cm³]</td>
<td>PV = Cᵥ.n</td>
</tr>
</tbody>
</table>

Steady State Flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Hydrograph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>10.066</td>
<td>[cm³]</td>
<td></td>
</tr>
<tr>
<td>Time (t)</td>
<td>10</td>
<td>[sec]</td>
<td></td>
</tr>
<tr>
<td>Darcy Flux Jw</td>
<td>0.01618</td>
<td>[cm/sec]</td>
<td>J_w = \frac{V}{tCᵥ}</td>
</tr>
<tr>
<td>Average Pore Water Velocity v</td>
<td>0.02651</td>
<td>[cm/sec]</td>
<td>v = \frac{J_w}{n}</td>
</tr>
<tr>
<td>Dimensionless Time [10 cm³]</td>
<td>0.0087</td>
<td>[sec]</td>
<td>T = \frac{vT}{L}</td>
</tr>
<tr>
<td>Time for 1 Pore Volume</td>
<td>1150.45</td>
<td>[sec]</td>
<td></td>
</tr>
<tr>
<td>T/20 Residence time</td>
<td>58</td>
<td>[sec]</td>
<td></td>
</tr>
<tr>
<td>Volumetric Water Content</td>
<td>2.720268519</td>
<td>[g/cm³]</td>
<td></td>
</tr>
<tr>
<td>ρw at 25°C</td>
<td>0.977</td>
<td>[g/cm³]</td>
<td></td>
</tr>
</tbody>
</table>

Subsurface Denitrification in a Permeable Reactive Barrier

Fenton

column or mini reactor experiments. The retention time is then multiplied by the groundwater flow velocity to calculate the thickness \(b\) of the trench using the following equation (Carey, 2002):

\[
b = v.t.SF
\]

where \(v\) is groundwater velocity in the reactive media (m day⁻¹) and SF is a safety factor. The length and depth of the PRB may be calculated during the hydrogeological characterization of the site (Table 3). Underestimation of retention time to achieve water quality targets will result in decreased denitrification rates. In column experiments using a newspaper carbon source, with inlet concentration of 100 mg NO₃⁻ l⁻¹ and varied flow rate from 0.5 to 1.5 m d⁻¹ complete removal of nitrate was achieved at flow rates up to 0.8 m d⁻¹. At 1.5 m d⁻¹ nitrate removal decreased by 30% (Volokita, 1996). Similar results have occurred in the field where denitrification rate increases up to a certain hydraulic conductivity or flow rate. Above this limiting flow rate the retention time for denitrification is not achieved and nitrate concentrations leave the column. Increasing flow rate through two sections of a denitrification wall (mm day⁻¹) changed over time due to hydraulic gradient. The rate of nitrate removal (mg N cm⁻³ h⁻¹) increased with increased groundwater flow rate. In section (A) groundwater flow rate varied from 7 mm day⁻¹ in November to 23 mm day⁻¹ in June with a subsequent increase in removal rate from 0.8 to 4.8 mg N cm⁻³ h⁻¹ (Schipper, 2000).

**DISCUSSION AND CONCLUSION**

Woodchip and woodchip mixed with soil as PRB reactive materials may enhance nitrate removal through denitrification and depending on hydraulic loading rate, may have a long lifespan. The growth of willow plantations, or waste wood materials not used for fuel could provide a C source for PRBs. Studies have shown that woodchip rather than sawdust may avoid clogging of reactive walls and prevent groundwater bypassing the PRB. Maintaining hydraulic conductivity at the aquifer/reactive wall junction is important for successful remediation. The optimal location of the PRBs and associated groundwater monitoring networks should be identified on each farm. Specifications for the implementation of these technologies on-site should be developed and future national policy needs to change to incorporate remediation technologies. A thorough laboratory investigation of possible solid carbon reactive materials to enhance anaerobic
denitrification is important for a successful implementation of a PRB. The amounts of reactive media needed are dependent on the retention time needed for achievement of water quality targets. The costs of various solid carbon sources should be investigated. The long term suitability of these reactive materials (durability) and maximum trench denitrification rates should also be investigated.

ACKNOWLEDGMENTS

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REFERENCES


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