MANIPULATION OF CARBON MEDIA, TEMPERATURE AND HYDRAULIC EFFICIENCY TO INCREASE NITRATE REMOVAL RATE IN DENITRIFICATION BEDS

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Abstract

The accumulation of reactive nitrogen (Nr) in terrestrial and aquatic environments is a global environmental issue that causes or contributes to climate change, stratospheric ozone depletion, and deterioration of coastal and terrestrial waters. Point source discharges of Nr from municipal and septic treatment systems, agricultural tile drainage, and industrial discharges contribute to these issues. Practical, low-cost methods are needed to reduce the Nr load into the environment from small-volume point source discharges. Denitrification beds are one such method. Improving the nitrate removal rate of denitrification beds will lead to reduced bed volumes, lower construction costs that likely facilitate greater uptake of the technology and reduced accumulation of Nr in the environment.

The main objective of this thesis was to test a number of approaches that might increase the rate of nitrate removal rate in a denitrification bed under non-nitrate limiting conditions, including: manipulation of carbon source, temperature and hydraulic flow.

To date, operational denitrification beds have used wood media as the carbon source which sustains nitrate removal rates of between 2–10 g N m^{-3} of media d^{-1} and relatively high permeability. While previous laboratory experiments have investigated the potential of alternative carbon sources, these studies were typically of short duration and small scale and did not necessarily provide reliable information for denitrification bed design purposes. To address this issue, nitrate removal, hydraulic and nutrient leaching characteristics of nine different carbon substrates were compared in 0.2 m^3 barrels, at 14°C and 23.5°C over a 23 month period. The relationship between hydraulic efficiency and nitrate removal of the different media was also investigated. Findings from the barrel trial were field tested in pilot scale (2.9 m^3) denitrification beds receiving municipal effluent dosed with KNO_3, over a 15 month period. The pilot scale trial tested whether nitrate removal could be improved by using an alternative carbon media (maize cobs) and increasing bed temperature through passive solar heating. The influence of bed flow regime (horizontal-point, horizontal-diffuse, downflow and upflow) on hydraulic efficiency and nitrate removal was also investigated.

This thesis demonstrated that more labile carbon sources, such as maize cobs, had significantly higher nitrate removal rates (15.0 to 21.8 g N m^{-3} d^{-1}) than wood media (3.0 to 4.9 g N m^{-3} d^{-1}) over the duration of the barrel trial. Nitrate removal rates increased with increasing temperature with mean Q_{10} of 1.6 for all media. The hydraulic efficiency of fragmented wood media decreased with increasing grain-size. However, nitrate removal rate was not dependent on hydraulic efficiency of the media, which was attributed to the significant secondary porosity of the media allowing denitrification to occur both on the surface and within the media particle. In the pilot scale trial, bed temperature increased by 3.4°C due to passive solar heating, but did not cause a measureable increase in nitrate removal rate due to variability in removal rates and possibly low temperature responsiveness of maize cobs for removing nitrate. Flow regime affected the hydraulic efficiency of denitrification beds and nitrate removal rates were lower in flow regimes with poor hydraulic efficiency. This was attributed to short-circuit flow reducing the bed volume that contributed to nitrate removal.

The results indicate that a four-fold reduction in denitrification bed size could potentially be achieved by using maize cobs as the carbon substrate, as opposed to wood fragments, and increasing bed temperature by incorporating passive solar heating techniques.

The findings of this thesis indicate that future research on improving the nitrate removal rate of denitrification beds under non-nitrate limiting conditions should focus on carbon substrates, increasing bed temperature, and hydraulic design of beds rather than on hydraulic efficiency of media. For example, research on coupling improved solar heating design with an appropriate inlet/outlet structure and location.

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TABLE OF CONTENTS

Chapter 1

General Introduction

1.1 Introduction

Global anthropogenic production of reactive nitrogen (Nr) increased by approximately 225% from 1970 to 2000 and exceeded all natural terrestrial production (Galloway et al., 2003). This has resulted in accumulation of Nr in the environment causing or contributing to global environmental issues including: an increase in atmospheric ozone and aerosols associated with respiratory illness, cancer, and cardiac disease in humans (Pope et al., 1995; Follett and Follett, 2001; Wolfe and Patz, 2002); climate change and stratospheric ozone depletion (Cowling et al., 1998); acidification and loss of biodiversity in surface waters (Vitousek et al., 1997); and eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal and terrestrial surface waters (Howarth et al., 2000).

The global anthropogenic increase in nitrogen is due to cultivation of nitrogen-fixing crops, combustion of fossil fuels, and production of ammonia fertilizers. Reactive nitrogen creation and accumulation is projected to increase in the future as human populations and per capita resource use increase (Galloway et al., 2003).

In New Zealand, nitrogen loss from farming activity to water bodies is considerable due to nitrogen fixation by pasture legumes, application of nitrogen fertilizer in excess of plant demand and stocking rates (Parfitt et al., 2006). Nitrogen fertilizer use increased by almost 700% from 1989 to 2003 (Parfitt et al., 2006). Leaching of excess nitrogen beneath farmland has caused elevated nitrate concentration in groundwaters, eutrophication of surface water waterways, and algal blooms in nationally significant lakes (Larned et al., 2004; Vant and Smith, 2004). In the groundwater fed lakes of the Rotorua and Taupo districts, water quality is predicted to continue to decline, regardless of immediate reduction in nitrogen leaching, due to long groundwater residence times (Morgenstern et al., 2004; 2006a; 2006b).

Nitrogen can enter receiving environments from point and non-point source discharges. Point source discharges can originate from a range of systems including: municipal and septic wastewater treatment systems, farming drains, and industry discharges. Practical methods are needed to reduce the Nr load into the environment from these point source discharges. Although numerous technologies for removing nitrogen from wastewaters exist (Oakley et al., 2010) these methods are often unaffordable for treatment of small volume point source discharge.

Denitrification beds (Blowes et al., 1994; Robertson et al., 2005a; Schipper et al., 2010b) offer a practical solution for the removal of nitrate from small-volume point-source discharges for which more expensive treatment options may be uneconomic. The beds are relatively low cost to install and require minimal maintenance compared to more expensive and complicated treatment options. However, there are considerable information gaps regarding the functioning and optimisation of denitrification beds that need to be resolved in order to increase their use to treat a range of effluents.

1.2 Denitrification beds

A denitrification bed is essentially a lined cavity or container filled with organic matter (typically wood fragments) through which nitrified effluent or discharge is passed. The organic matter supports biological denitrification that converts nitrate to dinitrogen gas under anaerobic conditions. There is evidence from laboratory and field studies that the dominant nitrate removal process occurring in denitrifying bioreactors is denitrification and not anaerobic ammonia oxidation (anammox) or dissimilatory nitrate reduction to ammonia (DNRA) (Greenan et al., 2009; Gibert et al., 2008). To date, denitrification beds have been used to removal nitrate from municipal, septic and dairy shed effluents; hydroponic hothouse and agricultural tile drains; geothermal water and in small streams (Fig. 1.1, Schipper et al., 2010a).

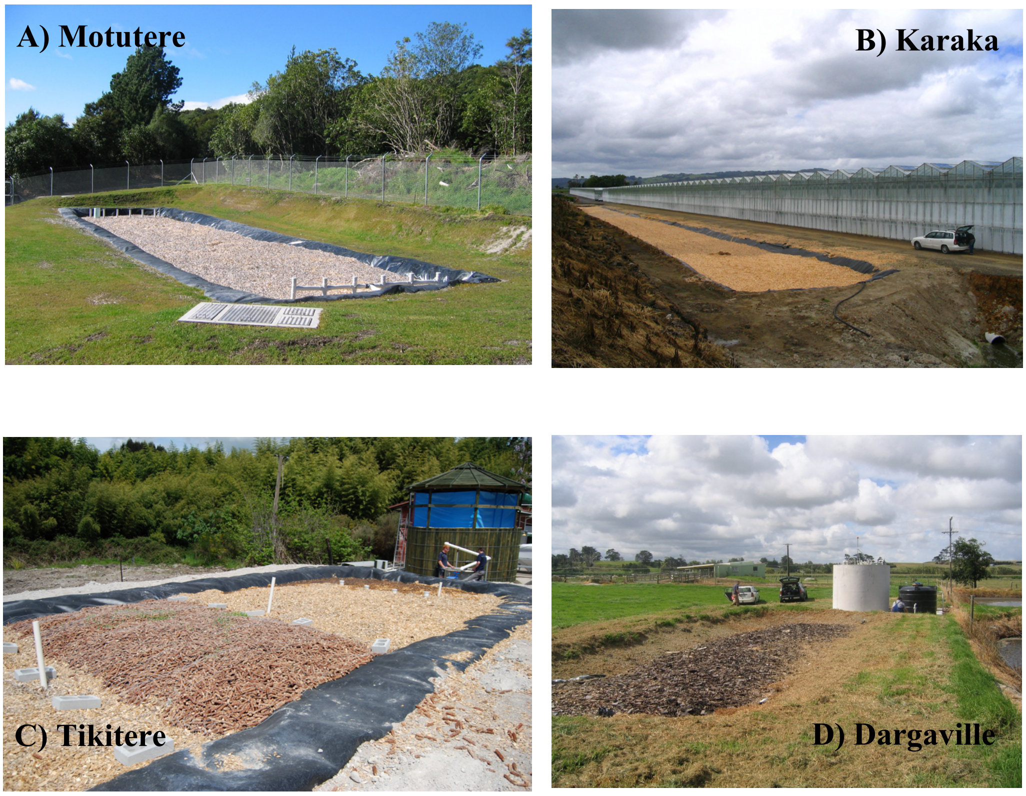

Figure 1.1 Photos of four operation denitrification beds. A) Motutere, (Lake Taupo, NZ) treating municipal effluent nitrified by an SBR plant. B) Karaka, (Auckland, NZ) treating hydroponic glasshouse discharge. C) Tikitere, (Rotorua, NZ) treating nitrogen in a geothermal stream. Note trickling filter in the background for nitrifying the water before flowing into the bed. The carbon substrate is a combination of maize cobs and woodchips. D) Daraville, (NZ) treating dairy shed effluent. Note the MBR plant in the background for nitrifying the effluent.

Other passive, low cost wastewater treatments systems also typically rely on the manipulation of the denitrification process to treat nitrate contaminated waters. These other treatment methods include constructed wetlands, pond systems, land disposal, and subsurface treatment (e.g., peat beds).

The advantages of denitrification beds over these traditional passive low cost reactive nitrogen treatment options are that denitrification beds are capable of greater than 99% removal of nitrate, have a relatively small footprint and low installation cost. One essential requirement for denitrification bed operation is that the nitrogen must be in the oxidised form, typically as nitrate. Therefore an upstream nitrifying process may be required.

Factors regulating the rate of nitrate removal in a bed include the concentration of available organic carbon of the substrate, concentration of nitrogen oxides (mainly nitrate) and dissolved oxygen, presence of denitrifying bacteria, pH, and temperature (Schipper et al., 2010a).

To date, field scale beds have used varying fractions and grain-sizes of wood particles as the carbon media. These wood-based denitrification beds are capable of sustained nitrate removal and hydraulic performance for more than 15 years (Robertson et al., 2010). Nitrate removal rates range from 2–10 g N m^{-3} d^{-1} (Schipper et al., 2010a) and are the main design criteria that dictate size of constructed beds. Identifying practical approaches that increase nitrate removal will result in decreased beds size and likely construction costs. Higher nitrate removal rates have been achieved in laboratory scale studies using alternative carbon media, but the longevity of these media are unknown.

Temperature is one of the most important factors influencing microbial growth. As temperature rises (within a given range) chemical and biological reaction rates increase and growth becomes faster (Madigan et al., 1996). Generally the increase in reaction rate can be approximated by the temperature coefficient (Q_{10}) which is the factor by which a reaction rate increases for every 10°C rise in temperature (Anderson and Janssen, 2006). Consequently, nitrate removal rate in a denitrification bed will increase with increasing temperature in non-nitrate limiting conditions (Schipper et al., 2010a). Raising denitrification bed temperature by incorporating techniques (such as solar heating) into the bed design may increase the nitrate removal rate of the bed.

Short-circuit flow in a denitrification bed may also potentially decrease nitrate removal rate by decreasing interaction of nitrate with potentially active sites of denitrification. Short-circuiting effectively reduces treatment volume where denitrification in zones of slow or stagnant water becomes nitrate limited. The degree of short-circuiting in a bed can potentially be affected by inlet-outlet location and design, as well as hydraulic properties (e.g., porosity and grain-size) of the carbon substrate.

1.3 Objectives of this study

Denitrification beds containing woodchips have previously been used to treat point source discharges. Identifying simple, low cost, effective ways of increasing the nitrate removal rate of a bed could reduce construction costs due to smaller foot print area. Lower construction costs could promote greater uptake of this technology and ultimately reduced Nr discharge to the environment. The overall aim of this thesis was to test a number of approaches that might increase denitrification bed performance, including manipulation of carbon source, temperature and hydraulic flow.

Specifically the objectives of this study were to:

1. Measure the long-term nitrate removal performance of different carbon substrates, to determine if removal can be increased above removal rates for woodchips.
2. Determine the temperature sensitivity of nitrate removal for different substrates.
3. Determine whether hydraulic performance and nitrate removal rate were dependent on woodchip size.
4. Determine if bed temperature and nitrate removal could be increased by passive solar heating of operational beds.
5. Determine if different inlet/outlet structures, coupled to solar heating, alters hydraulic efficiency and nitrate removal rate in denitrification beds.

1.4 Thesis outline

This thesis contains six chapters. The Introduction (Chapter One) is followed by a review of denitrification bed related research (Chapter Two). The review reports results of previous denitrification bed and carbon substrate column studies, including nitrate removal rates, temperature and hydraulic properties. In addition, areas of denitrification bed performance in which information is lacking are identified in Chapter Two. Chapters Three to Five contain the research results of this thesis. Chapter Three addresses objectives 1 to 3 in a 23 month study of nitrate removal in large barrels containing nine different carbon media. Results of these objectives have been published as a journal paper (Cameron and Schipper, 2010). Chapter Four addresses the hydraulic performance (objective 3) of different carbon substrates in the same barrel study. Results of objective 3 have been submitted as a journal paper (Cameron and Schipper, submitted). Chapter Five addresses objectives 4 and 5 in a 15 month denitrification bed field study treating municipal effluent and has been published as a journal paper (Cameron and Schipper, 2011). Chapter Six synthesises findings presented in previous chapters, provides general conclusions regarding the influence of tested techniques on nitrate removal and discusses future research topics.

The appendix contains two journal papers on denitrification bioreactors for which Stewart Cameron was a contributing author. The papers were produced at the same time as work on this thesis was undertaken. While the information presented in these papers is not part of the main objectives of this thesis (to test methods of improving nitrate removal performance of denitrification beds), both papers are directly relevant to application of denitricification bed technology for reducing nitrate discharge to the environment. Schipper et al. (2010a) is review paper of passive technologies for overcoming the carbon limitation of denitrification for enhanced nitrate removal. Schipper et al. (2010b) presents performance results of three large denitrification beds used to remove nitrate from municipal, dairy-shed and hydroponic glasshouse effluents.

Each chapter of this thesis is written to stand alone in the format of journal papers. In some chapters minor repetition occurs between introduction and methodology sections. Also, each chapter contains a reference list so an inclusive reference list is not included at the end of the thesis.

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Chapter 2

A Review of Nitrate Removal and Hydraulic Performance of Carbon Media for Denitrification Beds

2.1 Introduction

The accumulation of reactive nitrogen (Nr) in terrestrial and aquatic environments is recognised as a global environmental issue (Galloway et al., 2008). Reactive nitrogen contributes to the degradation of ground- and surface-water quality, resulting in contamination of potable water supplies, algal blooms and loss of aquatic habitat. Three major sources of Nr are: application of nitrogen fertilizers for the purpose of food production, fixation associated with leguminous crops, and combustion of fossil fuels (Seitzinger et al., 2006).

The effects of Nr on receiving environments have been extensively summarised by Galloway et al. (2003; 2004; 2008). Reactive nitrogen can enter terrestrial and aquatic environments via point and non-point sources. Non-point sources include the diffuse movement of Nr from: agroecosytems (Smil, 1999; Galloway and Cowling, 2002), forests (Aber et al., 1998; Dise and Wright, 1995), grasslands (Tartowski and Howarth, 2000), and aquatic environments (Galloway et al., 2003) including groundwater, surface water (stream, rivers and wetlands) and marine coastal regions. The origin of non-point source Nr in a system is often undiscernible due to the diffuse input and complexity of the system. In contrast, point sources of Nr are discernable, confined and occur at a single location, e.g. pipe, channel, conduit, well, etc. Examples of point sources of Nr are discharge from a municipal wastewater treatment plant or stormwater drain; industrial discharge from a factory, and flow from an agricultural tile drain. This literature review focuses on point source discharges of Nr, although treatment options of non-point source Nr is also briefly discussed in the following paragraph.

A number of approaches have been used to reduce the mass of Nr entering the environment. Treatment processes are commonly used to remove Nr from point source municipal and industrial wastewater discharges including: ammonia volatilization, selective ion exchange, reverse osmosis, and combined nitrification/denitrification systems (Oakley et al., 2010). Improved land management practices are increasingly being advocated and implemented to reduce non-point source Nr loss from agricultural and livestock farming activities (Sims et al., 1995; Drury et al., 1996; Jaynes et al., 2004.). Riparian zones and wetlands are used to reduce non-point source Nr load to surface waters (Mitsch and Grosselink, 2000; Kadlec and Wallace, 2009; Hill, 1996). Despite these efforts, considerable cumulative mass of Nr entering terrestrial and aquatic environments continues to originate from discrete agricultural, industrial and household point source discharges as the above approaches for removing Nr can be bypassed, may be expensive or not appropriate for the location. Therefore, cost effective approaches for removing Nr from point source discharges are also required.

Denitrification beds offer one possible approach for cost effective removal of nitrate from small volume point source discharges. The bed utilise the naturally occurring process of microbial denitrification to convert nitrate to dinitrogen gas. The process requires nitrate to be in contact with a carbon source in an anaerobic environment (Seitzinger et al., 2006).

A denitrification bed is essentially an excavated and lined cavity or container containing particulate organic carbon matter (e.g., woodchip) through which nitrified effluent is passed (Blowes et al., 1994; Schipper et al., 2010). Other passive, wastewater treatment systems also typically rely on the manipulation of the denitrification process to treat nitrate contaminated waters. These other treatment methods include constructed wetlands, pond systems, land disposal, and subsurface treatment (Mitsch and Grosselink, 2000; Kadlec and Wallace, 2009; Shilton, 2005; Sparling et al., 2006; Barton et al., 2005).

The advantages of denitrification beds over these other passive Nr treatment options are that denitrification beds are capable of more than 99% removal of nitrate, with a relatively small footprint and low installation/maintenance costs. However, one essential requirement for denitrification bed operation is that the nitrogen must be in the oxidised form, typically as nitrate, as other forms of nitrogen (ammonium and organic nitrogen) pass through the bed untreated. Therefore an upstream nitrifying process may be required.

Column studies to date have demonstrated that a wide variety of carbon substrates can be used to support biological denitrification for wastewater treatment (e.g., wood, cardboard, soil, wheat straw, cellulose, alfalfa, and greenwaste; Vogan, 1993; Gibert et al., 2008; Greenan et al., 2006). However, existing denitrification bed trials have all incorporated wood, or a significant component of wood, as the carbon substrate (Schipper et al., 2010a). Therefore, the use of alternative carbon substrates are unproven under field conditions in operational beds.

The types of point source discharges for which denitrification beds may be applicable include: farm dairy effluent, hydroponic hothouse effluents, small-scale municipal systems (Schipper et al., 2010b), septic systems (Robertson et al., 2005a), agricultural tile drains, (van Driel et al., 2006a; Jayes et al., 2008; Christianson et al., 2011; Woli et al., 2010) and landfill leachates (Robertson and Anderson, 1999). The beds would also be suitable for removal of nitrate from some tertiary treated industrial discharges (e.g., abattoir) but have not as yet been reported in the literature. The beds are appropriate as a final nitrate removal process after which the effluent water can be discharged to receiving waters.

Greater uptake of denitrification bed technology would reduce the mass of Nr entering the environment via point source discharges that contribute to degradation of aquatic ecosystems. Greater uptake is partially dependent on improving the nitrate removal rate in beds. Improving the nitrate removal rate will lead to reduced bed volumes, construction costs and likely greater uptake of the technology.

This chapter reviews the literature on denitrification beds with an initial description of the microbial processes of denitrification and nitrification. Subsequently this chapter focuses on review of:

1. Nitrate removal rates of denitrification beds (Section 2.3).
2. Factors limiting nitrate removal with a particular emphasis on different carbon substrates (Section 2.4.1), temperature (Section 2.4.2), and hydraulic performance (Section 2.4.3).

This review draws from literature on denitrification beds but also on studies of denitrification in denitrification walls, soil and groundwater. A denitrification wall is a vertical wall containing organic carbon material that removes nitrate from shallow groundwater (Robertson and Cherry, 1995).

2.2 Denitrification and nitrification

2.2.1 Denitrification process

Denitrification is the reduction of nitrogen oxides to nitrogen gases including dinitrogen gas, nitric oxide, and nitrous oxide along the following pathway:

$$\begin{array}{lcccccccc} \mathrm{NO_3^-}\ \text{(aq)} & \rightarrow & \mathrm{NO_2^-}\ \text{(aq)} & \rightarrow & \text{NO (gas)} & \rightarrow & \mathrm{N_2O}\ \text{(gas)} & \rightarrow & \mathrm{N_2}\ \text{(gas)} \\ \text{Nitrate} & & \text{Nitrite} & & \text{Nitric oxide} & & \text{Nitrous oxide} & & \text{Dinitrogen} \end{array}$$

Denitrification can occur by both biological and chemical processes (Tiedje, 1988). Biological denitrification can be achieved by heterotrophic and autotrophic bacteria (Soares, 2000). Heterotrophic bacteria utilise organic carbon substrates for the reduction of nitrate under anaerobic conditions. In autotrophic denitrification, hydrogen or reduced sulphur compounds can serve as the substrate and carbon dioxide or bicarbonate serve as the carbon source and can occur in aerobic conditions (Madigan et al., 1997). Biological denitrification is a dissimilatory process performed by bacteria. Assimilative nitrate reduction is where nitrate is reduced to ammonia by plants, fungi or bacteria (Tiedje, 1998). There are other processes that remove nitrate from a system and should not be confused with biological denitrification including: dissimilatory nitrate reduction to ammonia (DNRA; Tiedje, 1998), ammonification of nitrate and anaerobic ammonia oxidation (anammox; Kunen, 2008).

Chemical denitrification is catalysed by abiological agents (Tiedje, 1998), including various metals: manganese, magnesium, zinc, iron and aluminium (Della Rocca et al., 2006; Sabzali et al., 2006). The final reduction product(s) is governed by temperature, pH and the metal involved. Generally, chemical denitrification is considered to be minor in comparison to biological denitrification.

The focus of this thesis is on dissimilatory biological denitrification and other process of removing nitrate from a system are not discussed in detail. Hereafter, the use of the term denitrification in this thesis refers to dissimilatory biological denitrification, unless otherwise stated. Denitrification is an anaerobic respiration process by which facultative heterotrophic denitrifying bacteria (e.g. *Pseudomonas* sp and *Bacillus* sp) simultaneously oxidise organic carbon compounds (as an electron donor) and utilise nitrogen oxides as the terminal electron acceptor, (Delwiche, 1981) i.e.,

$$4NO_3^- + 5CH_2O \rightarrow 2N_2\,(g) + 5CO^-_2\,(g) + 3H_2O + 4OH^- \qquad (1)$$

More than one enzymatic pathway has been identified for the reduction of nitrate to dinitrogen (Atlas, 1995). Some species of bacteria can complete the entire pathway while other pathways involve several species. The process involves four consecutive reactions by metalloenzymes: nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase. Denitrifiers are represented in all main phylogenetic groups and are ubiquitous in most soils and aquatic environments (Zumft, 1997).

In the presence of oxygen, denitrifying bacteria may be capable of normal aerobic respiration and thus these organisms are generally considered to be facultative anaerobes.

Denitrification is the major pathway by which potentially damaging nitrogen oxides are returned to the atmosphere as harmless molecular nitrogen. It is an important process in natural and modified wetlands and riparian zones for the removal of nitrate from ground and surface waters. It is also commonly promoted to remove nitrate in municipal, industrial and septic treatment systems, with an additional carbon source often added to increase denitrification. Therefore, it is an important process for the return of nitrogen from terrestrial and aquatic environments to the atmosphere.

Factors regulating the rate of denitrification include: the concentration of available organic carbon and nitrogen oxides; presence of denitrifying bacteria; pH;

temperature; and most importantly anaerobic conditions (Seitzinger et al., 2006; Tiedje, 1988; Parkin et al., 1985). How some of these factors can be used to improve nitrate removal rate in denitrification beds are discussed in Section 2.4.

Denitrification is inferred to be the main mechanism for nitrate removal in denitrification beds. Very high rates of denitrifying enzyme activity have been measured in beds (Warneke et al., 2011) compared to rates in denitrification walls (Schipper et al., 2005; Moorman et al., 2010) and natural and constructed wetlands (Duncan and Groffman, 1994). Furthermore, Warneke et al. (2011) measured rates of insitu denitrification that were sufficient to account for nitrate removal rates. There has been no evidence for anammox or DNRA being a significant process in the beds as ammonium concentrations are generally low in denitirifcation beds unless added with incoming effluent (Robertson et al., 2000). Indeed in a laboratory experiment using ^{15}N isotope enrichment, Greenan et al. (2006) showed that less than 4% of nitrate removed from columns filled with woodchips was due to DNRA.

2.2.2 Nitrification process

Reactive nitrogen must be in an oxidized form, typically as nitrate, for denitrification beds to remove nitrogen from influent water. Many sources of Nr are in the reduced form such as ammonium and require a nitrification step before the effluent enters the bed. Therefore, the nitrification process can be vital for removal of nitrogen from point source discharge by denitrification beds and it is appropriate to provide a brief description of this biological process.

Nitrification is the biological oxidation of ammonia to nitrate, in which nitrite is the intermediate form. The microorganisims responsible for the transformation include *Nitrosomonas* and *Nitrobacter* (Prescott et al., 1993). At temperatures below 10^{o}C, the bacterial metabolism decreases significantly, and below 4^{o}C it stops completely. Dissolved oxygen concentrations above 1 mg L^{-1} are needed for nitrification to occur. The nitrification step is much slower and more likely to be disrupted than the denitrification step (Madigan et al., 1997).

Nitrification can occur naturally in topsoils and the vadose zone as ammonia bearing water infiltrates to groundwater. In water treatment systems, the aeration for nitrification is commonly achieved by passing the effluent through a trickling filter or by the use of blowers to aerate the effluent.

2.3 Denitrification bed performance (rates of nitrate removal)

It has been well established that denitrification beds remove nitrate from incoming waters and effluents but the extent of nitrate removal varies between studies (Schipper et al., 2010a). The performance of a denitrification bed can be described by the percentage removal of nitrate between influent and effluent. However, percentage removal does not take into account the volume of carbon incorporated in the bed. For comparative purposes it is more meaningful to describe denitrification performance as a reaction rate using mass of nitrate removed per unit volume of organic media per unit time (e.g., g N m^{-3} of media d^{-1}) or per unit of mobile fluid volume (e.g., g N L^{-1} d^{-1}; Robertson et al., 2005a; van Driel et al., 2006b). Such units are scalable and can be used for denitrification bed design when influent volumes and concentrations are known. The rate also allows comparison of nitrate removal performance between different denitrification bed designs and studies.

Table 2.1 provides a summary of long-term nitrate removal rates for a variety denitrifying reactors in units of g N m^{-3} d^{-1}, which has been updated from the summary of removal rates presented by Schipper et al. (2010a). All of the removal rates are for reactors that contain all, or component of, wood media of varying particle size. For denitrification beds, long-term sustainable rate varies between about 2 to 10 g N m^{-3} d^{-1} for operating bed temperatures of 8 to 20°C and influent nitrate concentrations of 5 to 250 mg L^{-1}. Higher shorter term nitrate removal rates (up to 32 g N m^{-3} d^{-1}) for operational wood based beds have been reported (Blowes et al., 1994; Robertson et al., 2000; Schipper et al., 2010b), but are not sustained over the longer-term operation of the bed. Schipper et al. (2010b) showed that denitrification beds were capable of removing all of the nitrate from the influent stream when nitrate limiting conditions occurred in the bed.

Table 2.1 Avearge rates of nitrate removal for a range denitrifying bioreactors in the field. Many of the systems recorded here had complete nitrate removal which would limit the rate of denitrification and consequently are likely underestimates of potential removal rate. Units are g N m^{-3} d^{-1} where m^{-3} refers to volume of bioreactor. (Adapted from Schipper et al., 2010a).

System design	Study	Size of bioreactor (m^3)	Typical nitrate inputs (g N m^{-3})	Temperature annual average (°C)	Average rate of N removal (g N m^{-3} d^{-1})
Walls	Robertson et al. (2000)	1	50	14	1.7
	Schipper et al. (2005)	78	5–15	12	1.4*
	Jaynes et al., 2008	79	87	10	0.62
	Fahrner, 2002	160	>60	19	12.7
Beds	Robertson et al. (2000)	2	5	10	10
	Robertson et al. (2005)	9	17	15	1.8*
		108	38	15	2.4*
		120	35	15	2.5*
		360	14	15	5.1*
	van Driel et al. (2006a) upflow reactors	0.7	9	9	2.1
		0.2	13	13	3.7
	Robertson and Merkley (2009)	40	5	8	3.2
	Robertson et al., 2009	17	10	7.7	3.4
	Schipper et al. (2010)	83	53	15–25	1.4*
		294	5.5	NR	0–11*
		1320	250	20	9.7
	Leverenz et al. (2010)	7.7	82	22	NR
	Woli (2010)	40	15	NR	6.4

*Nitrate removal rate limited by nitrate concentrations

NR Not reported

Lower average reaction rates (0.95 to 2.5 g N m^{-3} d^{-1}) were reported by van Driel et al. (2006a) in lateral and vertical flow denitrification beds utilising sawdust and woodchip. The lower reaction rates in these beds were attributed to more frequent occurrence of nitrate limiting conditions and relatively low average water temperatures (7° to 9°C). Similar reaction rates (0.7 to 3.6 g N m^{-3} d^{-1}) were achieved in column studies and denitrification wall trials that utilised a mix of sawdust and sand/aquifer material (matrix), at about 20% sawdust to matrix ratio (Schipper and Vojvodic-Vukovic, 1998; Healy et al., 2006).

Reaction rates achieved in denitrification wall studies are generally an order of magnitude less than denitrification bed reaction rates most likely due to the lower proportion of carbon media to wall matrix (typically 15–30% by volume), compared to 100% carbon media utilised in denitrification beds. Lower reaction rates achieved in column studies of wood media compared to operational beds are generally attributed to the presence of dissolved oxygen in the influent water that must be removed by microbial activity before denitrification can occur (Tiedje, 1988).

Van Driel et al. (2006a) compared reaction rates measured in the two denitrification beds to rates reported for constructed wetlands in the US and Sweden. The reaction rates for the constructed wetlands were generally an order of magnitude lower than the denitrification beds.

2.4 Factors constraining denitrification bed performance

Factors that regulate the rate of denitrification include the concentration of available organic carbon and nitrogen oxides, presence of denitrifying bacteria, pH, temperature, and most importantly anaerobic conditions (Seitzinger et al., 2006; Tiedje, 1988; Parkin et al., 1985).

Anaerobic conditions are required for denitrification as oxygen is a more energetically favourable electron acceptor than nitrogen oxides and is preferentially respired by the facultative denitrifying bacteria. However, completely anoxic conditions are not required and denitrification can occur at diminished rate at dissolved oxygen concentrations up to 0.2 g m^{-3} (Seitzinger et al., 2006). Denitrification can also occur at anaerobic microsites within a more oxic system. Dissolved oxygen in the influent water of denitrification beds may allow aerobes to out-compete denitrifiers for available carbon. This is most likely an issue when hydraulic retention time (HRT) is short (<1 hr; Robertson, 2010) such as in small beds with high flow rates but less of an issue in large beds with longer HRT. Healy et al. (2006) attributed low nitrate removal rates (3.7 to 7.3 g N m^{-3} d^{-1}) in a 0.036 m^3 denitrification bed trial to high influent DO concentration.

The availability of organic carbon to microbes is dependent upon the carbon substrate used in bed construction. Carbon substrate and temperature have been shown previously to effect nitrate removal rates in denitrification column studies and denitrification bed trials (Vogan, 1993; Gibert et al., 2008; Greenan et al., 2006; van Driel et al., 2006a; Robertson et al., 2000, 2009; Robertson and Merkley, 2009; Schipper et al., 2010a). Additionally, short-circuit flow through a bed may reduce nitrate removal due to decrease in the volume of the bed in contact with nitrate. Therefore, the influences of these three factors (carbon substrate, bed temperature and bed hydrology) on nitrate removal rate in a bed are discussed in more detail in the following three sections (2.4.1, 2.4.2 and 2.4.3). A briefer discussion on how concentration of nitrogen oxides, presence of denitrifying bacteria and pH influences denitrification is provided in section 2.4.4, as these factors were not investigated in this thesis. This study focused on improving denitrification bed performance when nitrate was non-limiting.

2.4.1 The effect of carbon substrate on nitrate removal

The availability of organic carbon as an electron donor for denitrification becomes critical if the system is receiving excess nitrate. Organic carbon plays two roles in regulating denitrification. Firstly, aerobic micro-organisms utilise organic carbon to respire oxygen creating an anaerobic environment for denitrifiers to compete for remaining carbon and, secondly to act as electron donor for denitrification.

Generally the nitrate removal rate of a denitrification bed or wall is carbon limited if there is excess nitrate (Schipper et al., 2005; Warneke et al., 2011). The long-term availability of carbon for denitrification is then dictated by the rate of microbial decomposition of the organic carbon media by fermentative bacteria which release carbon to other anaerobic microbes including denitrifiers (Tiedje, 1988).

Selection of organic carbon material for use in operational denitrification beds is governed by site specific factors, such as permeability requirements, hydraulic retention time, required rate of nitrate removal, size restrictions of the bed, acceptable frequency of maintenance, and local availability of the organic carbon materials.

Laboratory and field trials have demonstrated that a wide variety of carbonaceous material can be used to induce denitrification in groundwater environments and in wastewater treatment process including:

- Sawdust (Vogan, 1993; Schipper and Vojvodic-Vukovic, 1998; Robertson and Anderson, 1999; Healy, 2006).
- Woodchip (Robertson et al., 2000; Healy, 2006; Schipper et al., 2010a).
- Combination of bark, sawdust and woodchips (Robertson et al., 2005a).
- Combination of grow bark, wood chips and composted leaf mulch (Blowes et al., 1994).
- Wheat straw, alfalfa, wood pulp (Vogan, 1993).
- Grain seed (type unspecified) (Robertson et al., 2000).
- Corn (Erickson, 1974; Fay, 1982; Xu et al., 2009).
- Soil (Stewart et al., 1979), soil and sawdust (Healy, 2006).
- Newspaper (Volokita et al., 1996a).
- Raw cotton (Volokita et al., 1996b).
- Jute pellets and soil (Wakatsuki et al., 1993).
- Vegetable oil (Hunter et al., 1997).
- Rice husk (Shao et al., 2009).

The highest reported nitrate removal rates are from column studies. For example, Vogan (1993) using cellulose, alfalfa, and wheat straw as the carbon substrate reported removal rates of between 27 to 116 g N m^{-3} d^{-1}. Xu et al. (2009) using corn cobs achieved a removal rate of about 200 g N m^{-3} d^{-1}. However, column studies are generally short-term (1–6 months) and reported removal rates are not indicative of longer-term sustainable removal rates that are required for denitrification bed design purposes (Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 2001; Jaynes et al., 2008). Stewart et al. (1979) found that humus rich soil was ineffective for long-term nitrate removal from septic tank effluent due to relatively rapid depletion of available carbon.

The carbon source most commonly used in passive in-situ denitrification trials are the wood-based by-products sawdust and woodchip. This is because these materials are commonly available, relatively low cost, support high permeability, have a high C:N ratio (e.g., 300:1; Robertson and Anderson, 1999) and have long durability. Wood based products do not support as high initial nitrate removal rates as more labile carbon sources such as corn cobs but they are likely to sustain removal for longer duration. Although removal rates of up to 32 g m^{-3} d^{-1} have been reported for wood based beds (Blowes et al., 1994) longer-term removal rates are between 2 to 10 g m^{-3} d^{-1} (Schipper et al., 2010a). The commercially available Nitrix filter used in denitrification bed trials by Robertson et al. (2005) contained bark, sawdust and woodchips and provided removal rates of 2 to 5 g N m^{-3} d^{-1}, however, testing of this system was generally conducted under nitrate limiting conditions and maximum nitrate removal rates could be higher.

While alternative and more liable carbon sources (e.g., corn) may support higher denitrification rates, they may require more frequent replacement because of carbon depletion and decreased permeability in the bed as the carbon structure breaks down (Erikson et al., 1974; Fay, 1982).

Comparative studies have not been published on the benefit of using hardwood by-product as opposed to by-product from softer, faster growing tree species (e.g. *Pinus radiata*, D.Don). It is possible that hardwood by-products may maintain physical properties for longer duration due to greater density and/or physical stability. However, hardwood by-product is not as readily available and may be more expensive. Robertson et al. (2000) used hardwood sawdust as the primary carbon source (in conjunction with leaf compost and grain seed) in denitrification walls, however, these authors made no inference as to any denitrification performance advantage over softwood sawdust.

2.4.1.1 Particle size of carbon media

Higher nitrate removal rate might be expected for a given media with smaller grain-size due greater surface area. However, Carmichael (1994) observed that the rate of nitrate consumption was not correlated with surface area of the sawdust, in laboratory studies using sawdust of varying grain size. Robertson et al. (2000) speculated that denitrification was associated with reaction rims that penetrate, by diffusion, into the carbonaceous solids, rather than being restricted to the grain surfaces. They supported this suggestion by examination of media after 4 years of operation, which revealed that the larger centimetre-sized wood particles exhibited dark coloured rims that extended several millimetres into the particles, while the centre of the particles remained light coloured and appeared unaltered from their original condition. They interpreted this to mean that the darker rim indicated where the zone of denitrification was occurring, although no supporting measurements were made. The smaller particles were dark coloured throughout.

Van Driel et al. (2006a) compared two denitrification beds, one constructed with predominantly coarse-grained wood particles (wood chip) and the other constructed with fine grained wood particles (sawdust). They measured similar rates of nitrate removal for these two particle sizes (5.9 vs 5.5 g N m^{-3} d^{-1} in the coarse and fine grained particles, respectively). They suggested that this was caused by the dual porosity characteristics of the media as proposed by Robertson et al. (2000), which allowed denitrification to occur several millimetres into the wood particles rather than being restricted to the particle surfaces.

2.4.2 The effect of bed temperature on nitrate removal

Temperature is an important factor controlling the rate at which denitrification occurs (Sedlak, 1991). This is because enzyme activity generally increases with increasing temperature, typically over the range 0 to about 40^{o}C, due to increase in kinetic energy of molecules. Enzyme activity begins to decline above an optimum temperature limit as enzymes start to denature. Generally, the change in reaction rate with change in temperature can be approximated by the temperature coefficient (Q_{10}) which is the factor by which a reaction rate increases for every 10°C rise in temperature (Anderson and Janssen, 2006).

While many studies of denitrification beds have acknowledged the temperature dependence of denitrification reaction rates, few studies have quantified the temperature-reaction rate relationship in field conditions. The variability of other factors that influence nitrate removal (e.g., influent nitrate concentration and chemistry) makes it difficult to isolate the effect of temperature under field conditions. Canadian-based studies (van Driel et al., 2006a; Robertson et al., 2000) reported a range of denitrification rates achieved in denitrification beds for water temperatures up to 22°C. The removal rates reported in these studies increased from 2–7 g N m^{-3} d^{-1} at 2–5°C up to 4–30 g N m^{-3} d^{-1} at 10–22°C. However, in the study of van Driel et al. (2006a), precise calculation of nitrate removal rates at temperatures >12°C were compromised because denitrification was constrained as all the nitrate had been removed. Temperature dependence of nitrate removal has been shown in a column study using shredded paper (Volokita et al., 1996a). Nitrate removal was approximately three times higher at 25 to 32°C than at 14°C, but denitrification rates were not reported.

Temperature dependence of denitrification rate is also indicated in denitrification wall studies. Schipper and Vojvodic-Vukovic (2001) reported reaction rates of 0.014 to 0.43 g N m^{-3} d^{-1} for temperature range of 11° to 22°C. In comparison, Fahrner (2002) measured higher removal rates of 15 g N m^{-3} d^{-1} when soil temperatures regularly exceeded 30°C.

While it is acknowledged that temperature is an important factor in constraining denitrification rate in a bed, no reported study has shown a definitive relationship between temperature and nitrate removal rate under field conditions.

2.4.3 The potential influence of short-circuit flow on nitrate removal

There are few reported studies on short-circuit flow in denitrification beds. Information on short-circuit flow presented in this thesis has largely been drawn from other types of systems, e.g., treatment wetlands and constructed ponds. Ideal flow through a denitrification bed, for the purpose of maximising nitrate removal, is plug flow. Plug flow is characterised by a uniform velocity profile. Non-ideal flow is characterised by short-circuiting. Short-circuit flow can reduce the mass of pollutants removed in a treatment wetland (Kadlec et al., 1993; Carleton, 2002). In a denitrification bed, short-circuiting could potentially cause zones of low or nil denitrification which would reduce the active volume of the bed. Short-circuiting within a hydraulic system can be quantified using tracer tests. Short-circuiting is indicated when theoretical hydraulic retention time (HRT) exceeds mean tracer retention time (Kadlec and Wallace, 2008). Location and design of inflow structures in constructed ponds and treatment wetlands are important aspects for reducing short-circuiting (WPCF, 1990; Shilton and Sweeney, 2005). Persson (2000) investigated the influence of pond shape, inlet/outlet locations and inlet/outlet type on the hydraulic efficiency of pond systems. He found that ponds with single inlets/outlets and large width:length ratios had poorer hydraulic efficiency than ponds with multiple inlets, baffles or small width:length ratios. Christianson et al. (2011) found that HRT greatly exceeded tracer retention time in a study looking at the effect of denitrification bed geometry on hydraulic properties. They attributed the non-ideal flow to the hydraulics of the media and poor functioning of the bed inlet and outlet.

A range of solid carbon sources have been investigated for their ability to support nitrate removal but little is known about hydraulic performance (such as short-circuiting) through different carbon media. Specifically, if the physical and hydraulic properties of a media (particle size, particle sorting and porosity) influence hydraulic performance; and if changes in hydraulic performance increase or decrease nitrate removal rates. Factors affecting hydraulic efficiency are presence of large connected void spaces (Villholth et al., 1998), flow fingering caused by profile heterogeneities (e.g., gas entrapment or biofilm growth (Hendrickx et al., 1993; Glass and Nicholl, 1996), and movement of water between the mobile (primary or inter-granular porosity) and immobile phases (secondary or intra-granular porosity).

The considerable secondary porosity of wood has been proposed as the reason for similar nitrate removal rates of different particle sizes (Robertson et al., 2000), with the inference that the denitrification reaction occurs both within the wood particle and on the particle surface. Presumably water and nitrate within the inter-granular pore space diffuses into and out of the media particle.

The components of primary and secondary porosities that contribute to fluid flow through a media are considered the effective porosity. Tracer tests in denitrification beds have shown that the effective porosity of wood media can exceed primary porosity estimated by gravimetric drainage (Robertson, 2010; Chun et al., 2009); indicating that secondary porosity contributed to hydraulic flow by movement of water into and out of the wood particle. Robertson (2010) reported the primary, secondary and effective porosities of fresh pine wood fragments were 0.48, 0.38 and 0.68, respectively. Other solid carbon media that could potentially be used in denitrification beds (e.g., maize cobs~~)~~ are also likely to have dual porosity characteristics due to low particle density, but have not been previously reported. Also, the change in porosity values due to change in media particle size (sawdust versus larger woodchip media) and the subsequent effect on hydraulic efficiency and nitrate removal has not been reported.

2.4.4 Other constraining factors (presence of denitrifiers, nitrate concentration and pH) on nitrate removal

Other factors that influence denitrification but were not investigated as part of this thesis to increase nitrate removal of denitrification bed include: presence of denitrifiers, nitrate concentration, and pH. For completeness, the influence of these factors on nitrate removal in denitrification beds is briefly discussed below.

Denitrifiers

Denitrifiers are widely disbursed and often in abundance throughout the environment. For example, one gram of soil can contain tens to hundreds of thousands of dentrifying bacteria (Tiedje, 1988). Consequently, denitrification is generally not constrained by absence of denitrifiers (Tiedje, 1988) and inoculation of denitrification beds is generally not required.

Nitrate concentration

A positive relationship between nitrate concentration and nitrate removal (largely by denitrification) has been demonstrated over a range of land- and water-scapes (Seitzinger et al., 2006). Simply, higher loading provides for more nitrate available for denitrification. In a wood-based denitrification bed with excess nitrate, the denitrification reaction is generally considered to be a zero-order process (van Driel et al., 1996a; Robertson, 2000). The reaction may become a first-order process when nitrate become limiting at concentration below about 1 mg L^{-1} (Roberston, 2010; Schipper et al., 2010a) or at reduced temperatures (Leverenz et al., 2010). While, Chun et al. (2010) found that first-order decay provided a better fit to a nitrate break-through curve from a 60 m^3 denitrification bed the difference in fit between the two decay functions was small and reliability of the results possibly compromised by other aspects of the modelling approach (e.g., dispersivity and the use of a single porosity model). Denitrification is likely to follow Michelis-Menten kinetics with regard to nitrate concentration which means that nitrate reduction will increase with increasing nitrate concentration until nitrate availability exceeds the Km of denitrifying bacteria. Healy et al. (2006) trialled two influent nitrate concentrations of 200 mg L^{-1} and 60 mg L^{-1} in a laboratory study. They found that the highest percentage reduction (97%) in nitrate concentration occurred in the column receiving the lower 60 mg L^{-1} nitrate influent.

pH

While denitrification can occur over a range of pH conditions, the optimum range is generally considered be pH 6 to 8 (Bremner and Shaw, 1958). It is likely that pH influences denitrification by selecting for denitrifying bacterial population adapted to a particular range of pH thus influencing the size of the population. Lower denitrification activity has been reported in more acid conditions (Parkin et al., 1985). Also, pH may cause an indirect effect on denitrification by influencing carbon availability to denitrifying bacteria (Kosinen and Keeney, 1982).

2.5 Longevity of nitrate removal rate and hydraulic conductivity of carbon substrate

The operational longevity of denitrification bed carbon media is an important aspect for uptake of the technology for the treatment of point source wastewater discharge. The carbon media must have a minimum operating lifespan for economic viability, including maintenance and the cost of carbon media replenishment. The two factors that affect the longevity of a carbon media are the continuous supply of carbon for denitrification and maintenance of adequate saturated hydraulic conductivity (K).

Results from the longest running field trial of a denitrification wall have shown that nitrate removal was maintained for 15 years (Robertson et al., 2009). The removal rate after 15 years (~4 g N m^{-3} d^{-1}) was about 50% of the removal rate measured during the first year. Similarly, Long et al. (2011) found that nitrate continued to be removed by a wall after fourteen years of operation.

Rates of carbon decline are not solely dependent on the removal by denitrification but also by other processes dependent on site specific conditions, including O_2 inputs and rate of other anaerobic process such as fermentation. The decomposition of solid carbon material is greatly reduced under saturated anaerobic conditions. Moorman et al. (2010) found that 70% of the wood was lost from the fluctuating water table horizon in a denitrification wall after 8 years operation, compared to only 13% of the wood being decomposed below the water table. They estimated that wood below the water table had a half life of 36.6 years. Below the water table, the wall lost about 1% mass of wood per year, to processes including denitrification. Long et al. (2011) reported a 50% reduction in total carbon mass content of a denitrification wall after 14 years operation, but denitrification rates were nearly as high as when the wall was installed.

Assuming that denitrification is the dominant nitrate attenuation mechanism, mass balance calculations using Equation 1 can be used to provide an estimate of bed/wall longevity beyond the operating history (e.g., Blowes et al., 1994; Robertson and Cherry, 1995; Robertson and Anderson, 1999; Robertson et al., 2000; van Driel et al., 2006a). The results of the mass balance calculations using Equation 1 by van Driel et al. (2006a) indicated that carbon consumption from denitrification was less than 2% per year in two denitrification beds. Carbon consumption by denitrification was estimated by Robertson et al. (2000) after 6 to 7 years of bed/wall operation to be less than 10 to 20% of the initial carbon mass installed during construction. Carbon loss also occurs from other processes such as aerobic activity, fermentation, dissolved organic carbon leaching, and sulphate reduction. Robertson and Cherry (1995) inferred that these reactions likely each consume less carbon than denitrification. Robertson et al. (2000) supported this conclusion by visual inspection of the wall and bed materials in year 6 of operation which showed that carbon solids (sawdust, woodchip mulch) had darken in colouration but otherwise remained similar in texture to the original material with no obvious indication of biomass build-up or permeability deterioration. However, visual inspection of the material does not take into account the possibility that degraded material may have been removed from the system. Schipper and Vojvodic-Vukovic (2001) cautioned that the mass balance approach to estimating longevity of wall carbon material may overestimate the media lifetime as organic matter degradation will continue in the absence of nitrate.

The slow degradation rates of wood media in denitrification beds means that hydraulic conductivity (K) is maintained for years. To date, there have been no reported hydraulic failures of denitrification beds due to loss of substrate permeability caused by degradation of wood media. The reported K of wood media is large ranging from ~100 m d^{-1} for sawdust up to several thousand m d^{-1} for coarser woodchips. While reduction in K from start-up has been reported it was attributed to accumulation of gas bubbles as physical inspection of the media showed no sign of breakdown in the physical structure of the wood particles (Robertson and Cherry, 1995). The K of more labile carbon media will likely decline faster than wood media as the less robust physical structure declines.

However, to date there have been no long-term (field or laboratory) trials of alternative carbon media to determine longevity of hydraulic performance.

2.6 Experimental approaches to improve performance of denitrification trials

Initial studies of denitrification beds and walls were to determine nitrate removal rates (Section 2.3). Subsequently, studies were undertaken on factors constraining nitrate removal rates in these systems (Section 2.4). There is now some emphasis being placed on increasing the nitrate removal rate of denitrification beds and reducing construction costs. Several different approaches have been undertaken to determine the potential performance of denitrification bed technology. These include: laboratory column studies of different carbon substrates (Vogan, 1993; Carmichael, 1994; Healy et al., 2006) and trialling of small-pilot-scale demonstration beds of different designs typically treating a component of a discharge stream (Blowes et al., 1994; Robertson et al., 2000). Fewer studies have monitored operational scale beds treating the entire discharge stream (Robertson et al., 2005a; Schipper et al., 2010b; Warneke et al., 2011).

Column studies have the advantage of being cheaper to undertake than field trials and their smaller scale (<0.2 m^3) allows for the trialling of more carbon substrates at minimal additional cost (e.g., wood, cardboard, soil, wheat straw, cellulose, alfalfa, and greenwaste; Vogan, 1993; Gibert et al., 2008; Greenan et al., 2006). The disadvantage of column studies is that achieved denitrification rates may not be reproducible under operational field conditions and temperatures. Small scale demonstration beds (<3 m^3) somewhat address the performance uncertainties of up-sizing and field temperatures (e.g., 1 m^3, reactor Robertson et al., 2000; 0.7 m^3 upflow reactor, van Driel et al., 2006a). They also provide a better indication of how bed shape and hydraulic design will affect nitrate removal. As flow rates and bed size are relatively small, construction costs can be minimal (<$500). However, as demonstration beds often only treat a component of the total discharge there is uncertainty as to whether a larger version will perform similarly. Also, the performance of small scale beds can be compromised by variability in nitrate input which is generally controlled in column studies.

Operational sized beds provide the best indication of denitrification bed performance in a working environment. However, construction costs (>$50K) can be prohibitive for many research budgets due to the potentially large bed size required to treat all of a point source discharge.

The design of a denitrification bed has implication for denitrification performance and maintenance requirements. Bed geometry, inlet-outlet design, hydraulic gradient and carbon media distribution can affect HRT, short circuiting and denitrification performance. To date a number of different denitrification bed designs have been used in both pilot scale trials and operational beds, including:

- Horizontal flow (van Driel et al., 2006a; Healy et al., 2006; Schipper et al., 2010b; Woli et al., 2010; Leverennz et al., 2010; Christianson et al., 2011; Chun et al., 2010).
- Upflow (Robertson et al., 2005a; van Driel et al., 2006a).
- Combined nitrification sand trickling filter and denitrification bed system (Robertson and Anderson, 1999).
- In-stream (Robertson and Merkley, 2009).

No defintitive study has been undertaken on comparison of the hydraulic efficiency or nitrate removal rate between different bed designs. To date all horizontal flow beds have incorporated a single pipe for the inlet and outlet. This type of configuration may be prone to short-circuiting as flow in the bed can potentially travel directly between the inlet and outlet pipes. Short-circuiting in horizontal flow beds may be reduced by incorporating inlet and outlet structures that disperse influent and accept effluent over a greater cross sectional area of the bed. Horizontal flow beds have recently been installed in the Taupo and Rotorua areas of New Zealand, that incorporate a diffuse inlet and outlet to promote more plug-like flow characteristics through the beds (Fig. 1.1a). However, to date no hydraulic or nitrate removal performance data are available for these beds. Christianson et al. (2011) looked at the difference in hydraulic dispersion between three different horizontal flow bed geometries (channel, rectangular and trapisodial). They found that the channel design provided the most plug-like flow dispersion characteristics.

Freeze and Witherspoon (1967) were the first researchers to recognise that high permeability layers focus flow lines capturing flow from adjacent zones. They noted that zones of capture increased as K contrast with adjacent material increased. This phenomenon has application for denitrification bed design as it provides a potential mechanism tool to manipulate flow patterns within the bed. In response to this possibility, trials have been undertaken on denitrification walls and beds that incorporate high-permeability layers (van Driel et al., 2006b; Robertson et al., 2005b).

Van Driel et al. (2006a) trialled two denitrification beds (horizontal flow bed and upflow bed) that utilised alternative layers of fine (sawdust) and coarse wood particles to modify flow through the beds. The coarse particles were approximately 10 times more permeable than the fine particles. The horizontal flow bed incorporated a coarse layer in the core of the bed that was sandwiched between fine layers (Fig. 2.1a). Tracer test showed that 90% of the flow occurred within the coarse layer. Van Driel et al. (2006a) initially anticipated that the coarse layer would be less reactive; thus the fine layers were included to provide zones of higher reactivity. The up-flow bed of van Driel et al. (2006a) utilised a fine layer overlying a coarse layer (Fig. 2.1b). The influent flowed directly into the coarse layer via perforated pipe. Flow then migrated upwards through the fine layer. Tracer test showed this design dispersed flow throughout the basal coarse layer followed by relatively uniform upward flow through the fine layer. van Driel et al. (2006a) reported similar nitrate removal rates (5.9 vs 5.5 g N m^{-3} d^{-1} in the horizontal- and up-flow, respectively) for the two reactors.

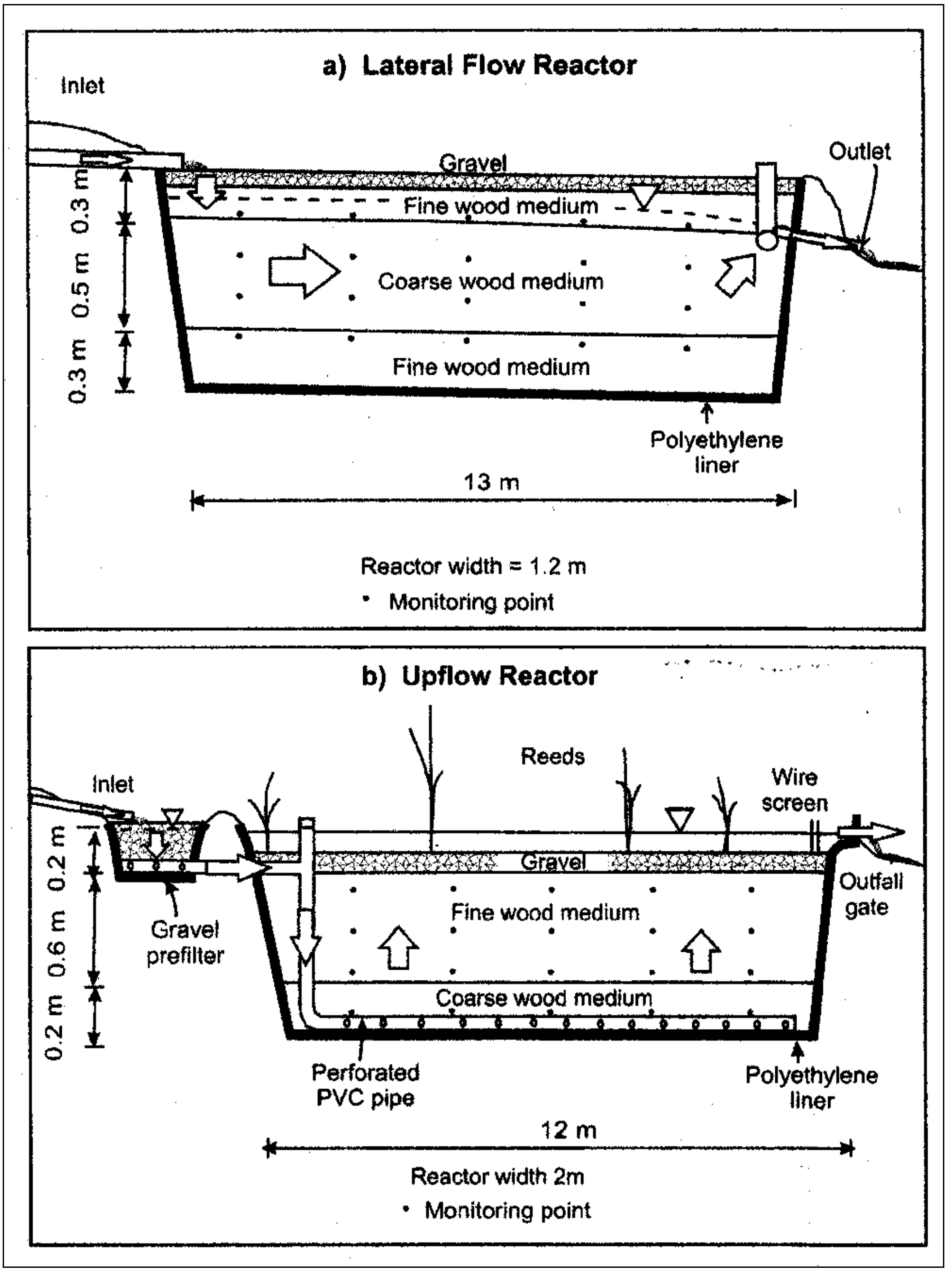

Figure 2.1 Design sketches of a) the horizontal flow denitrification bed, and b) up-flow denitrification bed (from van Driel et al., 2006a).

Robertson and Anderson (1999) trialled a combined unsaturated sand infiltration layer overlying a saturated bed of sawdust to treat landfill leachate. Maintenance of saturated conditions in the sawdust bed was achieved by a low permeability material underneath the sawdust. Nitrogen attenuation occurred by a two step process in which the leachate ammonium was first oxidised to nitrate in the unsaturated sand layer and then converted to dinitrogen gas by denitrification in the underlying sawdust layer. The system reportedly lowered influent inorganic nitrogen concentrations (averaging 24.8 mg L^{-1}) by 89%.

Robertson et al. (2005a) presented results of four operational denitrification beds (Nitrix filter; Fig. 2.2) treating septic system effluent from a house, trailer park, communal residence and inn. These beds contained a mixture of bark, sawdust and woodchip material with a diameter range of 0.5 to 50 mm. The unique aspect of this bed design was the partition that separates the downward inflow from the upward outflow chamber connected by perforated PVC pipe.

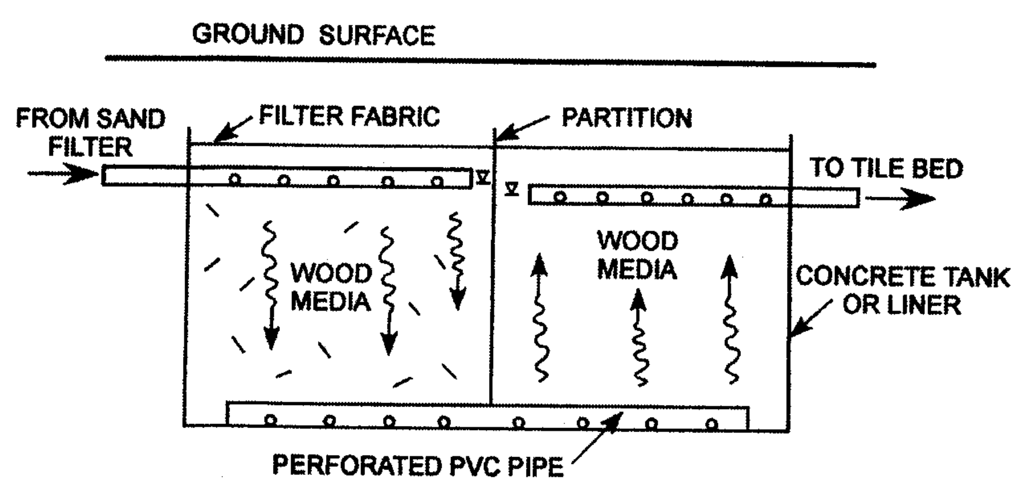

Figure 2.2 Schematic view of the Nitrix denitrification filter design and flow-through characteristics (from Robertson et al., 2005a).

While a number of different bed designs have been used to remove nitrate there is absence of comparative study on hydraulic efficiency of different designs and if change in hydraulic efficiency has any influence on rates of nitrate removal. The only inference that could be drawn from the literature for improving hydraulic efficiency is that "channel" cross-sectional bed profile had less short-circuit flow than rectangular and trapezoidal profile for horizontal flow beds (Christianson et al., 2011); and it is likely advantageous to use diffuse input of influent and beds with larger width:length ratio (Perrson, 2000).

2.6.1 Identified design issues of denitrification beds

The wide spread adoption of denitrification beds for the treatment of nitrate in point source discharge is dependent upon mitigating or managing potential operational issues. These issues can be addressed by appropriate denitrification bed design.

Factors which affect the ongoing operation of denitrification beds include:

- Suspended sediment in the influent causing blockage or reducing the efficiency of the inlet structure, and/or inflow area of the bed.
- Degradation of the upper layer of the denitrification bed resulting in significant permeability reduction.
- Biofilm build up in the outlet structure causing hydraulic head build up in the bed.
- Short-circuit flow within the bed that reduces the effective bed volume.
- Gas accumulation in the bed that reduces hydraulic conductivity.

Blowes et al. (1994) noted that frequent maintenance of the denitrification bed inflow area was required due to plugging by the suspended sediment load in tile drain discharge. Therefore, an appropriate pre-filtering mechanism may be required for some denitrification bed applications. Van Driel et al. (2006a) incorporated a gravel pre-filter in their denitrification bed treating agricultural tile drainage.

Robertson et al. (2005a) found that degradation of a fine-grained (sawdust) inlet layer also substantially reduced permeability. This problem was resolved by replacing the inlet sawdust layer with a course-grained woodchip media. Robertson et al. (2005a) noted that beds that were originally constructed with coarser wood media in the inlet area did not have inlet area permeability problems.

Van Driel et al. (2006a) noted that biofilm developed in the denitrification bed outlet pipe following prolonged periods of low flow. This caused hydraulic head build-up in the reactor but did not reduce flow. The biofilm was easily removed by simple agitation. Hydraulic head build-up in the bed may cause overtopping at higher flow rates. Therefore, outlets need to be designed to permit easy cleaning of the plumbing to remove biofilm and de-fouling included in the maintenance plan.

The design and location of bed inlet and outlets was considered the cause of tracer retention times being almost twice the theoretical HRT in a study looking at effect of denitrification bed geometry on hydraulic performance (Christianson et al., 2011). The result suggested that areas of little or no flow occurred around the single pipe inlet and outlet areas which reduced effective bed volume.

A reduction in carbon media K due to gas bubbles has been reported in column studies (Soares et al., 1991) and in denitrification walls (Schipper et al., 2004). Soares et al. (1991) found that the decrease in K due to gas accumulation was correlated to denitrification activity. Gas bubble formation are also likely to decrease the effective porosity of the carbon media.

2.7 Potential adverse effects of denitrification beds

Although denitrification beds have been shown to successfully remove nitrate from point source wastewater discharge, there can be some adverse effects from bed operation that need to be managed.

The potential adverse effects of denitrification bed operation are:

- Elevated biological oxygen demand (BOD) in discharge of effluent during start-up period (Robertson and Cherry, 1995; Robertson et al., 2005a; Healy et al., 2006; Della Rocca et al., 2006).
- Hydrogen sulphide (H_2S) gas production and emissions from effluent discharging from the bed. (Van Driel et al., 2006a; Robertson and Merkley, 2009; Robertson et al., 2009).
- Production of greenhouses gases (e.g. carbon dioxide, nitrous oxide and methane (Jaynes et al., 2008; Greenan et al., 2009; Warneke et al., 2011).

Biological oxygen demand

The BOD test is widely used as an indicator of the strength of municipal and industrial wastes and is an important test used in protecting aquatic life from oxygen deficiency. It is the primary regulatory tool used in limiting discharge of wastewaters to water (McCutcheon et al., 1993). Water quality guidelines used in New Zealand (Ministry of Health, 2005) limit BOD_5 to <5 g m^{-3} to protect against nuisance bacterial slime growth (Davis-Colley and Wilcock, 2004).

Denitrification beds typically have high BOD (>100 mg/L) during start-up and for up to several months thereafter as the soluble organic constituents (tannic acids etc.) are leached from the reactive media (Robertson et al., 2005a; Schipper et al., 2010a). As these soluble constituents comprise only 1% to 2% of the wood mass (Robertson et al., 2005a), BOD subsequently stabilises at much lower values (10 to 40 mg/L) after several months operation depending on factors such as HRT, temperature, and wastewater characteristics. Dissolved organic carbon (DOC) can also be used as an indicator of excess carbon leaching. Healy et al. (2006) noted washout of significant amounts of DOC (37 to 171 mg L^{-1}) during the initial stages of operation but reduced to between 11 and 43 mg L^{-1} after 6–7 weeks operation. It is likely that use of more labile carbon sources in denitrification beds for the purpose of increasing nitrate removal rate will result in higher rates BOD leaching during the first months of operation.

Temporarily elevated BOD values may not always be of concern depending on the final disposal environment, e.g., discharge to groundwater. However, in cases where high initial BOD concentrations are considered unacceptable, pre-leaching the reactive media, prior to installation needs to be investigated. The effects of pre-leaching on long-term treatment effectiveness would also need to be explored.

The onset of sulphate reducing conditions, which may occur when nitrate is fully depleted, also appears to increase BOD. Under these conditions, sulphide oxygen demand may also contribute to BOD. Robertson et al. (2005a) noted that sulphate reduction appears to be more active during the summer when higher temperatures lead to increased reaction rates and nitrate is depleted more quickly. Any sulphide that is present in the effluent is presumably re-oxidized to SO_4 when the effluent is discharged to aerobic environments; however, sulphide can be toxic and method to minimise its discharge needs to be investigated.

Hydrogen sulfide

Van Driel et al. (2006a) noted the occasional presence of H_2S odour in the effluent discharging when effluent temperatures exceeded 10^oC and during low flow conditions, most likely due to sulphate reduction. This presumably resulted from longer retention times and nitrate depletion during the low flow conditions.

H_2S gas at low concentration has an unpleasant odour similar to rotten eggs. As the gas is heavier than air it can accumulate in low lying areas. Over exposure to the gas can have severe health affects. At high concentrations H_2S can cause collapse and death in both humans and animals.

Greenhouse gases

Incomplete denitrification can lead to production of the intermediate N_2O. Anaerobic degradation of organic media also results in the production of CO_2 and possibly CH_4. All three of these are greenhouse gases (GHC) of concern. GHGs have been measured in the outflow of a stream bed bioreactor (Elgood et al., 2010), in a denitrification wall (Moorman et al., 2010), column study (Greenan et al., 2009) and in a large denitrification bed (Warneke et al., 2011). Reported release of N_2O from reactors varies between 0.6 to 4.3% of nitrate removed (Elgood et al., 2010; Warneke et al., 2011). Emissions of CH_4 from a reactor would be expected to increase when nitrate concentrations are low as methanogenes begin to outcompete denirifiers for carbon supply. While CO_2 is released from denitrifying bioreactors (Elgood et al., 2010; Warneke et al., 2011) it does not necessarily contribute to a net increase in CO_2 concentrations in the atmosphere as the carbon may decay to CO_2 in any case.

2.8 Conclusions

Denitrification beds are an effective way to remove nitrate from point source discharges. To date field-scale beds have used fragmented wood particles (sawdust and woodchip) as the carbon source. The wood media maintains nitrate removal rates of between 2 to 10 g N m^{-3} d^{-1} for greater than 15 years. Higher nitrate removal rates have been achieved in laboratory scale studies using alternative carbon media, but the longevity of these media are unknown and likely to be less than wood.

A denitrification bed is a cost effective method of removing nitrate from point source discharges compared to alternative passive options (e.g. constructed wetlands) or more sophisticated treatment methods (e.g., carbon dosing). The beds require low maintenance and are capable of removing more than 99% of the nitrate from influent water, which many alternative technologies struggle to accomplish. Greater uptake of denitrification bed technology could be achieved by reducing the cost of bed construction, leading to a reduction in the mass of nitrate discharged to the environment. Reducing the required bed volume and footprint area through improving nitrate removal performance of a bed is one approach that could be taken to reduce construction costs. The key aspects of denitrification bed design and operation that could be investigated for the purpose of identifying practical techniques to improve nitrate removal performance are:

1. Increasing the available carbon concentration in the bed by either using media that provide greater sustained concentration of available carbon than wood media or by increasing the decomposition rate of the media. The media must also have and maintain adequate permeability to avoid hydraulic failure.
2. Determine the optimal organic media particle size to provide greatest nitrate/carbon contact while maintaining adequate permeability.
3. Reduce short-circuit flow through the bed by using media of optimal particle size for providing plug flow conditions.
4. Increasing the operational temperature of the bed to enhance denitrifying bacteria growth.
5. Reduce short-circuit flow through the bed by using inlet and outlet design and locations that provide most plug-like flow conditions.
6. Reduce dissolved oxygen concentration of influent so that denitrification occurs in the upstream section of the bed. Elevated DO concentration of influent water means that denitrification will not occur until DO

concentration are reduced to less than about 1 mg L^{-1} by aerobic microbial processes.

7. Maintain pH in the bed so that conditions are optimised for the growth of denitrifying bacteria population.

Bullet points 1 to 5, are addressed in this thesis for the purpose of increasing the nitrate performance of denitrification beds compared to existing operation bed designs. Bullet points 6 and 7 are not addressed in this thesis.

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Chapter 3

Nitrate Removal and Hydraulic Performance of Organic Carbon for use in Denitrification Beds

This chapter was published as the following journal paper and is presented in this thesis in journal format.

Cameron, S.G., Schipper, L. A., 2010. Nitrate removal and hydraulic performance of organic carbon for use in denitrification beds. Ecological Engineering 36: 1588–1595

The contribution of contributing authors were:

Cameron, S. G.: Experimental design, trial setup, sampling, data analysis and primary write-up.

Schipper, L.A., Experimental design, advisor and primary review.

A photograph of the barrel trial that was not included in Cameron and Schipper (2010) is presented as Figure 3.1 on the following page.

Figure 3.1 Photograph of barrel trial. The photograph shows the 0.2 m^3 barrels housed within the 7.5 m long shipping container. The unheated 14°C barrels are located on the floor of the container. The heated 23.5°C barrels with thermal lining are located on the wooden shelving. The heat pump that maintained temperature in the container is at the top right hand corner of the photo. The 200 mm diameter PVC tube mixing manifolds are on the left hand side of the entry to the shipping container. The manifolds were used to mix the dosed KNO_3 solution with the influent water before being piped to the barrels.

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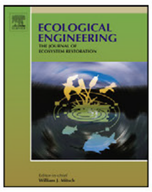

Nitrate removal and hydraulic performance of organic carbon for use in denitrification beds

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ABSTRACT

Denitrification beds are a cost-effective technology for removing nitrate from point source discharge. To date, field trials and operational beds have primarily used wood media as the carbon source; however, the use of alternative more labile carbon media could provide for increased removal rate, lower installation costs and reduced bed size. While previous laboratory experiments have investigated the potential of alternative carbon sources, these studies were typically of short duration and small scale and did not necessarily provide reliable information for denitrification bed design purposes. To address this issue, we compared nitrate removal, hydraulic and nutrient leaching characteristics of nine different carbon substrates in 0.2 m^3 barrels, at 14 and 23.5 °C over a 23-month period. Mean nitrate removal rates for the period 10–23 months were 19.8 and 15 $g\,N\,m^{-3}\,d^{-1}$ (maize cobs), 7.8 and 10.5 $g\,N\,m^{-3}\,d^{-1}$ (green waste), 5.8 and 7.8 $g\,N\,m^{-3}\,d^{-1}$ (wheat straw), 3.0 and 4.9 $g\,N\,m^{-3}\,d^{-1}$ (softwood), and 3.3 and 4.4 $g\,N\,m^{-3}\,d^{-1}$ (hardwood) for the 14 and 23.5 °C treatments, respectively. Maize cobs provided a 3–6.5-fold increase in nitrate removal over wood media, without prohibitive decrease in hydraulic conductivity, but had higher rates of nutrient leaching at start-up. Significant difference in removal rate occurred between the 14 and 23.5 °C treatments, with the mean Q_{10} temperature coefficient = 1.6 for all media types in the period 10–23 months.

1. Introduction

Global anthropogenic production of reactive nitrogen, from cultivation of crops, combustion of fossil fuels, and production of nitrogen fertilizers increased by about 225% from 1970 to 2000 and exceeded all natural terrestrial production (Galloway et al., 2003). This has resulted in accumulation of reactive nitrogen in the environment contributing to loss of biodiversity, and habitat degradation in coastal and terrestrial surface waters (Howarth et al., 2002). Reactive nitrogen creation and accumulation is projected to increase in the future as human populations and per capita resource use increase (Galloway et al., 2003).

Point source discharge is one of the contributing sources of reactive nitrogen into the environment, including: municipal and septic treatment systems, agricultural tile drainage, and industrial discharges. Practical methods are needed to reduce the reactive nitrogen load into the environment from point source discharges. Although numerous technologies for removing nitrogen from wastewaters exist (e.g. breakpoint ion exchange, ammonia volatilization, selective ion exchange, reverse osmosis, and combined nitrification/denitrification systems), these methods are often unaffordable for treatment of small volume point source discharge. Even when these treatments are applied, often some nitrogen remains in the final effluent.

Denitrification beds (Blowes et al., 1994) offer a practical solution for the reduction of reactive nitrogen concentrations in point source discharges, when more expensive treatment options are uneconomic. The bed is essentially a lined cavity or container with organic matter through which nitrified effluent is passed. This organic matter supports microbial denitrification that converts nitrate (NO_3) to nitrogen gas (N_2). There is evidence from laboratory and field studies that the dominant nitrate removal process occurring in denitrifying bioreactors is denitrification and not Anammox or dissimilatory nitrate reduction to ammonium (DNRA) (Greenan et al., 2006; Gibert et al., 2008).

Other passive, low-cost wastewater treatments systems (e.g., constructed wetlands, pond systems, land disposal, and subsurface treatment) also typically rely on the manipulation of the denitrification process to treat nitrate contaminated water. The advantages of denitrification beds over alternative options are that beds are capable of greater than 99% removal of nitrate (Robertson

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Table 1
Grain size, porosity and hydraulic retention time (HRT) of the reactors at start of the barrel tests.

Media	Variety	Grain size[a] (mm)	Drainable porosity	Dry media weight[b] (kg)	HRT[c] (h)
Sawdust	*Pinus radiata* (softwood)	2 ± 1.8	0.46	35.4	33.1
4 mm woodchip		4 ± 2.0	0.48	27.2	34.9
6 mm woodchip		6 ± 3.3	0.53	32.9	38.4
15 mm woodchip		15 ± 5.3	0.54	30.0	38.9
61 mm woodchip		61 ± 19	0.56	30.1	40.1
Hardwood	Eucalyptus (Red Duke)	11 ± 4.5	0.52	47.2	37.5
Maize cobs		45 ± 11	0.61	19.9	43.9
Wheat straw		13[d]	0.75	8.9	54.3
Green waste		6 ± 9.7	0.47	42.3	34.0

[a] Mean arithmatic value ± 1 SD (sorting).
[b] Average dry weight of media included in each barrel.
[c] HRT (hydraulic retention time) = volume of media × porosity/flow rate.
[d] Measured manually by ruler and excludes length of wheat straw stalk.

et al., 2005; Schipper et al., 2010a), have a relatively small footprint, require minimal maintenance compared to more expensive and complicated treatment options and have a lower installation cost.

Nitrate removal rates for denitrification beds utilising wood media range from 2 to $10\,\mathrm{g\,N\,m^{-3}\,d^{-1}}$ (Schipper et al., 2010b). Many short-term small-scale studies have tested a variety of carbon sources to support nitrate removal (e.g., wood and wheat straw – Vogan, 1993; Soares and Abeliovich, 1998; cotton – Volokita et al., 1996; Della Rocca et al., 2006; wood, cardboard and corn husks – Greenan et al., 2006; wood, soil and mulch – Gibert et al., 2008). The highest reported rates were up to $105\,\mathrm{g\,N\,m^{-3}\,d^{-1}}$ measured in laboratory studies using rice husk media (Shao et al., 2009). However, the duration of most of these laboratory studies has been less than 6 months and involved small volumes of carbon sources during which time nitrate removal rates decline due to depletion of readily available carbon (e.g., Soares and Abeliovich, 1998; Greenan et al., 2006). For bed design purposes, longer term rates of nitrate removal for a variety of carbon media are needed.

While more labile carbon media might support greater nitrate removal rates, these media may also have higher leaching concentrations of soluble carbon and ammonium (Della Rocca et al., 2005; Greenan et al., 2006; Shao et al., 2009; Vogan, 1993; Robertson and Cherry, 1995; Schipper et al., 2010b). Elevated soluble carbon in discharge waters can reduce dissolved oxygen (DO) in surface water adversely effecting biota. Similarly, ammonium is toxic to fresh water biota at concentrations above $0.32\,\mathrm{g\,N\,m^{-3}}$ (ANZECC, 2000).

Different carbon media are likely to sustain different hydraulic conductivities, which is critical for maintaining effluent flow through the bed. Reduction of hydraulic conductivity over time can occur as cell structure degrades, from the production of gas bubbles (Soares et al., 1991; Schipper et al., 2004), from secondary mineral precipitates (Blowes et al., 1994) or from biomass growth. While some long-term studies of wood media denitrification trials have reported no reduction in media permeability (Van Driel et al., 2006a), there is no information on long-term permeability of more labile carbon media.

In this study, we measured nitrate removal rates supported by nine different carbon media in large barrels for 23 months. The carbon media included five different particle sizes of wood product to determine whether particle size modified nitrate removal rates. We also measured hydraulic conductivity of the media to determine whether there would be change in effluent transport over time. Nitrate removal, carbon and ammonium leaching, and hydraulic conductivity were measured in two separate temperature treatments (14 and 23.5 °C). The study had longer duration and larger volume of carbon media compared to previously reported laboratory scale experiments. Hydraulic residence time (HRT) of effluent in the barrels (33–54 h) was similar to reported times for larger scale denitrification beds (Van Driel et al., 2006a,b). This provided for improved reliability when applying the results from this study to the design of larger scale denitrification beds. It also addressed the issue of comparing carbon media performance measured by different researchers under different experiment design and duration, due to the number of different carbon media tested in this study.

2. Methodology

The experiment was housed in a 7 m long temperature-controlled shipping container. Nine different carbon media were placed in $0.2\,\mathrm{m^3}$ barrels (2 replicates each) and were continuously loaded with water dosed with nitrate. The trial included two independently plumbed temperature treatments to give a total of 36 barrels. Mean temperature for the unheated and heated treatment was 14 and 23.5 °C, respectively. Selection criteria for media included: availability, suitable hydraulic properties, and cost.

2.1. Media

The nine media included (Table 1): five different grain sizes of *Pinus radiata* (radiata pine), eucalyptus (Red Duke) woodchip, maize cobs, green waste and wheat straw. The five grain sizes of *P. radiata* media were obtained from the same source (Waste Pro Solutions, Rotorua). Eucalyptus woodchip, sourced from Norske Skog paper mill in Kawerau, was included in the trial as a hardwood comparison to the softwood *P. radiata* media. The deseeded maize cob media were sourced from Corsen's Seed and Grain in Gisborne. The cobs were a waste product from the production and processing of maize seed. Green waste was sourced from the Taupo District Council composting facility. Green waste was mixture of miscellaneous shrubbery leaves and stems that had been mulched for compost production. The dried wheat straw was purchased from an agricultural contractor in Palmerston North.

2.2. Barrel design

Carbon media ($0.17\,\mathrm{m^3}$) was loaded into barrels and weighed (Table 1). Wheat straw media required compression to load sufficient media. Media was held in place by a secured stainless steel mesh ring. A subsample of each media was analysed for moisture content and grain size.

Flow through the barrels was from top to bottom (Fig. 1). Design influent flow rate was $40\,\mathrm{mL\,min^{-1}}$ ($0.056\,\mathrm{m^3\,d^{-1}}$) controlled by 1 mm ID micro-tubing. Flow rate through each barrel was measured

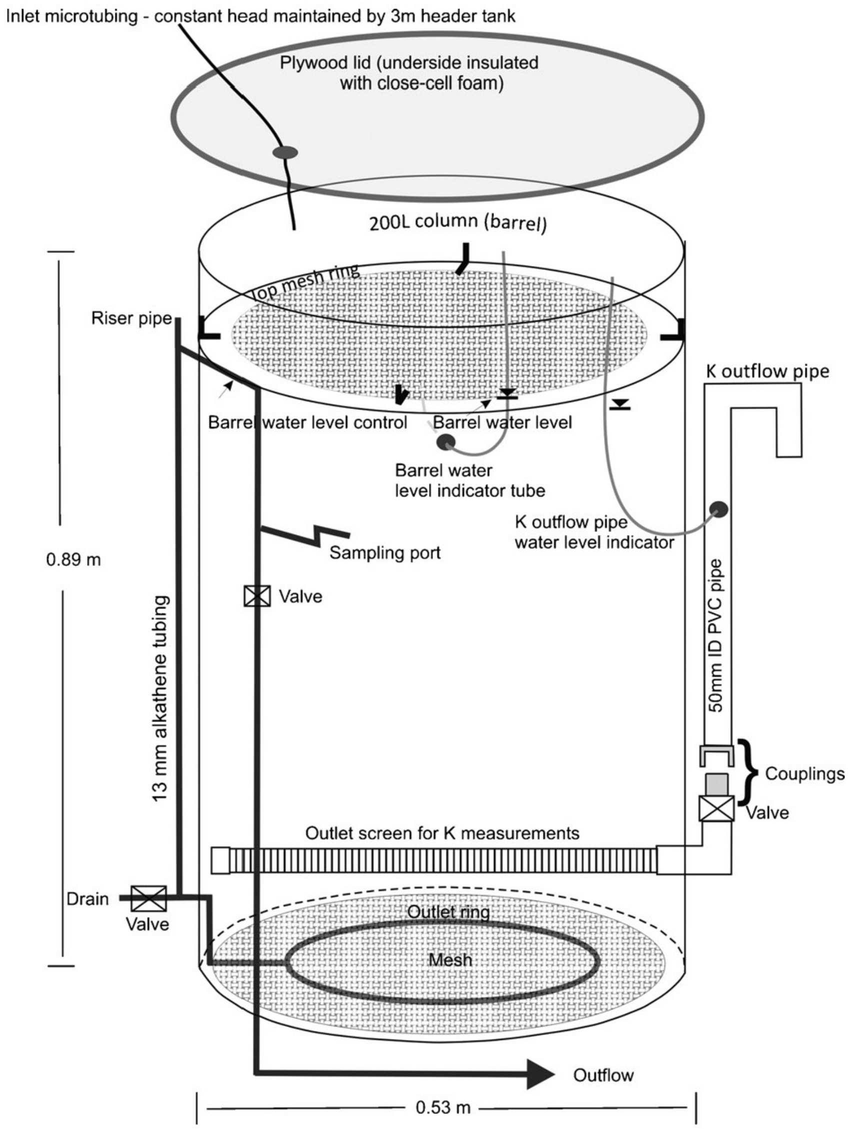

Fig. 1. Barrel design.

by the time to fill a calibrated volumetric flask. A perforated outlet ring, installed at the bottom of the barrel, promoted uniform flow through the media reducing preferential flow. The water level in the barrel was kept at about 20 mm above the top of the media by riser pipe to maintain a constant hydraulic head. 50 mm ID pipes, fittings and PVC screen were installed near the base of the barrel for measuring hydraulic conductivity of the media (described below). Thick carpet underlay (12 mm thickness) was wrapped around heated barrels to reduce heat lose. Plywood lids, with closed cell foam glued to the underside, were placed on the top of each barrel for insulation.

Municipal potable water dosed with potassium nitrate (KNO_3) served as the influent water to the trial. Mean inlet NO_3–N concentration into the 14 and 23.5 °C barrels was 159 and 141 mg L^{-1}, respectively, throughout the study. High influent nitrate concentrations were required to maintain non-nitrate limiting conditions in the more labile carbon media treatments. Stable hydraulic head pressure (about 3 m) was maintained to the inlet lines by header tanks to facilitate uniform influent flow rate. Metering pumps were used to inject KNO_3 solution at the required rate into mixing manifolds installed in the inlet line. Temperature inside the shipping container was maintained by 8 kW heat pump, and resulted in a temperature gradient from about 15 °C at the floor to 20 °C at the ceiling in the container. The unheated barrels were located on the floor of the container and the heated barrels located above on shelving.

Temperature in the heated barrels was maintained by heating influent water to about 36 °C, prior to nitrate dosing, with a thermostatically controlled heating element installed in the header tank. In the heated barrels, temperature decreased from the top at about 28–30 °C to the base of the barrel at about 18–20 °C. The mean of these temperatures throughout the trial was 23.5 °C. Vertical temperature gradient in the unheated barrels varied between 0 and 2 °C and the average temperature was 14 °C. The mean difference between the two temperature treatments throughout the trial was 9.5 °C.

Table 2
Mean nitrate removal rates (g N m^{-3} d^{-1}) for periods 1–10 months and 10–23 months after start-up.

	Media	1–10 months						10–23 months						
		14 °C[a]	23.5 °C[a]	Significance			Q_{10}[c]	14 °C[a]	23.5 °C[a]	Significance				Q_{10}[c]
				Media		Temp				Media		Temp	Interaction	
					Group[b]						Group[b]			
	Sawdust	5.0 ± 2.7	11.6 ± 3.4		a		2.4	2.2 ± 0.2	5.0 ± 0.2		ab			2.4
	4 mm woodchip	5.7 ± 0.1	10.4 ± 0.3		a		1.9	2.9 ± 0.3	4.8 ± 1.0		a			1.7
Pinus radiata	6 mm woodchip	5.3 ± 1.2	12.3 ± 0.6		a		2.4	3.1 ± 0.5	5.3 ± 0.2		ab			1.8
	15 mm woodchip	6.0 ± 3.7	11.1 ± 4.0		a		2.0	3.6 ± 1.0	5.3 ± 1.4		b			1.6
	61 mm woodchip	7.8 ± 1.8	9.6 ± 2.1	$F_{(8,35)} = 25.0$, $P < 0.001$	a	$F_{(1,35)} = 51.9$, $P < 0.001$	1.3	3.3 ± 1.0	4.2 ± 0.2	$F_{(8,35)} = 29.8$, $P < 0.001$	ab	$F_{(1,35)} = 33.7$, $P < 0.001$	$F_{(8,35)} = 4.13$, $P = 0.006$	1.3
	Mean (softwood)	6.0 ± 1.1	11.0 ± 1.0				1.9	3.0 ± 0.5	4.9 ± 0.2					1.7
	Hardwood	3.8 ± 0.3	7.4 ± 1.1		a		2.0	3.3 ± 0.8	4.4 ± 1.0		ab			1.4
	Maize cobs	34.6 ± 3.0	43.0 ± 2.4		c		1.3	19.8 ± 0.1	15.0 ± 1.2		c			0.8
	Wheat straw	18.7 ± 4.2	22.7 ± 1.7		b		1.3	5.8 ± 1.4	7.8 ± 1.6		d			1.4
	Green waste	22.0 ± 1.5	25.6 ± 0.6		b		1.2	7.8 ± 0.2	10.5 ± 1.1		e			1.4
Mean							1.8							1.6

[a] Mean nitrate removal rate ± 1 standard deviation.

[b] Nitrate removal rate for the media with the same letter (a, b, c, d, e) are not significantly different at 95% confidence level using Fisher's least significant difference procedure.

[c] Measure of the rate of change of a biological or chemical system as a consequence of increasing the temperature by 10 °C.

2.3. *Water quality sampling*

Effluent samples were collected at the dedicated sampling port (Fig. 1) of each barrel. Sampling of the barrel influent and effluent was generally monthly for the first 16 months then at 3-month intervals between months 16 and 23. Influent and effluent samples were analysed for NO_3–N, temperature and pH for all samplings. Effluent Total Kjiedahl Nitrogen (TKN), ammonium–nitrogen (NH_4–N) and carbonaceous biological oxygen demand (BOD) were measured during eight sampling events.

Samples for nitrate and ammonium analysis were passed through a 0.45 μm filter. Samples for BOD and TKN samples were unfiltered. The TKN samples were preserved with sulphuric acid. After collection, all samples were stored at 4 °C until analysis.

NO_3–N was analysed by Ion Chromatography using *Standard Method* 4110-B (APHA, 2005) while NH_4–N was analysed by phenol/hypochlorite colorimetry using *Standard Method* 4500-NH3-4-114 (APHA, 2005). TKN samples were analysed by sulphuric acid digestion with copper sulphate catalyst and (Total Kjeldahl digestion) phenol/hypochlorite colorimetry, according to *Standard Methods* 4500-Norg C. (modified), 4500 NH3 F (modified) (APHA, 2005). BOD samples were incubated for 5 days, with a nitrification inhibitor added, and measurements obtained by DO meter, according to *Standard Methods* 5210 B (APHA, 2005).

pH and temperature of the effluent water were measured using a CyberScan PD300 meter and pH electrode with temperature sensor and compensation.

2.4. *Hydraulic properties*

Drainable porosity (Brutsaert, 2005) of each media was measured from the volume of water that drained from the bottom of an initially saturated barrel over a 24-h period. Grain size distribution of media was determined by sieving for the finer grain-size component and by manual measurement for the larger grain-size component of the media. Reported grain size (Table 1) is the mean arithmetic value and the standard deviation (degree of sorting). The HRT of effluent within each media treatment (Table 1) was calculated by volume of media multiplied by porosity divided by flow rate.

Hydraulic conductivity (K) was determined on all barrels at 1 and 22 months after start-up. The K of the column media was calculated using the Darcy equation ($q = KIA$) from the flow rate through the barrel and the hydraulic head loss between water level in the barrel and the outflow pipe (Freeze and Cherry, 1979) (Fig. 1); where q was the flow rate (m^{-3} d^{-1}), I was hydraulic gradient, and A was the cross sectional area of the barrel.

2.5. *Data analysis*

Nitrate removal rate (g N m^{-3} d^{-1}) was calculated as the difference between mass of nitrate in barrel inflow and outflow, with mass calculated as concentration (g N m^{-3}) multiplied by flow (m^{-3} d^{-1}) divided by the volume of media (m^3).

Two-way analysis of variance using Statistica (Release 8, StatSoft Inc., Tulsa, OK, USA) was undertaken to test for significant differences in nitrate removal rates between different media and temperature treatments for the periods 1–10 months and 10–23 months. The division into two periods was undertaken because the 1–10-month start-up period was characterised by rapid changes in nitrate removal rates and the 10–23-month period by more stable removal rates. Mean values for the two time periods were cube-root transformed prior to analysis to normalise the data. Reported differences were significant at the 5% level unless stated otherwise.

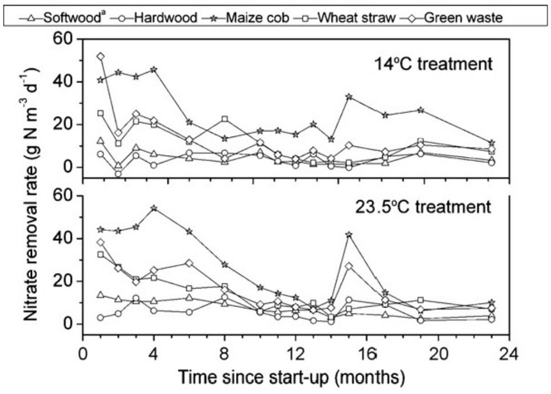

Fig. 2. Nitrate removal rates for the 14 and 23.5 °C treatments for the period 1–23 months. Superscript a: mean of all softwood media nitrate removal rates.

Reported error values for mean nitrate removal rates are 1 standard deviation.

The Q_{10} reaction rate (Anderson and Janssens, 2006), defined as the factor by which a reaction rate increases with a 10 °C rise in temperature, was calculated to determine the difference in nitrate removal rate between temperature treatments.

3. Results

3.1. Nitrate removal

Generally, nitrate removal rates declined for the first 10 months after which there was little further change in removal rate (Fig. 2). Removal rates differed significantly between media types for both the start-up (1–10 months) and longer term (10–23 months) periods (Table 2).

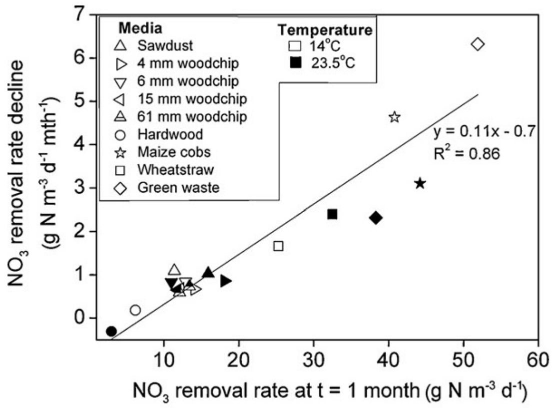

Fig. 3. Rate of decline of nitrate removal as a function of start-up nitrate removal rate. Nitrate removal rate decline was the slope of linear regression lines through the removal rates for the period 1–10 months.

Nitrate removal rates were consistently higher in the maize cob media in both the 14 and 23.5 °C treatments during the 23-month experiment (Fig. 2, Table 2). Nitrate was completely removed in the 23.5 °C maize cob barrels for the first 2 months and so nitrate removal rates were likely conservative. The longer term nitrate removal rate for maize cobs was about 6.5-fold greater than wood media and 2.5 and 3.4-fold greater than green waste and wheat straw media, respectively, in the 14 °C treatment. In the 23.5 °C treatment, the difference in removal rate between maize cobs and other media types was not as great.

Nitrate removal rate was significantly greater at 23.5 °C than at 14 °C for both the first 10 months and between 10 and 23 months (Table 2). The magnitude of the difference in nitrate removal rate for different media was temperature dependent for the period 10–23 months and higher nitrate removal rates occurred in the 14 °C maize cob media compared to the 23.5 °C maize cob media.

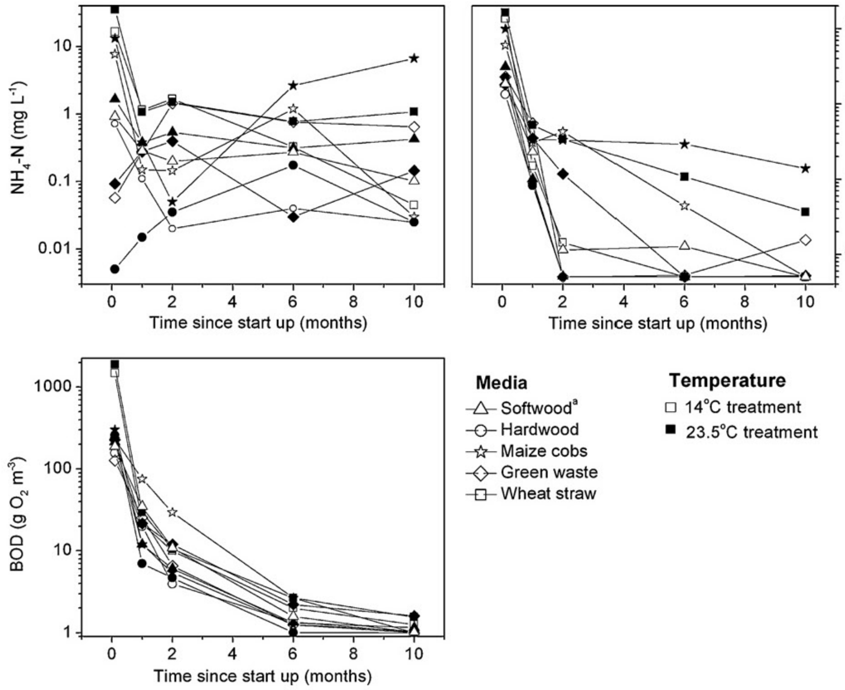

Fig. 4. Effluent NH_4–N, TKN and BOD concentrations for the period 1–10 months. Superscript a: mean of all softwood media.

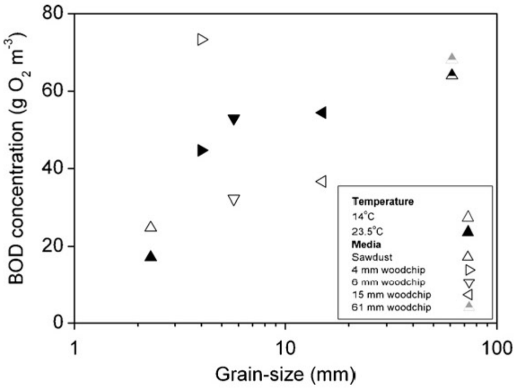

Fig. 5. Mean effluent BOD concentrations for first 10 months, as a function of softwood media grain size.

The nitrate removal rates were similar for the five particle sizes of *P. radiata* media for each temperature and so a single average nitrate removal rate is presented in Fig. 2. Similarly, there was no significant difference in nitrate removal rate between softwood and hardwood media (Table 2).

The decline in the rate of nitrate removal (expressed as $g\,N\,m^{-3}$ (of media) d^{-1} $month^{-1}$) during the first 10-month period was correlated by linear regression to the initial rate of nitrate removal measured at 1 month. Fig. 3 shows there is exponential correlation between rate of decline and initial removal with the highest rates of decline occurring in the more labile media (maize cobs, wheat straw and green waste).

3.2. Leaching of NH_4, TKN and BOD

Leaching concentrations of TKN and BOD were elevated for all media at start-up (Fig. 4). High start-up NH_4–N concentrations occurred in the wheat straw and maize cob media. These media also had the highest TKN and BOD start-up concentrations.

Leaching concentrations declined during the first 2–6-month period; however, the 23.5 °C maize cob treatment continued to leach NH_4–N and TKN at concentrations above 3 and $5\,mg\,L^{-1}$ respectively, beyond 6 months.

Generally leaching of NH_4–N, TKN and BOD was higher in the 23.5 °C barrels than in the 14 °C barrels for each media type. Also BOD leaching concentrations generally increased in the larger grain size softwood media, with the effect more pronounced in the 23.5 °C treatment (Fig. 5).

3.3. pH

Initial pH of the outflow from all treatments ranged between 2.5 and 6.6 depending on media type (Fig. 6). Wood media had the lowest start-up pH (hardwood = 2.5 and softwood = 4.3). Media pH concentration increased to 6.6, or higher within 3 months.

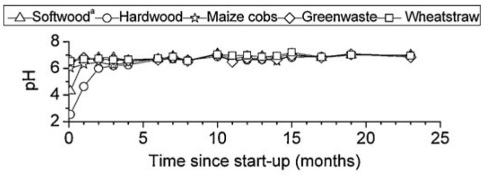

Fig. 6. Effluent pH concentrations for the period 0–23 months. Superscript a: mean of all softwood media.

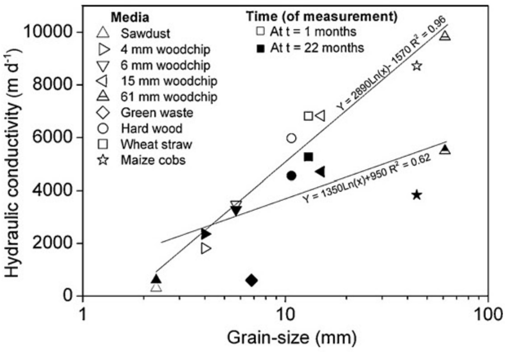

Fig. 7. Change in media hydraulic conductivity between 1 and 22 months, as a function of media grain size. Correlations exclude green waste as green waste grain size was poorly sorted (see Table 1).

3.4. Physical properties and hydraulic conductivity

Porosity, grain size and initial hydraulic retention time (HRT) data are presented in Table 1. K of the nine media ranged from $300\,m\,d^{-1}$ for sawdust to $10{,}000\,m\,d^{-1}$ for 61 mm woodchip, for the two K measurements taken at $t = 1$ and 22 months (Fig. 7). Between 1 and 22 months, K generally decreased in media with larger grain size but remained similar in the smaller grain sized media. For media coarser than 10 mm, the decline in K was greater as grain size increased.

4. Discussion

4.1. Carbon media

Nitrate removal rates (1–23 months) ranged from 0 to $52\,g\,N\,m^{-3}\,d^{-1}$ depending on media and temperature (Fig. 2). Nitrate removal for all media declined during the first 10 months, after which measured rates more reliably represent longer term nitrate removal. In order of magnitude, nitrate removal rates for both the 14 and 23.5 °C treatments were maize cobs > green waste > wheat straw > wood, for both the 1–10-month and 10–23-month periods (Table 2).

Mean nitrate removal rates for softwood media between 10 and 23 months (14 °C treatment = $3.0 \pm 0.5\,g\,N\,m^{-3}\,d^{-1}$; 23.5 °C treatment = $4.9 \pm 0.2\,g\,N\,m^{-3}\,d^{-1}$) were generally at the lower end of the range of removal rates from other long-term denitrification trials. Schipper et al. (2010b) summarised removal rates for field scale trials of wood media, when nitrate was non-limiting and rates ranged between 2 and $10\,g\,N\,m^{-3}\,d^{-1}$, at temperatures from 7.7 to 20 °C.

The more labile carbon sources (maize cobs, green waste, and wheat straw) supported significantly greater nitrate removal rates than wood media (Table 2). The long-term nitrate removal rate for maize cobs was 3–6.5 times greater than wood media for the 23.5 and 14 °C treatments, respectively. Greenan et al. (2006) also measured nitrate removal rates that were 6.5-fold greater for ground cornstalks than woodchips for a 180-day period. However, by day 180 the rate of nitrate removal by the cornstalks was nearly zero, whereas in the present study, maize cobs continued to remove nitrate at 19.8 ± 0.1 and $15.0 \pm 1.2\,g\,N\,m^{-3}\,d^{-1}$ for the 14 °C and 23.5 °C treatments respectively, after 10 months.

The nitrate removal rates for the 23.5 °C wheat straw and green waste treatments between 1 and 10 months (22.7 ± 1.7 and $25.6 \pm 0.6\,g\,N\,m^{-3}\,d^{-1}$, respectively) were similar to rates measured in a column study which included sawdust, wheat straw and cellulose mixed with silica sand (Vogan, 1993). Vogan (1993) measured nitrate removal rates of between $18–26\,g\,N\,m^{-3}\,d^{-1}$ and

29–39 g N m^{-3} d^{-1}, for wheat straw and cellulose respectively, for 74 days at 22 °C. In the current study, wheat straw and green waste continued to remove nitrate beyond 10 months at approximately twice the rate of wood media.

While hardwood had lower nitrate removal rate than softwoods for the first 10 months (Fig. 2), there was no statistically significant difference in long-term nitrate removal rate (10–23 months). Rates may have been lower in the hard wood barrels due to the initially very low pH (2.5) which was less than the optimum pH for denitrifiers (Coyne, 2008). Gibert et al. (2008) and Greenan et al. (2006) also measured similar denitrification rates for softwood and hardwood.

The removal rate for 15 mm woodchip was significantly greater than that of 4 mm woodchip between 10 and 23 months (Table 2). There was a tendency for the nitrate removal rate to increase with increasing grain size in the 14 °C softwood treatments, but there was no such tendency in the 23.5 °C treatments. An increase in removal rate with increasing grain size may be associated with the longer HRT of the coarser grain sized softwood media (Table 1) because of its higher porosity (e.g. 0.56 vs. 0.46, Table 1). In contrast, Carmichael (1994) observed that the nitrate consumption rate was not correlated with the specific surface area of sawdust. Furthermore, Van Driel et al. (2006a,b) measured similar rates of nitrate removal in denitrification beds constructed with coarse (5.9 mg N L^{-1} d^{-1}) and fine grained wood particles (5.5 mg N L^{-1} d^{-1}). They suggested that this was caused by the dual porosity characteristics of the media where denitrification occurs several millimetres into the wood particles rather than being restricted to just the particle surfaces (Robertson et al., 2000).

4.2. Temperature controls on nitrate removal

Nitrate removal rates were greater at 23.5 °C than at 14 °C for all media in the first 10 months ($F_{1,35} = 51.9$, $P < 0.001$) and in the long term ($F_{1,35} = 33.7$, $P < 0.001$) for all media except maize cobs. Q_{10} values (Table 2) were generally lower for the wood and maize cob media for the latter time period, possibly because carbon availability to support denitrification had declined. The latter time Q_{10} values for softwood media (mean $Q_{10} = 1.7$) were lower than Q_{10} values (2.7–3.5) calculated from nitrate removal rates for the temperature range 3–13 °C reported by Van Driel et al. (2006a,b) for a denitrification bed study utilising wood products. The difference in Q_{10} values between these two studies could be due to several factors such as differences in scale, temperature range and wood particle characteristics.

4.3. Leaching during start-up period

Leaching of soluble carbon and NH_4 during the start-up of denitrification beds and laboratory experiments is well documented (e.g., Robertson and Cherry, 1995; Vogan, 1993; Carmichael, 1994; Robertson et al., 2005; Schipper et al., 2010a, 2010b) although there is little comparative information for different carbon media. In the current study, leaching of NH_4–N, TKN and BOD were generally higher for the maize cob and wheat straw media than for the wood and green waste media during the first 10 months. NH_4–N and BOD leaching concentrations from wood media were generally less than environmental guideline values (ANZECC, 2000) by 2 months after start-up. In contrast, leaching from for the 23.5 °C maize cobs media continued to exceed NH_4–N guideline values beyond 10 months.

Leaching of NH_4–N, TKN and BOD was generally higher in the 23.5 °C barrels than in the 14 °C barrels, probably because higher temperatures supported faster microbial decomposition of carbon media releasing NH_4–N, organic nitrogen and carbon.

The HRT of the wood media increased with increasing grain size (Table 1) because porosity increases. BOD leaching also increased with grain size (Fig. 5) likely due to the longer HRT in the wood media. This effect was more pronounced in the 23.5 °C barrels than the 14 °C barrels. Longer HRT would provide for greater dissolution of carbon as effluent flowed through the media. Robertson and Cherry (1995) also reported that soluble carbon leaching from denitrification beds increased due to longer effluent residence time in the reactor.

To minimise leaching losses of NH_4–N and BOD during start-up, for discharge to sensitive environments, management of start-up denitrification bed temperature (perhaps by commissioning during winter) and HRT (by flow rate or hydraulic gradient), coupled with selection of appropriate media could be employed.

4.4. Hydraulic conductivity

Hydraulic conductivity decreased in the coarser grain size media but increased in the finer grain size media between 1 and 22 months (Fig. 7), with the magnitude of the change in K increasing as a function of grain size. Physical inspection of the media in the barrels at 23 months showed no obvious deterioration in media structure or visual sign of biofilm growth, but some tendency for larger grain sized particles to rest on their flat surfaces. The decline in K was assumed to be caused by a combination of gas bubbles (Soares et al., 1991; Schipper et al., 2004), media particle shape and tendency for settling of the media particles on their flat surface. The coarser grain sized (>10 mm) wood media had a flat surface which would trap gas bubbles whereas the finer grain sized media were more lath-like. Similarly, gas bubbles become entrapped in the "honey comb" structure of the (deseeded) maize cob media. While the reduction in K in the coarser grained media over the 22-month period was considerable (23–56%), K values remained high (>3800 m d^{-1}) and would not cause hydraulic failure in most cases. However, the longer term reduction in K needs to be considered for denitrification bed design.

Reduction in carbon media permeability due to gas bubbles (Soares et al., 1991; Schipper et al., 2004) and secondary mineral precipitates (Blowes et al. 2000) has been reported previously. However, Van Driel et al. (2006a,b) found no noticeable deterioration in K over the 24-month monitoring period of two wood particle bioreactors, one containing fine grained sawdust and the other coarse grained woodchip media.

There was no difference in decline of hydraulic conductivity between hard wood and the equivalent grain size of softwood media (15 mm woodchip). The 23-month duration of the experiment was insufficient for difference in rate of breakdown of wood media cell structure to affect media hydraulic conductivity.

5. Conclusions

Previous studies have shown that wood media is well suited to denitrification bed technologies as it provides sustained nitrate removal (Robertson, 2010; Schipper et al., 2010b), high hydraulic conductivity (Van Driel et al., 2006a), has a low C:N ratio (~300:1; Robertson and Anderson, 1999) and is available at low cost in many areas. The current work shows that maize cob media can provide a 3–6.5-fold increase in nitrate removal over wood media without significant loss in permeability. However, significant amounts of NH_4–N and BOD leached from the media during the first months of operation. Management practices such as commissioning beds during winter, reducing HRT at start-up, pre-leaching of media and recirculation could reduce these losses.

The nitrate removal rates for maize cob, wheat straw and green waste media remained higher than the removal rates for wood media at 23 months after start-up. How long higher nitrate removal rates will be sustained is not known, but utilisation of the more labile media in operational denitrification beds may require more frequent replacement of media. Higher nitrate removal rates, however, offer a significant economic advantage of being able to substantially reduce the size of the bed for the same level of nitrate removal. For example, the volume of a bed containing maize cobs would be about three times smaller than a wood chip bed based on nitrate removal rates at the end of the trial. A major constraint to use of denitrification beds will likely be cost and availability of space.

There was no difference found in nitrate removal rate for five different grain sizes of softwood media, or between softwood and hardwood media.

Long-term nitrate removal rate was 1.5 times higher ($Q_{10} = 1.6$) in the 23.5 °C barrels than in the 14 °C barrels. However, long-term nitrate removal rates for maize cob media were lower in the 23.5 °C barrels than in the 14 °C barrels. This was attributed to rapid depletion of carbon in the first 10-month period.

Hydraulic conductivity of media with grain sizes greater than 10 mm decreased by between 23 and 56% over the 22-month monitoring period but still remained very high and was unlikely to affect hydraulic performance. The decrease was correlated with grain size and attributed to gas bubbles accumulating beneath the larger media particles.

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Chapter 4

Hydraulic Properties and Hydraulic Efficiency of Organic Carbon Media for use in Denitrification Beds

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The contribution of contributing authors were:

Cameron, S.G., Experimental design, trial set-up, sampling, data analysis and primary write-up.

Schipper, L.A., Experimental design, advisor and primary review.

Abstract

Denitrification beds, utilising fragmented wood particles as the carbon source, have been successfully used to remove nitrate from point source discharge. Other more labile carbonaceous solids have provided higher short-term nitrate removal rates than wood in laboratory scale trials, but the longevity of these media is unproven. In addition, the nitrate removal rate of a bed is indicated to be temperature dependent. Improving the hydraulic efficiency of a denitrification bed, by reducing short-circuit flow, may also provide for increased long-term nitrate removal rate and reduced bed size and lower installation cost. In this study, we compared the hydraulic properties and hydraulic efficiency of nine carbon media, including five grain sizes of wood particles, in 0.2 m^3 barrels, at two temperatures (14^{o}C and 23.5^{o}C). The relationship between hydraulic efficiency and nitrate removal of the different media was also investigated.

We found that carbon substrate and temperature were more influential on nitrate removal rate than hydraulic efficiency of the media. While larger grain-sizes of wood media were less hydraulically efficient than smaller grain-sizes, the difference in hydraulic efficiency was small. We also found that primary porosity of the wood media increased with temperature, which may have been caused by contraction of the wood particles with increasing temperature due to loss of water from the cellulose to the liquid phase.

While hydraulic properties and hydraulic efficiencies varied between carbon media, the variation did not cause significant difference in nitrate removal rate. The results indicate that future work on improving nitrate removal performance of denitrification beds should focus on carbon availability of the substrate and increasing bed temperature, rather than on identifying more hydraulically efficient media.

4.1 Introduction

Point source discharges of nitrate-contaminated water are a global environmental issue (Galloway et al., 2003) contributing to degradation of coastal and terrestrial waters (Howarth et al., 2002). Cost effective technologies are needed to reduce nitrate concentrations in point source discharge. Denitrification beds are one such technology that have been used to remove nitrate from municipal and septic wastewater systems, hothouses and agricultural tile drain water; and within small streams (Schipper et al., 2010a). A denitrification bed is typically constructed as an excavated trench fitted with an impermeable liner that is then filled with a solid organic carbon media such as woodchips (Blowes et al., 1994). The major expenses of installing a denitrification bed are land area needed, and purchase price and transport of wood material. Reducing the cost of constructing a bed would contribute to greater uptake of the technology. One way to reduce the construction cost would be to improve nitrate removal per unit volume thus reducing the size of the bed needed.

Nitrate removal in a bed is dependent upon a range of conditions being met including carbon availability of the media (Greenan et al., 2006; Cameron and Schipper, 2010) and bed temperature (Robertson et al., 2000; van Driel et al., 2006a). Fragmented wood typically has been used as the carbon media providing sustained nitrate removal (2 to 10 g N m^{-3} d^{-1}, Schipper et al., 2010a) and relatively high permeability (Robertson, 2010); and is readily available at moderate cost. Addition of soluble carbon (e.g., vegetable oil) could increase short-term nitrate removal rate but can also result in a reduction in hydraulic conductivity of the system (Hunter, 2001). High nitrate removal rates (>100 g N m^{-3} d^{-1}) have been reported in short-term laboratory scale studies using more labile carbon media (e.g., maize cobs, wheat straw, rice husk) but the longevity of both the removal rate and permeability of these media are likely to be less than wood (Shao et al., 2009; Cameron and Schipper, 2010).

A range of solid carbon sources have been investigated for their ability to support nitrate removal (Cameron and Schipper, 2010). Short-circuit flow through the media may reduce nitrate removal by reducing effective bed volume, however, comparative studies of short circuit flow through different carbon media have not been reported. Factors affecting short-circuiting are the presence of large connected void spaces (Villholth et al., 1998), flow fingering caused by profile heterogeneities (e.g., gas entrapment or biofilm growth; Hendrickx et al., 1993; Glass and Nicholl, 1996), and exchange of water between the mobile (primary or inter-granular porosity) and immobile phases (secondary or intra-granular porosity).

Despite different particle size of wood media being used in denitrification trials nitrate removal rates are not different (van Driel et al., 2006b). The considerable secondary porosity of wood has been proposed as the reason for similar nitrate removal rates by different particle sizes (Robertson et al., 2000), with the inference that the denitrification reaction occurs both within the wood particle and on the particle surface. Presumably water and nitrate within the inter-granular pore space diffuses into and out of the media particle.

The components of primary and secondary porosities that contribute to fluid flow through a media are considered its effective porosity. The physical and hydraulic properties of a solid carbon media that may influence flow are particle size, particle size sorting, and porosity. Tracer tests in denitrification beds have shown that the effective porosity of wood media can exceed primary porosity estimated by gravimetric drainage (Robertson, 2010; Chun et al., 2009). Other solid carbon media that could potentially be used in denitrification beds (e.g., maize cobs; Cameron and Schipper, 2010) are also likely to have dual porosity characteristics due to low particle density, but this has not been previously reported.

One way to estimate the degree of short-circuiting is to measure the hydraulic efficiency. Hydraulic efficiency of saturated porous medium or a denitrification bed can be defined as the ratio between actual retention time and theoretical hydraulic retention time (HRT) (Martinez and Wise, 2003; Kadlec and Wallace, 2008). Actual retention time is typically estimated by inert tracer test while HRT is calculated by multiplying the volume of media by effective (or primary) porosity divided by flow rate.

We have previously reported long-term nitrate removal rates for nine different carbon media (including five particle size of wood media) at two different temperatures (14°C and 23.5°C) in a 200 L barrel study (Cameron and Schipper, 2010). Nitrate removal rates ranged from 2.2 ±0.02 to 19.8 ± 0.1 g N m^{-3} d^{-1}. Differences in removal rates were attributed primarily to availability of carbon and temperature, but the importance of short-circuiting was not measured. This trial also provided opportunity to examine the hydraulic efficiency of the different media at the two different temperatures and determine whether physical and hydraulic properties of the media influenced hydraulic efficiency and nitrate removal rates. Hydraulic efficiency was assessed by tracer tests. Primary and secondary porosities of the media were measured at both temperatures. Hydraulic efficiency of the media was compared to nitrate removal rates to determine if short-circuiting or longer retention time influenced nitrate removal. The HRT of effluent in the barrels (about 2 days) was similar to those reported for larger-scale denitrification beds (van Driel et al., 2006a, 2006b) and so this study provides relevance when applying the results to the design of larger scale denitrification beds.

4.2 Methodology

Detailed description of the experimental setup was given by Cameron and Schipper (2010). A 7 m long shipping container was used to house the trial. Nine different carbon media (Table 4.1) were placed in 0.2 m^3 barrels (2 replicates each) and were continuously loaded with water dosed with nitrate for a 23-month period. The trial included two independently plumbed temperature treatments to give a total of 36 barrels. Mean temperature for the unheated and heated treatment was 14°C and 23.5°C, respectively.

Table 4.1 Carbon media grain-size, hydraulic efficiency and nitrate removal rate. Reported error is ± 1 standard deviation

	Media	Grain-size	Total porosity at start of the trial ($m^3\ m^{-3}$)	Total porosity at the end of the trial ($m^3\ m^{-3}$)		Hydraulic efficiency (e_V)		Nitrate removal rate for the period 10 to 23 months ($g\ N\ m^{-3}\ d^{-1}$)	
		mm ± 1 SD		**14°C**	**23.5°C**	**14°C**	**23.5°C**	**14°C**	**23.5°C**
Pinus radiata (softwood)	Sawdust	2 ± 1.8	0.75	0.87 ± 0.04	0.87 ± 0.07	1.78 ± 0.1	2.12 ± 0.0	2.2 ± 0.2	5.0 ± 0.2
	4 mm woodchip	4 ± 2.0	0.86	0.86 ± 0.01	0.88 ± 0.02	1.84 ± 0.5	1.69 ± 0.3	2.9 ± 0.3	4.8 ± 1.0
	6 mm woodchip	6 ± 3.3	0.80	0.85 ± 0.07	0.80 ± 0.10	1.76 ± 0.3	1.99 ± 0.1	3.1 ± 0.5	5.3 ± 0.2
	15 mm woodchip	15 ± 5.3	0.84	0.86 ± 0.02	0.91 ± 0.08	1.49 ± 0.1	1.85 ± 0.1	3.6 ± 1.0	5.3 ± 1.4
	61 mm woodchip	61 ± 19	0.83	0.87 ± 0.01	0.89 ± 0.02	1.36 ± 0.1	1.76 ± 0.1	3.3 ± 1.0	4.2 ± 0.2
	Hardwood	11 ± 4.5	0.76	0.81 ± 0.02	0.82 ± 0.02	1.33 ± 0.1	1.81 ± 0.0	3.0 ± 0.5	4.9 ± 0.2
	Maize cobs	45 ± 11	0.80	0.94 ± 0.13	0.94 ± 0.03	1.64 ± 0.2	1.45 ± 0.3	19.8 ± 0.1	15.0 ± 1.2
	Wheat straw	13[a]	0.95	0.97 ± 0.12	0.98 ± 0.12	1.38 ± 0.1	1.46 ± 0.3	5.8 ± 1.4	7.8 ± 1.6
	Green waste	6 ± 9.7	0.79	0.83 ± 0.02	0.82 ± 0.02	1.62 ± 0.3	1.50 ± 0.1	7.8 ± 0.2	10.5 ± 1.1

[a] Measured manually by ruler and excludes length of wheat straw stalk

4.2.1 Barrel design

Flow through the barrels was from top to bottom (Fig. 4.1). Influent flow rate of about 0.056 m^3 d^{-1} was controlled by 1 mm ID micro-tubing. A perforated outlet ring, installed at the bottom of the barrel, supported uniform flow through the media. The water level in the barrel was held constant at about 20 mm above the top of the media by riser pipe to maintain media saturation and stable hydraulic head. 50 mm ID PVC screen, pipes and fittings were fitted near the base of the barrel for measuring hydraulic conductivity of the media. Carpet underlay was wrapped around heated barrels to reduce heat lose. Lids were placed on the top of each barrel for insulation.

Municipal potable water dosed with potassium nitrate (KNO_3) was the influent water for the trial. Stable hydraulic head pressure of about 3 m was maintained to the inlet lines by header tanks to facilitate uniform influent flow rate. Metering pumps were used to inject KNO_3 solution at the required rate into mixing manifolds installed in the inlet line providing a final influent NO_3-N concentration of about 150 mg L^{-1}.

A heat pump was used to maintain temperature inside the shipping container and resulted in a temperature gradient from about 15°C at the floor to 20°C at the ceiling. The unheated barrels were located on the floor of the container and the heated barrels located above on shelving.

Temperature in the heated barrels was maintained by heating influent water to about 36°C with a thermostatically controlled heating element installed in the header tank. In the heated barrels, temperature decreased from about 28 to 30°C at the top to about 18 to 20°C the base of the barrel. The mean of these temperatures throughout the trial was 23.5°C. The vertical temperature gradient in the unheated barrels varied between 0 to 2°C from top to bottom of the barrel and the average temperature was 14°C. The mean difference between the two temperature treatments throughout the trial was 9.5°C.

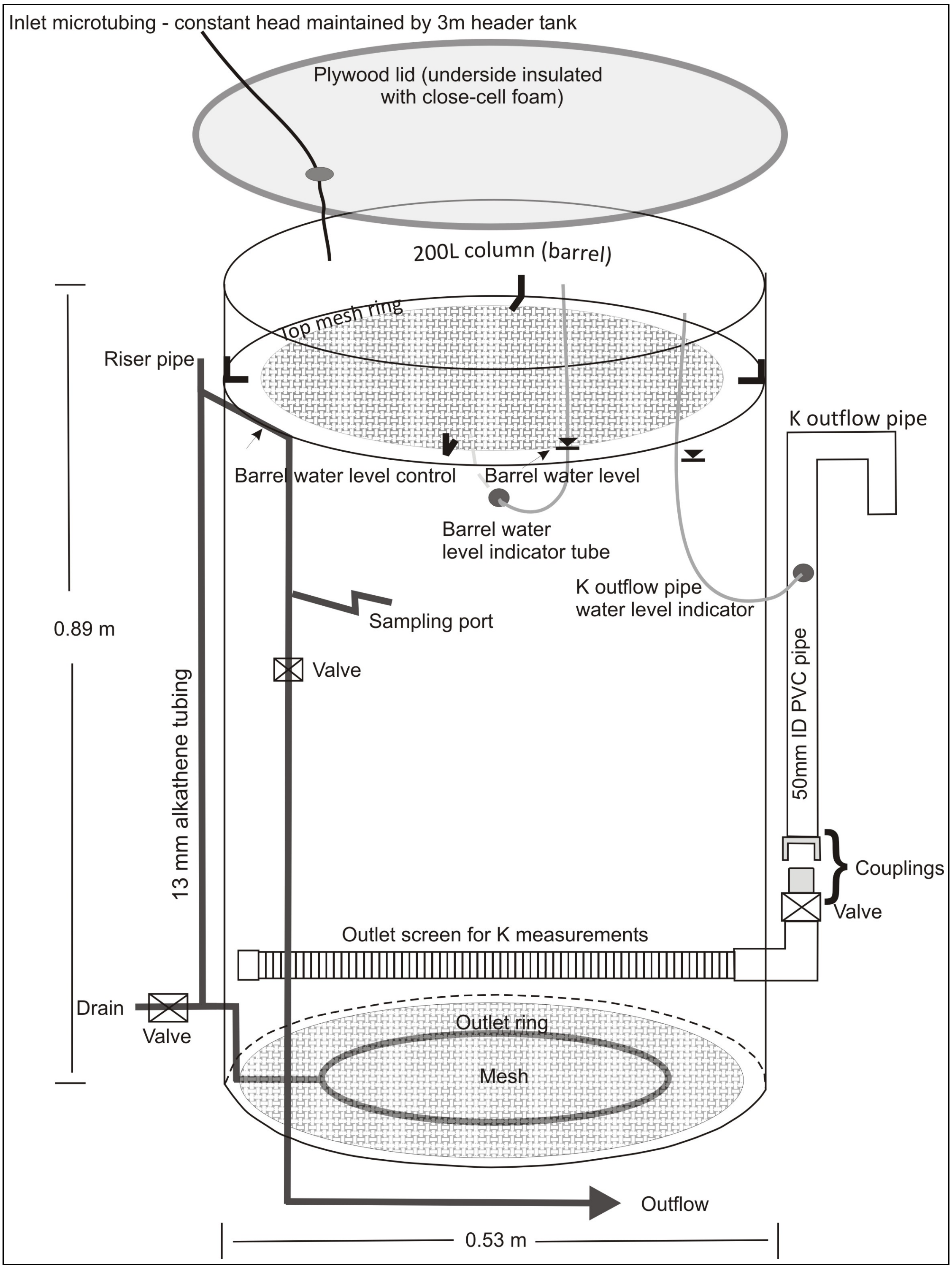

Figure 4.1 Barrel design.

4.2.2 Tracer test

A bromide tracer experiment was undertaken on all 36 barrels, 12 months after start-up to evaluate flow characteristics (including short-circuiting) through the different carbon media and the effect of temperature on hydraulic flow properties.

Potassium bromide (3 g) dissolved in 2.2 L of deionised water, providing a tracer concentration of 1 g L^{-1} Br, was added to each barrel. The tracer was added as an exponential decay input by inserting the inlet line into the tracer solution container, causing the tracer in the container to flow into the barrel. This method of tracer input was preferred over a pulse input as it did not involve a sudden input of high concentration KBr that may have preferentially flowed to the bottom of the barrel due to greater density than the surrounding water. Nor did the tracer input method alter flow rate into the barrels.

Based on the results of a preliminary tracer experiment, outlet samples were collected at 4 hour intervals for the first 30 hours, between 4 and 8 hours until approximately 80 hours and thereafter at daily intervals until 10 days. Six samples were collected from each tracer input solution container, during the first twelve hours, to check that tracer input matched the theoretical exponential decay input, which it did in all cases.

All samples were stored at $4^{o}C$ following collection until analysed. Analyses were undertaken using a Metrohm Br ion selective electode connected to a Metrohm 781 pH/ion meter.

4.2.3 Hydraulic properties

Measurements of the primary and secondary porosity for each media type were made prior to the start of the trial and at the end. The primary or drainable porosity (Brutsaert, 2005) of each media was measured from the volume of water that drained from the bottom of an initially saturated barrel over a 24 hour period. A sample of the drained media was then taken from the barrel, weighed and dried in an oven at $40^{o}C$ until constant weight was achieved. Secondary porosity was then estimated from the difference in wet and dry media weights. Total porosity was calculated as the sum of the primary and secondary porosities.

Theoretical HRT for each barrel was calculated by multiplying the volume of media (m^3) by primary porosity (%) divided by flow rate (m^3 d^{-1}). Additional residence time of water in the 20 mm depth of water above the top of the media and the 2.2 L container of tracer solution was added to the HRT value.

Grain size distribution of media was determined by sieving for the finer grained size component and by manual measurement for the larger grain-size component of the media. Reported grain size (Table 4.1) is the mean arithmetic value and the standard deviation (degree of sorting).

4.2.4 Data analysis

4.2.4.1 Tracer test

Residence time distribution (RTD) moment analysis was used to estimate the Br tracer retention time in the barrel (Levenspiel, 1972; Kadlec and Knight, 1996; Martinez and Wise, 2003). The RTD, also called the *E* curve, is calculated from:

$$E(t) = \frac{Q(t)C(t)}{M_O}$$

Where $E(t)$ = RTD (d^{-1}); $Q(t)$ = volumetric flow rate exiting the barrel ($m^3\ d^{-1}$) at time t (d); $C(t)$ = concentration of Br exiting the barrel ($g\ m^{-3}$) at time t; and M_0 = total mass of Br recovered at the outlet of the barrel (g).

Moment analysis of the RTD defines the parameters used to characterize hydraulic performance. The zeroth moment is the mass of tracer (M_o) that was recovered at the barrel outlet and is defined as:

$$M_O = \int_0^\infty Q(t)C(t)dt \cong \sum_{i=1}^{n} Q_i(t)C_i(t)\Delta t \qquad (1)$$

where n = number of samples. The normalized first moment is the centroid of the area under the RTD, which is the tracer retention time $\bar{t}$ (d).

$$\bar{t} = \int_0^\infty tE(t)dt \cong \sum_{i=1}^{n} t_i E_i t\Delta t \qquad (2)$$

The hydraulic efficiency (e_V) of media in the barrel can be defined as the ratio $\bar{t}$: HRT (Martinez and Wise, 2003; Kadlec and Wallace, 2008). In a saturated porous media absolute values of e_V depend on the type of porosity (primary, effective or total) used to calculate HRT. Typically an e_v value of 1 indicates uniform (plug) flow and values less than 1 are a measure of short circuiting. However, e_V values of greater than 1 can be calculated if primary porosity is used and it is less than effective porosity or movement of fluid into secondary porosity increases retention times.

4.2.4.2 Statistical analysis

All statistical analyses were undertaken using Origin version 8 software (MA, USA). Two-way analysis of variance was used to test for significant differences in tracer residence times, porosities and e_V between different media and temperature treatments. Tracer residence times were cube-root transformed prior to analysis to normalise the data. The Tukey Test was used for post-hoc comparison of means. A paired T-test was undertaken to determine if the means of the total porosity of the media at the start and end of the trail were significantly different. Linear regression was used to determine if the relationship between the primary and secondary porosity of media was significant. Non-linear (log) correlation was used to determine if the correlation between hydraulic efficiency and media grain-size was significant. All significant testing was at the 95% confidence level (CL). Reported error values are ±1 standard deviation.

4.3 Results

4.3.1 Tracer test retention time

Tracer retention times ($\bar{t}$) in the barrels with wood and maize cob media were between about 0 to 1.7 days longer in the 23.5°C media than in the equivalent 14°C media ($F_{(1,23)} = 9.9$; $P < 0.01$) (Figs. 4.2 and 4.3A). Tracer retention time was similar for other media between temperature treatments. Tracer retention time increased as particle size increased in the 23.5°C wood media ($P < 0.01$) but did not differ with particle size in the 14°C temperature treatment.

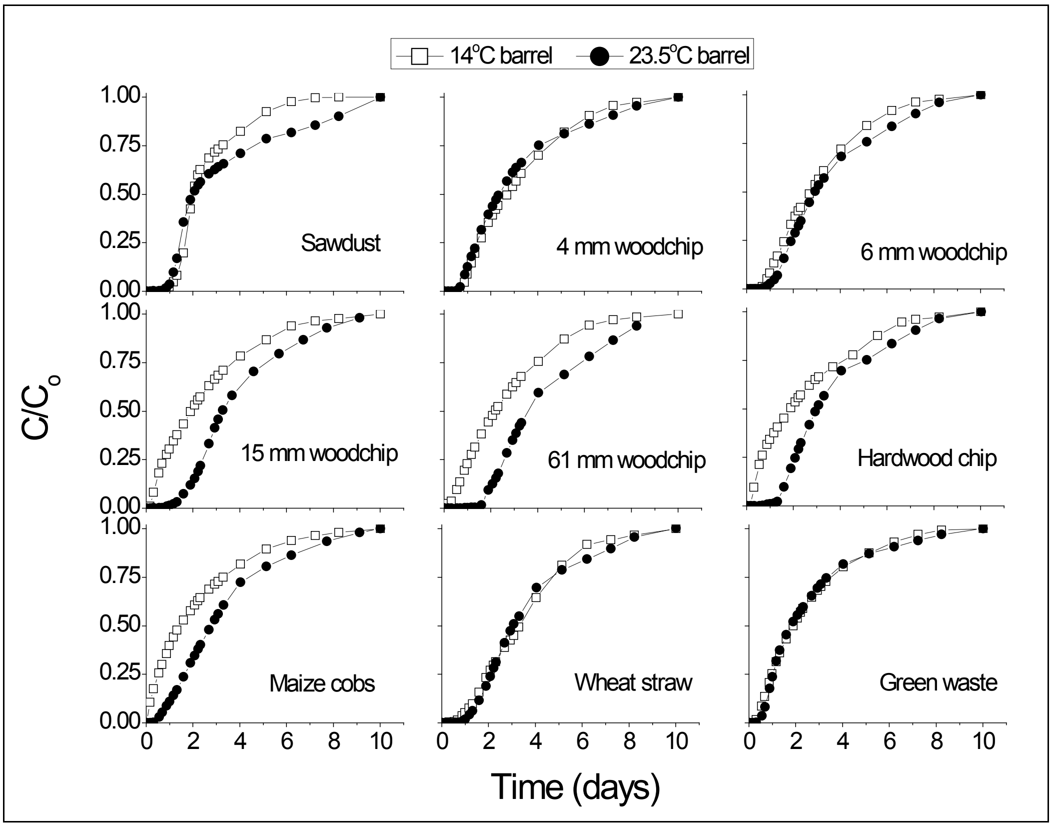

Figure 4.2 Normalised (C/Co) KBr breakthrough curves for tracer tests undertaken on the 0.2 m^3 barrels at 12 months after start of the trial. Each curve is an average of the breakthrough curve of two repeat treatments.

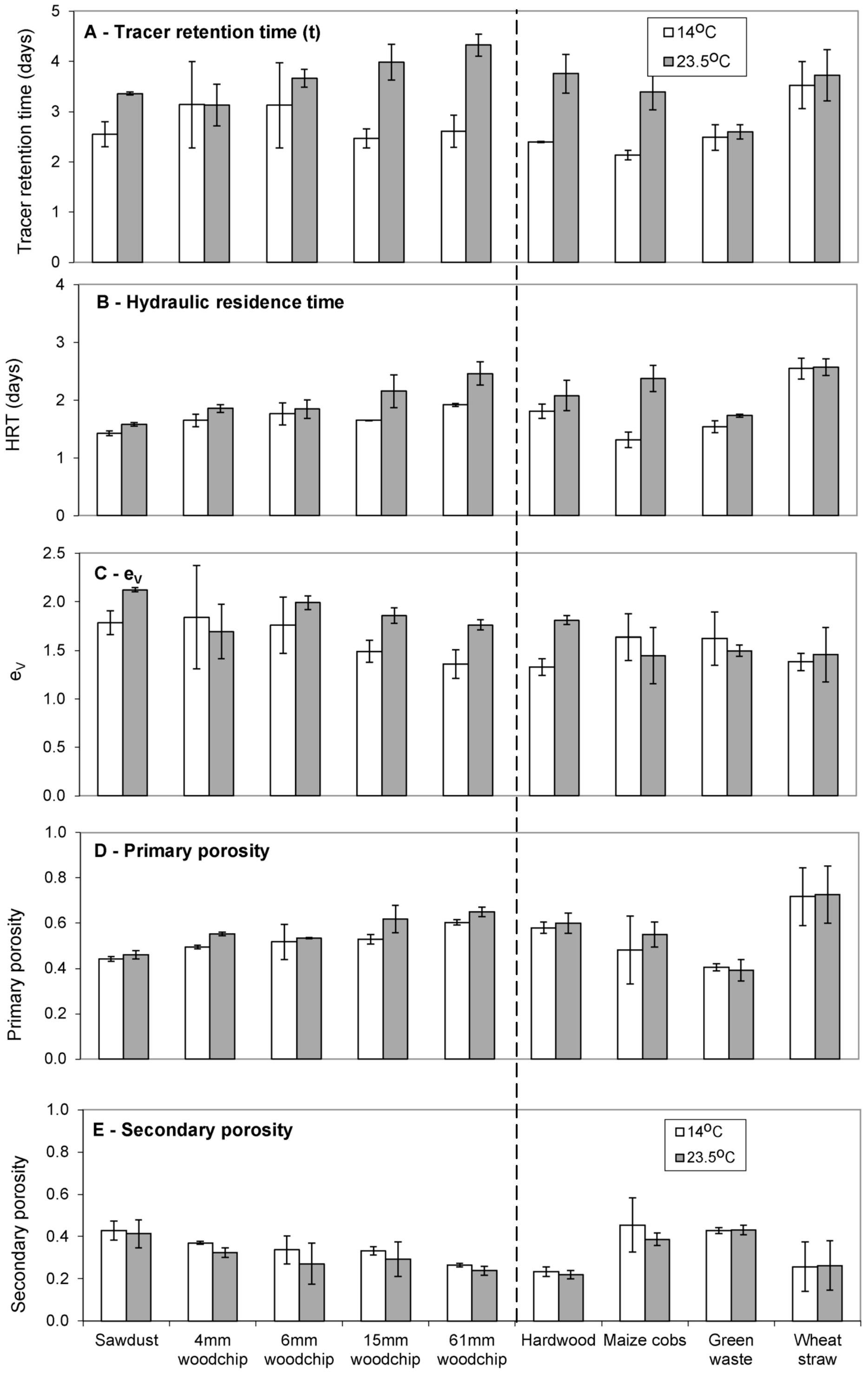

Figure 4.3 A) Tracer retention time ($\bar{t}$); B) theoretical hydraulic residence time (HRT); C) hydraulic efficiency (e_V); D) primary porosity; E) secondary porosity, of carbon media in the 200 L barrels. The porosity measurements were made at the end of the trial (23 months). The tracer tests were undertaken 12 months after the start of the trial. The vertical dashed line separates softwood (*Pinus radiata*) of increasing grain-size from other tested carbon media. Error bars are 1 standard deviation.

4.3.2 Porosity

Total porosity for all media ranged from 0.80 ± 0.10 to 0.98 ± 0.12 at the end of the trial and was similar within media type between temperature treatments (Table 1). The total porosity of all media increased slightly during the 23 month trial ($P < 0.01$). For example, total porosity of hardwood and wheat straw increased from 0.76 to 0.81 and 0.95 to 0.98, respectively.

There was no apparent pattern in the change of primary and secondary porosity of the media through the trial. Therefore, primary and secondary porosity measurements made at the start of the trial are not presented or further discussed. However, comparison of primary and secondary porosity of media at the end of the trial indicated a relationship between media grain-size, temperature and porosity. At the end of the trial, primary porosity increased with particle size for softwood media at both temperatures and was inversely related to secondary porosity ($P<0.01$) (Table 4.1 and Figs. 4.3D and 4.3E). Primary porosity of softwood media ranged from 0.44 for sawdust up to 0.65 for the 61 mm woodchip. The secondary porosity of all media was considerable with values ranging from 0.22 for hardwood up to 0.45 for maize cobs (Fig. 4.3E).

The primary porosity of softwood, hardwood and maize cob media was higher in the 23.5^{o}C treatment than in the 14^{o}C treatment ($F_{(1,27)} = 5.4$; $P < 0.05$) (Fig. 4.3D). Conversely, the secondary porosity was generally lower in the 23.5^{o}C treatment than in the 14^{o}C (Fig. 4.3E), although this difference was not significant ($F_{(1,27)} = 3.5$; $P = 0.08$). On average, the 23.5^{o}C softwood media had 10% higher primary porosity and a 12% lower secondary porosity than the corresponding 14^{o}C media. Hardwood and maize cobs had 3% and 14% increases in primary porosity and 6% and 15% decreases in secondary porosity, respectively, between the temperature treatments. There was no measurable difference in porosity for the green waste and wheat straw between temperature treatments.

4.3.3 Hydraulic efficiency and nitrate removal

The hydraulic efficiency (e_V) value of all media was greater than 1 (Fig. 4.3C), e_V ranged from about 1.3 for 14^{o}C hardwood up to 2.1 for 14^{o}C sawdust. Typically an eV value of 1 or greater indicates no short-circuit flow, or that physiochemical retardation of the tracer occurred.

Generally, there was little difference in e_V between media or temperature treatment (Fig. 4.3C), with the exception of sawdust and wheat straw which were significantly different from one another ($P < 0.05$). However, e_V was generally higher for the 23.5°C soft- and hard-wood media than for the corresponding 14°C media, with the exception of 4 mm woodchip, although the difference was only significant at $P=0.07$. Also e_V generally decreased with increasing grain-size in the softwood media in both temperature treatments ($P < 0.05$).

The nitrate removal rates of media in this trial were previously reported by Cameron and Schipper (2010) and removal rates for the period 10 to 23 months after start-up are included in Table 2.1. There was no correlation between hydraulic efficiency and nitrate removal rate when all media were considered, nor when only softwood media of varying grain-size were considered.

4.4 Discussion

4.4.1 Hydraulic efficiency and nitrate removal rate

The main objective of this study was to determine whether differences in hydraulic efficiency (e_V) of media might partially explain differences in nitrate removal rates which ranged from 2.2 ± 0.02 to 19.8 ± 0.1 for different carbon media (Table 4.1). However, we found no evidence to support this hypothesis.
The nitrate removal rates of media in this trial were previously reported by Cameron and Schipper (2010) for non-nitrate limiting conditions (Table 4.1). Removal rates were significantly higher in the 23.5°C media than in the 14°C media and were significantly higher for the more labile carbon media (maize cobs, wheat straw and green waste) than for both soft- and hard-wood media. However, nitrate rates were similar for different grain-size of softwood media within temperature treatments. In the current study, we found no correlation between nitrate removal rates reported by Cameron and Schipper (2010) and hydraulic efficiency. This was in spite of the significant differences in removal rates between temperature and media treatments and indication that hydraulic

efficiency of softwood media decreased with increasing grain-size. Clearly temperature and carbon availability of the media were more important for controlling nitrate removal rate than hydraulic efficiency. Decreases in nitrate removal rate could still occur in operational beds where there was greater short-circuiting, such as in poorly designed or located inflow and outflow structures (Christianson et al., 2011).

Techniques to improve the nitrate removal performance of denitrification beds should therefore focus on increasing bed temperature (e.g., Cameron and Schipper, 2011) and availability of carbon media to denitrifiers rather than on the hydraulic efficiency of carbon media due to particle size and porosity. For wood based beds, larger grain-size media should be used as larger grain-size had greater hydraulic conductivity (Cameron and Schipper, 2010) without any loss in nitrate removal performance. Greater hydraulic conductivity of media allows for higher hydraulic loading rates to a bed and reduces the risk of exceeding the hydraulic capability of the bed, which would result in surface flooding. Greater hydraulic conductivity may also cope better with long-term accumulation of suspended solids and be more resilient to different effluents and pulse events of poor quality effluents due to upstream system failure.

4.4.2 Hydraulic efficiency

Theoretically an e_V value of 1 indicates uniform (plug) flow. Values less than 1 suggest short-circuiting while values greater than 1 indicate physical or chemical retardation of tracer in the system. Temporary chemical retardation of the tracer was not considered to be the cause of e_V values exceeding 1 as generally more than 90% of the tracer was recovered from all barrels within 10 days. Rather, the high eV values were likely caused by: 1) movement of the tracer into and out of the secondary porosity of the media causing longer residence time of tracer in the barrel; 2) underestimation of HRT due to the primary porosity value used in the calculation being less than effective porosity; and 3) the log decay method by which the tracer was input into the barrels. Other treatment wetland studies have reported e_V values greater than 1 and suggested this indicates areas of physical retardation (Chazarenc et al., 2003; Kadlec and Wallace, 2008).

The log decay method of tracer input was unlikely to be responsible for high e_V because while it took 4.5 hours for 99% of the tracer to flow into the barrel the average $\bar{t}$ was about 1.2 days longer than HRT (Figs. 4.3A and 4.3B). Therefore, the most plausible explanation for high e_V was the movement of tracer into the secondary porosity and underestimation of HRT. The e_V values presented are a comparative measure of hydraulic efficiency between media treatments with higher values representing more plug-like flow and lower values suggesting greater short-circuiting.

Higher e_V of the 23.5°C soft- and hard- wood media compared to the corresponding 14°C media was attributed to the increase in primary porosity of the wood media with increasing temperature (Figs. 4.3 C and 4.3D).

A secondary objective of this study was to determine if the grain-size of the media influenced hydraulic efficiency. Hydraulic efficiency generally decreased with increasing grain-size of softwood media in both temperature treatments, suggesting slightly greater short-circuiting in the larger grain-size media (Fig. 4.3C). More short-circuiting may have taken place within the larger inter-granular pore spaces of the larger grain-sized media, as indicated by the higher primary porosity of these media (Fig. 4.3D). However, generally the difference in e_V of soft wood media was small suggesting that increasing grain-size only caused a minor increase in the degree of short-circuiting over the range of grain-sizes tested in this study.

4.4.3 Changes in porosity due to temperature

Measurement of primary and secondary porosity of the nine media was undertaken prior to the start of the trial at ambient air temperature. However, results of tracer tests indicated there was likely a difference in media porosity between temperature treatments. Therefore, primary and secondary porosity of the media in each barrel was re-measured at the end of the trial. Primary porosity was found to be higher in the 23.5°C wood and maize cob media than in the corresponding 14°C media and was inversely correlated to secondary porosity (Figs. 4.3D and 4.3E).

The 10% increase in primary porosity and 12% decrease in secondary porosity of the wood media in the 23.5^{o}C treatment, compared to the 14^{o}C treatment may be attributed to contraction of the media with increasing temperature, usually called negative thermal expansion. Contraction of water-saturated and moist wood in the temperature range 20 to 60^{o}C has been previously reported (Kubler et al., 1973; Salmen, 1990). The contraction has been attributed to the movement of water from the cellulose to the surrounding water phase as temperature increases up to about 60^{o}C (Westman and Lindström, 1981). The co-efficient of linear thermal expansion (α) of Norway spruce and redwood was about -10 to -25 x 10^{6} mm / (mm ^{o}C) at about 20 to 25^{o}C (Salmen, 1990; Kubler et al., 1973). Linear thermal expansion is a property of materials that can be expressed as $\Delta l = Lo \times \alpha \times \Delta T$, where Δl is the change in length of material in the direction being measured; Lo is the initial length, and ΔT is the change in temperature over which Δl is measured. This possible decrease in dimensions with increasing temperature was small but may have increased the space between particles (primary porosity) while reducing the pore space within the particle (secondary porosity). Contraction of the wood particle would also be expected to reduce the movement of water (and tracer) into and out of the smaller cavities and cause a decrease in secondary porosity.

Changes in wood media primary and secondary porosities due to temperature have not been previously reported. These changes suggest that the operating temperature of a denitrification bed may need to be considered when estimating its HRT due to increase in primary (and effective) porosity of wood media due to temperature. However, while the difference in porosity of media influenced hydraulic efficiency, we found no correlation between hydraulic efficiency and nitrate removal rate.

4.4.4 Changes in porosity with time

The 4% increase in average total porosity of all media during the trial was likely caused by loss of carbon from the media due to microbial decomposition and flushing of fines from the barrel due to water flow. The increase in total porosity during the trial was about 10% higher in the 23.5^{o}C media than in the 14^{o}C media, which may have been caused by greater microbial decomposition in the higher temperature media. Robertson (2010) also attributed greater secondary porosity of wood media that had been in a denitrification bed for 7 years, compared to younger media, to additional carbon loss that had occurred in the older media. Similarly, Xu et al. (2009) reported a 38% decrease in dry weight of corn cob media over their study period, which was attributed to carbon loss. Also, the contraction of wood with increasing temperature (Salmen, 1990) may have contributed to greater increase in total porosity of the 23.5°C wood media compared to the 14°C media. The 23.5°C wood media had a 20% greater increase in total porosity during the trial compared to the 14°C wood media.

4.5 Conclusions

The hydraulic efficiency (e_V) of carbon media was not an important influence on nitrate removal rate under non-nitrate limiting conditions. Rather nitrate removal rate was mainly dependent on temperature and carbon availability of the media (Cameron and Schipper, 2010). Under nitrate limiting conditions, hydraulic efficiency may be a more important influence as short-circuiting would reduce the contact between nitrate and active sites of denitrification.

While e_V was generally similar between media, there was tendency for e_V to decrease with increasing softwood media particle size and e_V was generally higher in the 23.5°C wood and maize cob media than in the corresponding 14°C media. The decrease in e_V with increasing particle size suggests short-circuiting increases with increasing grain-size. Higher e_V in the 23.5°C media was likely due to the greater primary porosity of these media which increased pore water volume and tracer residence time.

Primary porosity increased with softwood media particle size and was correlated to decrease in secondary porosity. The higher primary porosity and lower secondary porosity of the 23.5°C wood media may have been caused by contraction of the media particle with increasing temperature due to loss of water from the cellulose to the primary porosity water phase.

The results suggest that future research on increasing the nitrate removal performance of denitrification beds should focus on increasing bed operating temperature and incorporating labile carbon media rather than on the hydraulic efficiency of the media. Our results suggest that larger particle size media should be used as these provide for greater hydraulic load and reduced risk of over topping without any apparent loss of nitrate removal performance.

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Chapter 5

Evaluation of Passive Solar Heating and Alternative Flow Regimes on Nitrate Removal in Denitrification Beds

This chapter was published as the following journal paper and is presented in this thesis in journal format.

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Contribution of contributing authors were:

Cameron, S.G.: Experimental design, trial setup, sampling, data analysis, primary write-up.

Schipper, L.A., Experimental design, advisor, primary review.

A photograph of the pilot scale trial that was not included in Cameron and Schipper (2011) is presented as Figure 5.1 on the following page.

Figure 5.1 – Photograph of pilot scale denitrification bed trial. The poly-carbonate solar covers are on first (bed 1), third (bed 3) and fifth (bed 5) beds from the left. The 15 mm diameter white PVC tubes that can be seen protruding from beds 2, 3 and 5, housed the temperature probes. The loggers and batteries used to record temperature measurements were housed in three instrument boxes located between beds 1 and 2, beds 3 and 4, and beds 5 and 6 (lying on ground). The 5000 L SAF plant can be seen in the background on the left-hand side of the storage pond. The effluent from the beds discharged, by gravity drainage, into the storage pond.

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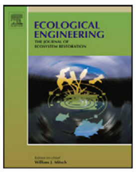

Evaluation of passive solar heating and alternative flow regimes on nitrate removal in denitrification beds

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ABSTRACT

Denitrification beds are a simple and relatively inexpensive technology for removing nitrate from point source discharges. To date, operational beds have used wood media as the carbon source, as it provides a sustained nitrate removal rate (2–10 g N m^{-3} of media d^{-1}) while maintaining permeability. In pilot-scale (2.9 m^{-3}) denitrification beds receiving municipal wastewater effluent dosed with KNO_3, we looked at improving nitrate removal by using alternative carbon media (maize cobs) and increasing bed temperature through passive solar heating. The influence of flow regime (horizontal-point, horizontal-diffuse, downflow and upflow) on short-circuit flow was also investigated.

The long-term nitrate removal rate (21.8 g N m^{-3} d^{-1}) of the maize cob beds over the 15-month period of the trial was 2–11-fold higher than sustained removal rates reported by other researchers for wood-based beds. While passive solar heating raised the mean bed temperature by 3.4 °C, it did not cause a measurable increase in the nitrate removal rate due to the variability in the removal rate exceeding the expected increase due to temperature.

Horizontal flow had more short-circuiting than vertical flow. Short-circuiting in the horizontal flow was attributed to flow being concentrated near the top surface due to the buoyancy effect of warmer water. Greater short-circuiting in the solar heated horizontal and upflow beds than in the corresponding unheated beds was attributed to the buoyancy effect being more pronounced in the solar heated beds.

Overall, downflow was deemed the most effective of the four tested flow regimes. It provided the highest increase in bed temperature due to solar heating, had the highest nitrate removal rate in the latter part of the trial and had more plug-flow characteristics. While passive solar heating raised bed temperature, we were unable to demonstrate a significant difference (at 95% CL) in nitrate removal rate between the unheated and solar heated beds because of the high variability in nitrate removal rate and the increase in short-circuiting in the solar heated horizontal and upflow beds.

1. Introduction

Excess nitrogen (N) in ground- and surface-waters has been identified as a global environmental issue (Galloway et al., 2003) contributing to loss of biodiversity, and habitat degradation in coastal and terrestrial waters (Howarth et al., 2002). The discharge of nitrogen-laden waters from domestic, municipal, industrial and farming origin contributes to the issue of elevated nitrogen in the aquatic environment.

Denitrification beds have been shown to be an effective method of removing nitrate (NO_3) from point source discharge originating from: municipal and septic systems (Schipper et al., 2010b; Robertson et al., 2005), agricultural tile drains (Blowes et al., 1994; van Driel et al., 2006) landfills (Robertson and Anderson, 1999), dairy sheds and hydroponic glass houses (Schipper et al., 2010b). The bed is essentially a lined cavity or container filled with solid organic carbon matter through which nitrified effluent is passed. Denitrification is inferred to be the dominant nitrate removal process occurring within the bed (Robertson et al., 2000; Schipper et al., 2010a; Greenan et al., 2006; Gibert et al., 2008), with nitrate (NO_3) being converted to nitrogen gas (N_2) by microbial denitrification.

To date, most of the field scale denitrification beds have incorporated wood products as the carbon media with longer-term nitrate removal rates for field scale denitrification beds ranging from 2 to 10 g N m^{-3} (of media) d^{-1} (Schipper et al., 2010a). Higher nitrate removal rates (up to about 200 g N m^{-3} d^{-1}) have been reported for more labile carbon media including: straw, leaf compost, cotton

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burr, newspaper, cardboard, corn stalks and maize cobs (Schipper et al., 2010a; Cameron and Schipper, 2010). However, there is indication that nitrate removal rates for the more labile carbon media decline more rapidly over time than the wood media (Soares and Abeliovich, 1998; Greenan et al., 2006; Cameron and Schipper, 2010).

Nitrate removal rates in denitrification beds are dependent upon a combination of carbon availability of the media (Greenan et al., 2006; Gibert et al., 2008; Cameron and Schipper, 2010), temperature (van Driel et al., 2006; Robertson et al., 2008, 2009; Cameron and Schipper, 2010; Schipper et al., 2010) and influent nitrate concentration (Schipper et al., 2010). Many authors have also noted the importance of hydraulic design on treatment performance of constructed wetlands and ponds (Brown, 1994; Persson, 2000; Martinez and Wise, 2003; Kadlec and Wallace, 2008), with plug flow considered to be the ideal (WPCF, 1990); however, this aspect has only been superficially addressed in the denitrification bed literature (van Driel et al., 2006).

This present study investigates the effect of temperature and hydraulic design on the nitrate removal rate of denitrification beds under non-nitrate limiting conditions. The influence of carbon availability of the media and influent nitrate concentration on nitrate removal are not discussed.

1.1. Temperature

Nitrate removal rates have been shown to increase with temperature (Robertson et al., 2008, 2009; Cameron and Schipper, 2010). Cameron and Schipper (2010) found that the mean Q_{10} (the factor by which a reaction rate increases with a 10 °C rise in temperature (Anderson and Janssens, 2006); Eq. (1)) for nine different carbon substrates was 1.6:

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{(10/(T_2-T_1))} \tag{1}$$

where R_1 and R_2 are the reaction rates at temperatures T_1 and T_2 (in °C), respectively; and $T_2 > T_1$.

Therefore, increasing bed temperature should increase nitrate removal rates, but heating using external power would be expensive, particularly for large beds. Passive solar heating techniques may offer an inexpensive approach for heating beds for little to no cost beyond initial construction. Passive solar heating captures energy from solar radiation without requiring moving parts (Stanley, 2004). Typically, the method incorporates a dark coloured object (thermal mass) to absorb short-wave radiation that is then released as longer wave length infrared radiation (heat). A clear cover, such as glass, over the object, allows sunlight to pass through but inhibits the transfer of the re-emitted lower energy wavelengths, thereby trapping the heat. The cover also inhibits mixing of the air beneath with cooler outside air. An effective thermal mass stores and continues to dissipate heat when solar radiation decreases at night. Denitrification beds are likely to be a good thermal mass as they contain considerable amount of water which has high heat storage.

1.2. Hydraulic efficiency

Short-circuit flow in a denitrification bed can also decrease the nitrate removal rate due to reduced interaction of nitrate with potentially active sites of denitrification. Short-circuiting may reduce the treatment volume by causing denitrification in zones of slow or stagnant water to become nitrate limited. The degree of short-circuiting in a bed can potentially be affected by inlet-outlet location and hydraulic design.

In treatment wetlands, the hydraulic design and relative location of inlets and outlets can influence hydraulic and nutrient treatment efficiencies (Kadlec and Wallace, 2008). For example, Persson (2000) and Persson and Wittgren (2003) demonstrated that hydraulic efficiency of constructed ponds varied with pond shape and inlet-outlet location and design using a computational fluid-dynamic model. In contrast to research on wetlands there is little information on the importance of different inlet and outlet structures of denitrification beds and the potential for short-circuiting.

The objectives of this study were to determine: (1) if solar heating could be used to increase the temperature of a denitrification bed and increase nitrate removal and (2) if different inlet/outlet structures altered hydraulic efficiency and nitrate removal rate in a denitrification bed. These objectives were tested in a small field-scale experiment using six denitrification beds (2.9 m^3), filled with maize-cobs and loaded with secondary treated municipal sewage. Clear polycarbonate covers were periodically placed on three of the beds to determine the extent of passive solar heating. Four different flow regimes (horizontal-point, horizontal-diffuse, downflow and upflow) were assessed. Temperature distribution in the beds, with and without solar covers, was measured and hydraulic efficiency determined using bromide tracer tests. The nitrate removal rate was also measured throughout.

2. Methodology

The experiment was undertaken in six denitrification beds constructed at the Taupo District Council municipal waste water treatment plant (WWTP), Taupo, New Zealand.

2.1. Bed design

Dimensions of the bed boxes were 2.4 m long × 1.2 m wide × 1.2 m high. The walls of beds were constructed from 13 mm thick plywood fitted with an interior impermeable PVC liner. The walls of the beds protruded 0.5 m above ground level to allow for gravity drainage from the bed outlets into an in-ground storage pond. Each bed was fitted with several inlet/outlet structures (Fig. 1a) to allow for testing of the four different flow regimes (Table 1). All inlet and outlet piping was 15 mm ID unless other wise specified. Horizontal-point flow had a single pipe as the inlet and outlet. The inlet and outlet structures of horizontal-diffuse flow had three vertical perforated pipes evenly distributed across the cross-sectional area of the bed and connected at the base. The downflow had perforated pipes in a rectangle pattern, which was evenly located over the top and at the bottom of the bed, as the inlet and outlet. Upflow used the same rectangular inlet and outlet piping as downflow, with the flow direction reversed. While in use, inlet and outlets were flushed with a small volume of tap water at about weekly interval to remove biofilm blockage.

The beds were filled with 2.9 m^3 of deseeded maize cobs as the carbon source. The media was weighed down with concrete paving stones because gas bubble formation caused the cobs to float.

The solar covers were made of corrugated polycarbonate roofing sheets fitted to a wooden frame that provided a tight fit over the top of the bed. Gaps between the ridges of the polycarbonate and frame were plugged with corrugated close-cell foam strips. Black polythene was placed between the solar covers and the bed. A 20 m coil of 20 mm ID black polyethylene tubing was placed between the polythene and the solar cover to heat the influent water before discharging into the bed. Residence time of influent in the coil was about 13 min.

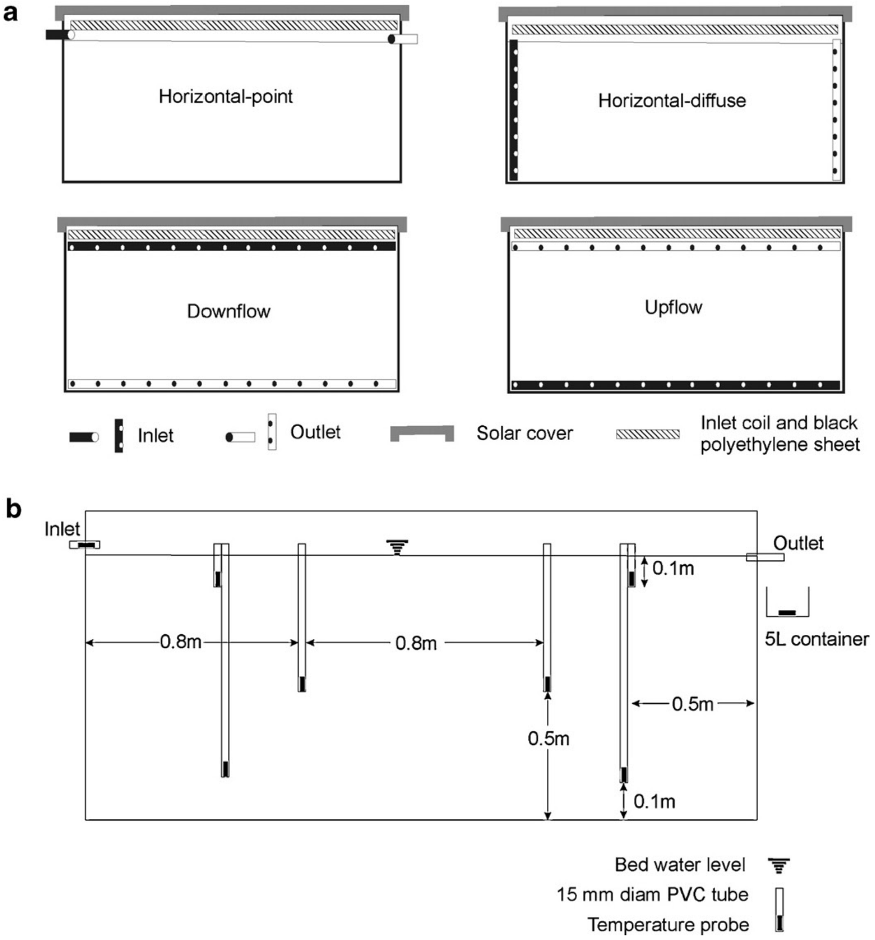

Fig. 1. Bed design. (a) Profiles of bed flow regimes showing inlet and outlet location, and solar heating apparatus. The dimensions of all beds were 2.4 m long × 1.2 m wide × 1.2 m deep. Water and media depth in the beds were 1 m. (b) Location of temperature probes.

Table 1
Summary of bed flow regimes and tracer tests.

Treatment	Flow regime	Period (months since start-up)	Tracer test reference no.	Solar cover	Number of beds	Theoretical HRT (days)	Tracer retention time (days)
1	Horizontal-diffuse	0–8	1 @ 5 months (autumn)	Not installed	3	5.3 ± 1.9	4.1 ± 0.7
	Horizontal-point			Not installed	3[a]	5.0 ± 0.5	2.6 ± 0.2
	Horizontal-point	4		Installed	1	No tracer test undertaken	
2	Horizontal-diffuse	9–13	2 @ 10 months (mid-spring)	Not installed	3	2.4 ± 0.2	1.3 ± 0.4
	Downflow			Not installed	3	2.4 ± 0.3	2.2 ± 0.2
3	Horizontal-diffuse		3 @ 13 months (summer)	Installed	1	3.6	1.5
				Not installed	2	3.4 ± 0.01	2.2 ± 0.3
	Downflow			Installed	2	2.9 ± 0.14	2.2 ± 0.1
				Not installed	1	4.3	3.4
4	Horizontal-diffuse	14–15	4 @ 15 months (summer)	Installed	1	3.8	2.2
				Not installed	2	4.0 ± 0.2	3.3 ± 0.2
	Upflow			Installed	2	4.4[b]	3.5[b]
				Not installed	1	4.6	4.3
	Mean					3.8	

[a] Solar heating of one horizontal-point bed was undertaken during month 4.
[b] Data not included for one bed which had periodic block of outflow during the tracer test.

2.2. *Influent*

Flow rate into each bed was measured by time to fill a container of known volume. Measurements were made during water quality sampling and tracer test experiments.

Secondary treated municipal effluent (3.4 $m^3\ d^{-1}$) was pumped from the WWTP clarifier outlet into a 5000 L submerged aeration filter (SAF) pilot treatment plant for nitrification of the effluent. KNO_3 was added to the SAF plant effluent to increase the NO_3-N concentration to approximately 200 mg N L^{-1} before discharging into the denitrification beds. The high influent nitrate concentration was required so that nitrate limiting conditions did not occur in the beds. A weir box, with six levelled v-notch weirs, was fitted to the outlet of the SAF plant to split the flow before it was piped by gravity drainage to the denitrification beds. Mean flow rate through each bed was 0.57 $m^3\ d^{-1}$. While flow into the beds was continuous, flow rate into each bed ranged from about 0.3 to 0.8 $m^3\ d^{-1}$ due to variation in discharge from the WWTP and periodic biofilm build-up in flow lines. Flow lines were routinely flushed with tap water to remove biofilm.

2.3. *Water quality sampling*

Influent and effluent samples were generally taken weekly and analysed for NO_3-N, and temperature. Influent and effluent pH, DO, Total Kjeldahl Nitrogen (TKN), ammonium-nitrogen (NH_4-N) and carbonaceous biological oxygen demand (BOD) were measured about every month. Samples for nitrate and ammonium analysis were passed through a 0.45 μm filter. Samples for BOD and TKN samples were unfiltered. The TKN samples were preserved with sulphuric acid. After collection, all samples were stored at 4 °C until analysis. NO_3-N was analysed by ion chromatography using *Standard Methods* 4110-B (APHA, 2005) while NH_4-N was analysed by phenol/hypochlorite colorimetry using *Standard Method* 4500-NH3-4-114 (APHA, 2005). TKN samples were analysed by sulphuric acid digestion with copper sulphate catalyst and (Total Kjeldahl digestion) phenol/hypochlorite colorimetry, according to *Standard Methods* 4500-Norg C. (modified), 4500 NH3 F (modified) (APHA, 2005). BOD samples were incubated for 5 days, with a nitrification inhibitor added, and measurements obtained by DO meter, according to *Standard Methods* 5210 B (APHA, 2005).

2.4. *Temperature measurements*

Temperature was measured using 58 temperature probes (Campbell Scientific 107) connected to data loggers (Campbell Scientific CR10x and CR500). Three point calibrations of the probes (0 °C, 20 °C and 40 °C) were undertaken at probe installation and removal. Logged temperature measurements were mean hourly values calculated from 10-min interval measurements. Eight probes were installed in each bed (Fig. 1b). Initially, the probes were installed at the same depth on the left and right side in only four of the beds. These probes showed that the temperature was practically identical across the width of the bed so the duplicate probes were shifted to the other two remaining beds. Inlet probes were installed within the inlet pipe to the bed while outlet probes were submerged in 5 L containers into which the beds discharged.

Air temperature at the site was measured by a temperature probe housed within a thermometer radiation shield located 1.5 m above ground surface.

2.5. *Tracer tests*

Four bromide (Br) tracer tests were undertaken on each bed to measure hydraulic efficiency of the different flow regimes and effect of solar heating on hydraulic efficiency. The flow regimes compared by tracer test and schedule are listed in Table 1. The KBr tracer (1 L of 8 g L^{-1} Br) was added as pulse input to the influent of each bed using a dosing pump over a 12-min period. A preliminary tracer test was undertaken to determine appropriate tracer concentration, outlet sampling frequency and duration. All samples were stored at 4 °C following collection until analysed. Analyses were undertaken using a Metrohm Br ion selective electrode connected to a Metrohm 781 pH/ion meter.

2.6. *Hydraulic properties*

To measure porosity of the media, a 200 L barrel filled with maize cobs was saturated with water until a constant water level was achieved after several days. To stop the cobs floating, a reinforced mesh cover was placed over the media and secured to sides of the barrel prior to filling with water. The primary (or drainage) porosity (Brutsaert, 2005) was measured as the volume of water drained after 24-h period. A sample of the drained media was then taken from the barrel, weighed and dried in an oven at 40 °C until constant weight was achieved. Secondary porosity was then estimated from the difference between the drained and dry media weights.

The theoretical hydraulic residence time (HRT) of effluent within the beds (Table 1) was calculated by multiplying the volume of media by primary porosity divided by flow rate.

Hydraulic conductivity (K) of the media in the horizontal flow beds was calculated using the Darcy equation ($q = KIA$) from the flow rate through the bed and hydraulic gradient between bed inlet and outlet (Freeze and Cherry, 1979) (Fig. 1a); where q was the flow rate ($m^{-3}\ d^{-1}$), I was the hydraulic gradient, and A was the cross-sectional area of the bed (m^2). Meaningful hydraulic gradient measurements could not be made for the vertical flow beds because there was only a small vertical variation in hydraulic head.

2.7. *Data analysis*

2.7.1. *Bed temperature*

Mean daily temperatures of each bed were estimated by: (1) calculating mean daily temperature for each of the eight in-bed temperature probes (Fig. 1b) from the 1-h interval data; (2) creating an 11 × 13 grid (143 nodes) of the mean daily temperature probe values using a Kriging method (Surfer version 8, Golden Software, CO, USA; Cressie, 1990); and (3) calculating the mean of the 143 node values as estimate of mean daily bed temperature.

Contours of bed temperature were produced from the 11 × 13 grid by Kriging method (Cressie, 1990) using Surfer version 8 software.

2.7.2. *Tracer test*

The retention time of the Br tracer in the bed was estimated by residence time distribution (RTD) moment analysis (Levenspiel, 1972; Kadlec and Knight, 1996; Martinez and Wise, 2003). The RTD, also called the E curve is:

$$E(t) = \frac{Q(t)C(t)}{M_0} \qquad (2)$$

where $E(t)$ = RTD (d^{-1}); t = time (d^{-1}); $Q(t)$ = volumetric flow exiting the bed ($m^3\ d^{-1}$); $C(t)$ = concentration of Br exiting the bed ($g\ m^{-3}$); and M_0 = total mass of Br recovered at the outlet of the bed (g).

Moment analysis of the RTD defines the key parameters used to characterize the hydraulic performance of a bed. The absolute zeroth moment yields the total mass of tracer that has been recov-

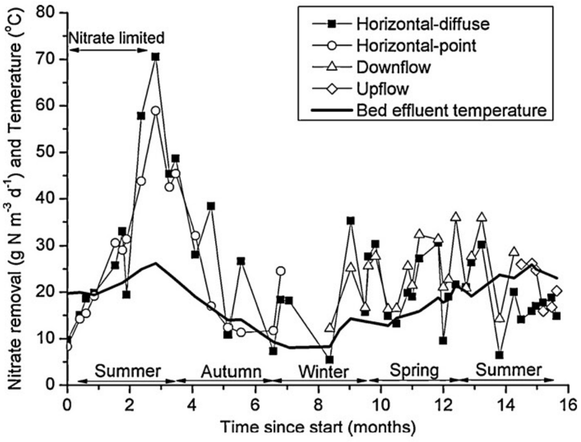

Fig. 2. Mean nitrate removal rate of different flow regimes, includes solar heated and unheated beds. Nitrate removal data are mean values of three beds. To maintain clarity error bars are not shown, but the mean coefficient of variation (σ/μ) was ~30% of the presented value. Bed effluent temperature is the mean of all six beds.

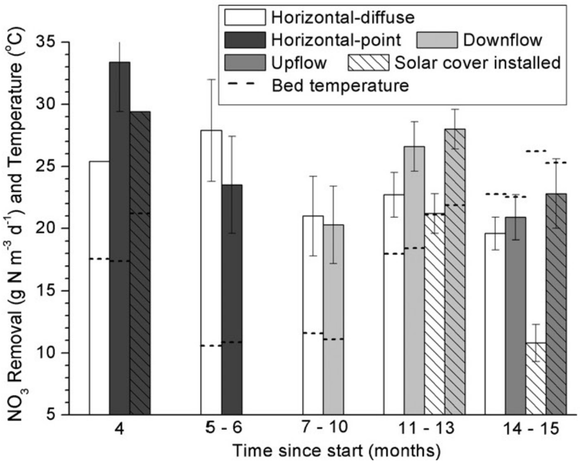

Fig. 3. Mean nitrate removal rate and mean bed temperature of different flow regimes. Error bars are standard error. Hashing shows when solar covers and inlet coil were installed. Dashed lines are bed temperature.

ered at the bed outlet and is defined as:

$$M_0 = \int_0^\infty Q(t)C(t)dt \cong \sum_{i=1}^{n} Q_i(t)C_i(t)\ \Delta t \tag{3}$$

where n = number of samples. The normalized first moment yields the centroid of the area under the RTD, which is the tracer retention time $\bar{t}$ (d).

$$\bar{t} = \int_0^\infty tE(t)dt \cong \sum_{i=1}^{n} t_i E_i t\ \Delta t \tag{4}$$

The hydraulic efficiency (e_V) of a denitrification bed (or wetland cell) can be defined as the ratio $\bar{t}$: theoretical HRT (Martinez and Wise, 2003; Kadlec and Wallace, 2008), where an e_V value of 1 is completely uniform flow and values less than 1 is measure of short-circuiting.

2.7.3. *Significance testing*

Paired T-tests were undertaken (Origin version 8 software MA, USA) to determine significance of differences between means of bed temperature and nitrate removal due to solar heating and flow regime. Linear correlation (Origin version 8 software MA, USA) was used to determine if there was significant correlation between nitrate removal and hydraulic efficiency. All significant testing was at the 95% confidence level (CL). All data are reported as mean values ± 1 standard deviation.

3. Results

3.1. *Nitrate removal*

Nitrate removal in the beds was nitrate limited for the first 2.5 months of operation due to low influent nitrate concentrations (50–100 mg N L^{-1}). Effluent nitrate concentration was less than detection (0.1 mg L^{-1}) during this period. Subsequently influent nitrate concentration was increased to about 200 mg N L^{-1} from 2.5 months onwards and the beds were not nitrate limited. Nitrate removal rate averaged 44.0 ± 20.6 g N m^{-3} d^{-1} between 2.5 and 5 months and then declined to 21.8 ± 8.3 g N m^{-3} d^{-1} between months 5 and 15 (Fig. 2).

The mean nitrate removal rate of the unheated beds was 23.3 ± 8.9 g N m^{-3} d^{-1} and in heated beds was 23.7 ± 6.7 g N m^{-3} d^{-1} for the period 4–15 months and was not significantly different (P > 0.05 at 95% CL). Solar heating of the beds was initiated at 4 months.

There was no significant difference in nitrate removal rate between flow regimes in the unheated beds (P > 0.05 at 95% CL) (Fig. 3). However, in the solar heated beds there was significant difference (P < 0.05 at 95% CL) with the nitrate removal rate in the horizontal-diffuse approximately 24% less than the downflow during months 11–13 and 54% less than upflow during months 14–15.

3.2. *Effect of solar heating on bed temperature*

The beds took about 7–10 days to heat-up after installation of solar covers and inlet coils (data not shown). Data from the heating-up period are excluded from analysis.

On average, passive solar heating increased bed temperature by 3.4 °C from 17.5 to 20.9 °C (P < 0.01 at 95% CL) (Figs. 4 and 5). Passing the influent through the inlet coil under solar covers, raised mean influent temperature by 3.6 °C during spring and early summer (11–13 months), and by 6.2 °C during mid summer (14–15 months).

The largest increase in bed temperature due to solar heating occurred in the downflow and horizontal-point flow regimes which raised temperature by 3–5 °C at mean daily air temperature of 13 °C (Fig. 5). However, the difference in bed temperature between flow regimes was not significant at 95% CL.

3.3. *Physical properties and hydraulic efficiency*

Total porosity of the maize cob media, estimated by gravimetric drainage and dry weight, was 0.87. Drainable (primary or effective) porosity was 0.8 and secondary porosity was 0.07.

The theoretical HRT of the beds varied between tracer tests (from 2.4 to 5.3 days) due to variation in flow rate between tests (Table 1). The average theoretical HRT of the beds for the four tracer tests was 3.8 days, based on an effective porosity of 0.8. The theoretical HRT exceeded the tracer retention time ($\bar{t}$) in all tracer tests.

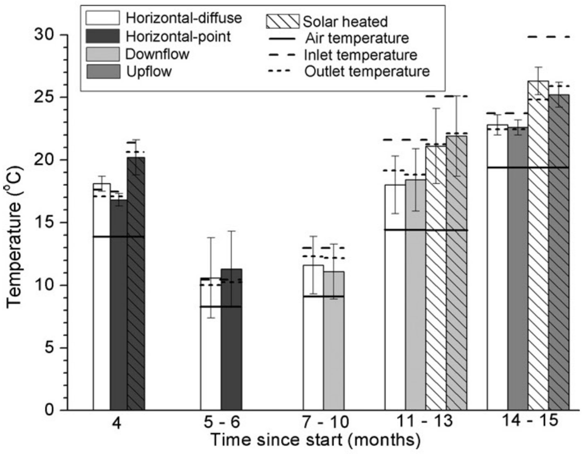

Fig. 4. Mean daily bed temperature, air temperature, inlet temperature and outlet temperature for different flow regimes. Error bars are 1 standard deviation. Hashing shows when solar covers and inlet coil were installed. Solid lines are bed temperature, long dash lines are inlet temperature, and short dash lines are outlet temperature.

Hydraulic efficiency ($e_V = \bar{t}$/theoretical HRT) of the flow regimes and effect of solar heating on e_V was assessed by Br tracer tests (Figs. 6 and 7). e_V ranged from 0.42 to 0.94, with lower values indicating more short-circuiting and e_V values approaching 1 indicating uniform flow. e_V was higher in: horizontal-diffuse flow than in horizontal-point flow (Tracer test 1; Fig. 6); both of the vertical flow regimes (downflow and upflow) than in lateral-diffuse flow (Tracer tests 2–4; Fig. 6); and the unheated horizontal and upflow beds than in the corresponding solar heated beds (Tracer tests 3 and 4; Fig. 6). e_V was similar in the unheated and heated upflow beds (Tracer test 3; Fig. 6).

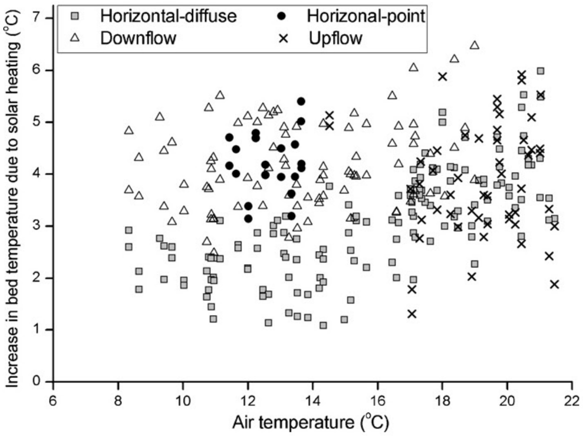

Fig. 5. Increase in mean daily bed temperature due to solar heating as a function of mean daily air temperature. Baseline for the temperature increase is the mean daily temperature of the non-solar heated bed of the same corresponding flow regime.

In the horizontal flow beds hydraulic conductivity (K) of the media decreased from about 1000 m d^{-1} at the start of the trial down to about 400 m d^{-1} at the end of the trial (data not shown). K was not able to be measured reliably in the vertical flow regimes due to the small vertical hydraulic gradient.

3.4. Water quality sampling

BOD in effluent of the beds decreased from about 500 g O$_2$ m^{-3} at the start of the trial down to about 20 g O$_2$ m^{-3} at 7 months. TKN leaching decreased from about 12 to 3 mg L^{-1} over the first 9 months while DO concentration decreased from between 3 and 6 mg L^{-1} at the inlet down to 0.5 to 1 mg L^{-1} at the outlet. Influent pH varied between 6.2 and 7.6. Effluent pH was 4 at the start of the

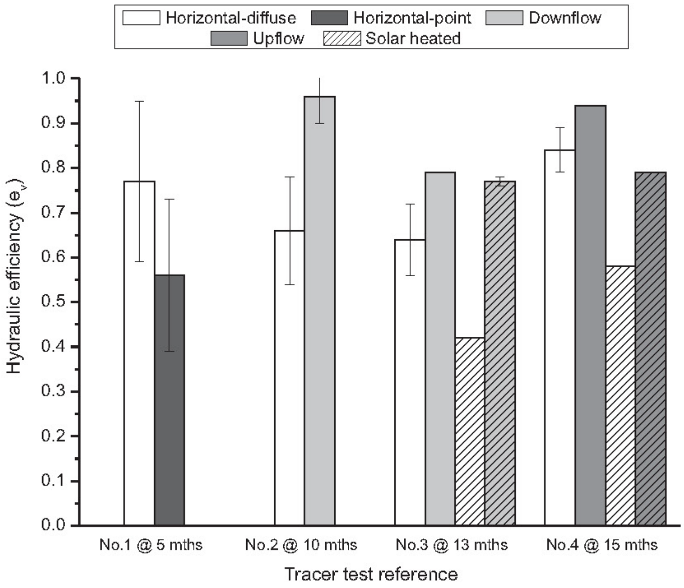

Fig. 6. Hydraulic efficiency of different flow regimes. Error bars are 1 standard deviation. Values with no error bar are from a single bed. Hashing shows when solar covers and inlet coil were installed.

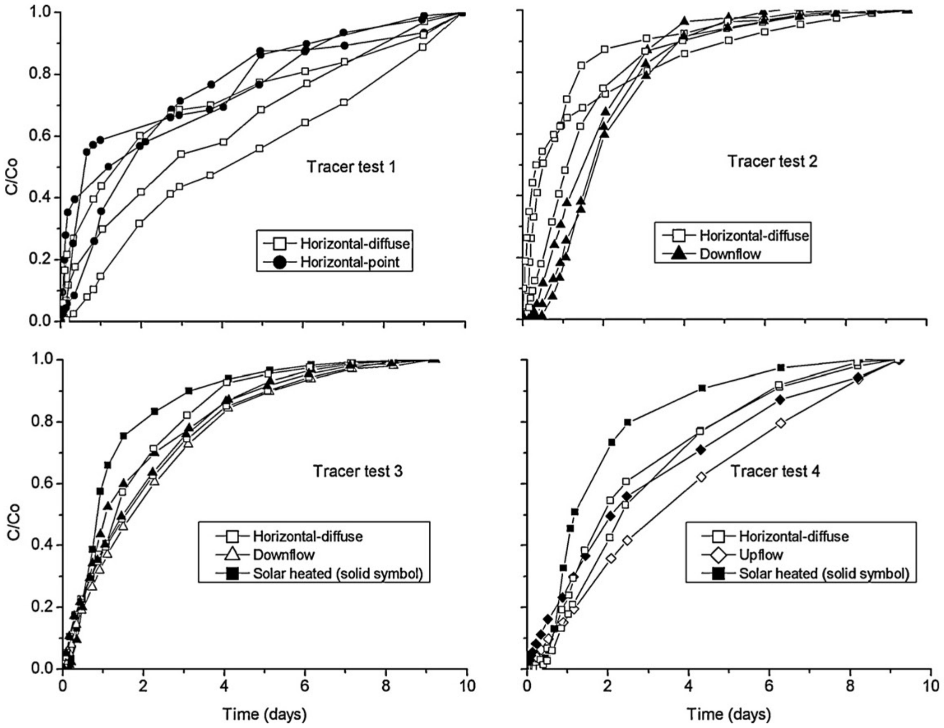

Fig. 7. Normalised tracer break-through curves. Where, vertical axis is cumulative mass of tracer recovered (C) divided by total mass of tracer recovered by the end of the test (C_o).

trial and gradually increased to about 7 during the next 5 months then remained fairly constant.

4. Discussion

4.1. Nitrate removal

Mean nitrate removal rate for the last 10 months was 21.8 ± 8.3 g N m^{-3} d^{-1} which more reliably represents longer-term nitrate removal (Fig. 2). The mean effluent temperature during this period was 21.9 °C. This removal rate was slightly higher than rates reported by Cameron and Schipper (2010) of 15.0 g N m^{-3} d^{-1} for maize cobs at 23.5 °C and generally greater than removal rates reported in long-term trial of denitrification beds with other carbon substrates. Schipper et al. (2010) summarised removal rates for field scale trials of wood media, when nitrate was non-limiting and rates ranged between 2 and 10 g N m^{-3} d^{-1}, at temperatures between 7.7 and 20 °C. Short-term column studies using corn cobs have reported much higher nitrate removal rates (e.g. 203 g N m^{-3} d^{-1} by Xu et al., 2009) but these are likely to overestimate long-term removal rates (Cameron and Schipper, 2010; Greenan et al., 2006).

4.1.1. Effect of solar heating on nitrate removal

Nitrate removal did not vary as a result of the 3.4 °C increase in bed temperature caused by solar heating (unheated = 23.3 ± 8.9 g N m^{-3} d^{-1}, heated = 23.7 ± 6.7 g N m^{-3} d^{-1}). The absence of significant increase (at 95% CL) in nitrate removal due to solar heating was attributed to two factors. Firstly, a 3.4 °C increase in temperature would be expected to increase nitrate removal rates by 4.0 g N m^{-3} d^{-1}, based on a Q_{10} value of 1.6, which was the mean Q_{10} value for carbon substrates reported by Cameron and Schipper (2010). An increase of 4.0 g N m^{-3} d^{-1} is within the variability of nitrate removal rates for unheated and heated beds with 1 standard deviation of 8.9 and 6.7 g N m^{-3} d^{-1}, respectively. Secondly, there was more short-circuiting in the solar heated beds for three of the four flow regimes which would have reduced the volume of bed available for denitrification (see Section 4.3.2).

Solar heating of denitrification beds is potentially a useful technique to improve the nitrate removal performance of a bed by about 12%, based on a Q_{10} of 1.6 (Cameron and Schipper, 2010) and a temperature increase of 3.4 °C. However, longer-term trials or trials with less variability in nitrate removal rate than occurred in this study are required to show significant increase in nitrate removal rate due to the increase in bed temperature from solar heating.

4.2. Bed temperature

Solar heating increased bed temperature for all flow regimes (Fig. 5). The magnitude of the increase in bed temperature increased with air temperature in the horizontal-diffuse and downflow beds. In contrast, there was no apparent relationship between air temperature and increase in bed temperature for the horizontal-point and upflow beds. This was likely due to solar heating of these flow regimes only being trialled for four and 6-week periods (Table 1) when there was only small variation in air temperature. Insulation of the bed walls and base would likely reduce heat loss along flow path and allow solar heating of the beds to be even greater.

Solar heating of horizontal-point and downflow appeared to be more effective for increasing bed temperature than horizontal-diffuse and upflow (Fig. 5). This was probably due to the inlet for both of these flow regimes being at the top of the bed and solar heating heated the beds from the top down. Heated water discharging from the inlet coil into the horizontal-point and downflow beds would have caused additional increase in near surface bed temperature.

Downflow may have been the most effective in raising bed temperature because of even downward movement of high temperature inlet water (Fig. 8b) that raised temperature throughout the bed; as evidenced by higher e_V of the downflow (0.77–0.96) compared to horizontal point (0.52) (Fig. 6). The lower e_V and vertical temperature profile of horizontal-point suggests short-circuiting of heated water across the top of the bed to the exit causing reduced vertical mixing and lower temperature at the base of the bed (Fig. 8a).

Raising the temperature of denitrification beds by passive solar heating has not been reported previously. The passive solar heating method used in this study was a simple and inexpensive (about US$17 per square meter of bed) way to increase bed temperature. There was no additional cost after installation aside from occasional maintenance.

4.3. *Hydraulic efficiency*

4.3.1. *Flow regime and hydraulic efficiency*

Flow regime influenced the degree of short-circuiting (Fig. 6), where $e_V = 1$ is uniform flow and $e_V < 1$ indicates increasing short-circuiting. Horizontal-diffuse ($e_V = 0.81 \pm 0.18$; Tracer test 1) had less short-circuiting than horizontal-point ($e_V = 0.56 \pm 0.17$; Tracer test 1). This was attributed to more direct flow across the top of the horizontal-point bed between the single pipe inlet and outlet than occurred in the horizontal-diffuse. Both vertical flow regimes had less short-circuiting than horizontal-diffuse (Fig. 6; Tracer tests 2–4). Again, this was attributed to increased flow near the top of horizontal-diffuse beds in comparison to the vertical flow systems.

Short-circuiting was exacerbated with heating of the influent in the horizontal-diffuse and upflow beds (Fig. 6). This difference was attributed to increased buoyancy of the warmer inlet water causing short-circuit flow near the surface of horizontal flow beds and vertical-upward preferential flow pathways in the upflow beds (Fig. 8b and c). There was no difference in short-circuit flow between the solar heated and unheated downflow beds.

4.3.2. *Nitrate removal and hydraulic efficiency*

Many authors have noted the importance of hydraulic design on treatment performance of constructed wetlands and ponds (Brown, 1994; Persson, 2000; Martinez and Wise, 2003; Kadlec and Wallace, 2008), with plug flow considered to be the ideal (WPCF, 1990). Plug flow is characterised by a uniform velocity profile. Short-circuiting would be expected to reduce nitrate removal if areas of slow or non-moving water become nitrate limited. However, in general there was no significant correlation between nitrate removal and short-circuiting (as measured by e_V), in spite of significant differences in hydraulic efficiency between flow regimes (Fig. 6). This lack of difference was likely due to the high variability in measured nitrate removal rates obscuring any real differences.

The only significant difference in nitrate removal was between solar heated beds. The solar heated vertical flow regimes had significantly higher nitrate removal than horizontal-diffuse ($P < 0.01$ at 95% CL) (Fig. 3). Horizontal-diffuse flow also had the most short-circuiting of the solar heated beds (Fig. 6). The lower nitrate removal rate in the solar heated horizontal-diffuse flow was attributed to short-circuiting caused by preferential flow near the bed surface due to buoyancy effect of warmer inlet water (Fig. 8b and c).

There have been very few studies of hydraulic efficiency in denitrification beds for comparison. van Driel et al. (2006) reported similar nitrate removal rates for a horizontal flow and an up-flow denitrification bed. The beds contained different spatial distribution of wood chip media particle size to improve hydraulic efficiency, however, comparison of hydraulic efficiency between the two beds was not reported.

Overall, downflow was indicated to be the most effective flow regime, when nitrate removal, hydraulic efficiency and increased bed temperature due to solar heating are considered. It provided the highest nitrate removal rate in the latter part of the trial and moderate hydraulic efficiency. Temperature contouring shows that downflow had more uniform temperature distribution pattern, than other flow regimes, suggesting more uniform velocity profile and plug flow characteristic (Fig. 8b and c).

Comparison of hydraulic efficiency between tracer tests cannot be made as porosity of the media appeared to increase with time. At the end of the trial when the beds were drained for decommissioning, media volume had decreased by approximately 40% from start of the trial. Some of the decrease in volume was likely due to greater packing density of the media as the beds were drained. Similarly, Xu et al. (2009) also reported a 48% decrease in packing height of corn cob media in a column study which they attributed to a measured 38% decrease in dry weight of the media over the study period. A decrease in media volume would cause an increase in porosity and theoretical HRT, causing apparent increase in hydraulic efficiency in the latter tracer test. However, the increase in porosity due to reduction in media volume may have been offset by gas bubble formation in the bed and accumulation of biomass around inlet areas.

4.4. *Porosity and hydraulic conductivity*

While total porosity measured at the start of the trial (Section 3.3) was similar to the value (0.88) reported by Cameron and Schipper (2010) for maize cobs, the primary porosity in the current study was considerably higher and secondary porosity considerably less than in the previous study (0.61 and 0.27, respectively). This difference was likely due to variety of maize cobs used in the trial. Total porosity of the maize cobs was also similar to values reported for wood media (0.82–0.86; Robertson, 2010) but the wood media secondary porosity was greater ranging from 0.31 to 0.40.

The reduction in hydraulic conductivity (K) of the media, from about 1000 m d^{-1} down to 400 m d^{-1}, was likely due to gas bubble formation. Considerable release of gas bubbles from the beds was observed throughout the trial. A similar magnitude decline in hydraulic conductivity of maize cob media was reported previously (Cameron and Schipper, 2010). Biofilm clogging in the bed inlet area may also have contributed to reduction in K. Accumulation of biofilm in the inlet areas of all beds was observed when the media was excavated during decommissioning of the beds.

4.5. *Leaching during start up period*

Effluent concentrations of BOD were greater than 20 g O$_2$ m^{-3} for the first 7 months. The concentrations were higher than those reported for denitrification beds incorporating wood media (Robertson and Cherry, 1995; Robertson et al., 2005), but similar to values reported by Cameron and Schipper (2010) for maize cob media. The discharge of effluent from denitrification beds, incorporating maize cobs, to some surface water bodies may not be appropriate due the high BOD leaching during the first 6 months of operation.

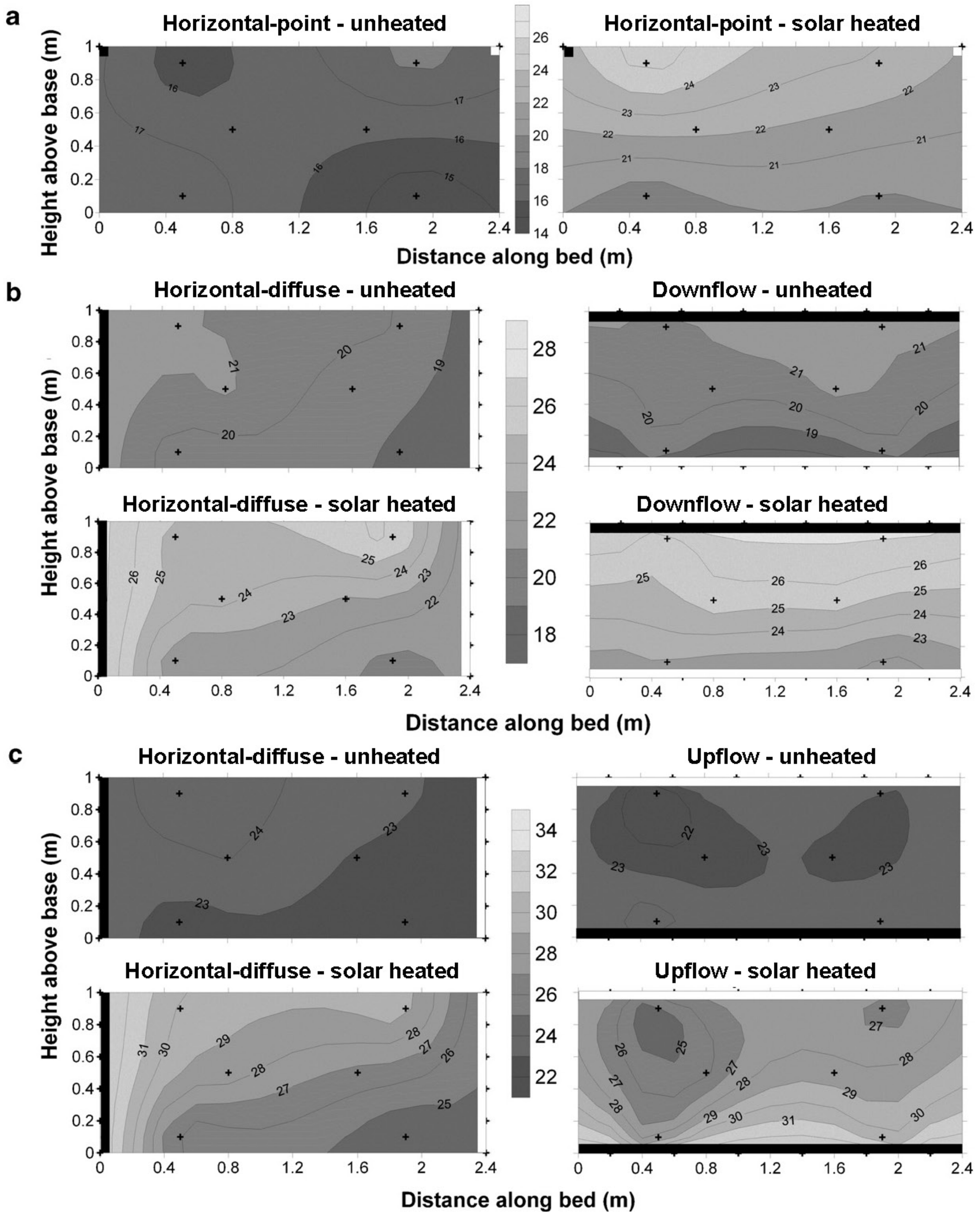

Fig. 8. Contour plot of mean daily bed temperature (°C) during period of solar cover installation (a) and tracer tests (b and c). Symbol ✚ are location of temperature probes, (■) is inlet and (□) is outlet. (a) Lateral diffuse (for period of solar heating beds at 4 months). (b) Lateral-diffuse and vertical-downward (for tracer test 3 undertaken at 13 months). (c) Lateral-diffuse and vertical-upward (for tracer test 4 undertaken at 15 months).

5. Conclusions

Maize cobs maintained a 2–11-fold higher nitrate removal rate ($21.8 \pm 8.3\,\mathrm{g\,N\,m^{-3}\,d^{-1}}$) over a 15-month period than long-term rates reported for wood chips (Schipper et al., 2010a). This removal rate was similar to the rate reported previously for maize cobs in a 23-month barrel trial (Cameron and Schipper, 2010).

Mean temperature of the beds increased by 3.4 °C due to solar heating with greater increases with increasing air temperatures. Generally, vertical flow regimes (upward and downward) were more effective than horizontal flow regimes (diffuse and point) for increasing bed temperature by solar heating due to short-circuiting near the top surface in the horizontal flow beds. Theoretically, the increased bed temperature due to solar heating should have increased nitrate removal by 4 g m^3 d^{-1}, but this difference was not detected due to the high observed variability in nitrate removal rates.

Generally, downflow was the most effective of the tested flow regimes. It was the most effective for increasing bed temperature with solar heating; had moderate short-circuiting and higher nitrate removal for the latter period of the trial; and had more even temperature distribution than other flow regimes as indication of plug flow.

While we have demonstrated increased temperatures through passive solar heating and compared inflow structures, observing an increase in nitrate removal in field scale experiments proved difficult due to high variability in nitrate removal rates. Passive solar heating of denitrification beds as described here is inexpensive and simple to maintain and may be beneficial to denitrification performance so long as it is coupled to inflow and outflow structures that do not result in increased short-circuit flow.

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Chapter 6

Summary and Conclusions

6.1 Introduction

Denitrification beds are a cost effective method for removing nitrate from point source discharges. These beds are capable of removing greater than 99% of influent nitrate and require minimal maintenance. To date, all operational and trial beds have used fragmented wood particles as the carbon source. The sustainable nitrate removal rate for beds using wood media has been reported as 2–10 g N m^{-3} d^{-1} (Schipper et al., 2010a). Increasing the nitrate removal rate of denitrification beds would lead to reduced bed size and potentially lower installation cost. This may facilitate greater uptake of the technology and ultimately reduce discharge of harmful reactive nitrogen to the environment. This thesis tested a number of approaches that might increase the nitrate removal rate of denitrification beds, including manipulation of carbon source, increasing temperature and improving hydraulic efficiency. The testing was undertaken in a barrel trial (0.2 m^3) over a 23 month period; and in a pilot scale (2.9 m^3) denitrification bed trial over a 15 month period.

The influences of hydraulic efficiency of media particle size and hydraulic efficiency of denitrification bed inlet/outlet on nitrate removal rate were tested. The hydraulic efficiency of media particle size was tested in the barrel trial in which the inlet/outlet structures were standardised. The hydraulic efficiency of the bed inlet/outlet was tested in the pilot scale trial in which the media (maize cobs) was standardized.

The main objectives and subsequent conclusions of this thesis are presented in the following section.

6.2 Thesis objectives and conclusions

6.2.1 Nitrate removal of different carbon substrates

Objective 1 – Measure the long-term nitrate removal rate of different carbon substrates to determine if removal can be increased above removal rates for woodchips.

More labile carbon sources, such as maize cobs, had significantly higher nitrate removal rate than wood media over the 23 and 15 month periods of the trials.

Nitrate removal rates of all tested media declined over the first 10 months after which there was no further decline. Mean removal rates for the period 10–23 months were more representative of long-term rates. The longer-term nitrate removal rate of maize cobs was 15.0–19.8 g N m^{-3} d^{-1} between 10 to 23 months and was significantly higher than the removal rate of softwood (*pinus radiata*) media (3.0–4.9 g N m^{-3} d^{-1}), without prohibitive decrease in hydraulic conductivity (Chapter 3, Cameron and Schipper, 2010; Table 2; Fig. 7). While other researchers have reported higher short-term nitrate removal rates (typically over a 1 to 6 month period) for more labile carbon sources than wood (Vogan, 1993; Xu et al., 2009; Shao et al., 2009), this study showed that the higher removal rates of maize cobs, wheat straw and green waste were maintained for at least 2 years in the barrel trial. Furthermore, maize cobs were shown to be suitable for use in larger scale operational reactors, as evidenced by sustained nitrate removal by maize cobs in the pilot scale beds receiving secondary treated municipal influent for the 15 month period. The long-term removal rate of maize cobs (21.8 g m^{-3} d^{-1}) was higher in the pilot scale trial (Chapter 5, Cameron and Schipper, 2011, Fig. 3) than previously reported long-term rates of operational beds using wood media (2–10 g N m^{-3} d^{-1}; Schipper et al., 2010a). However, it is likely that maize cobs will require more frequent replacement than wood media because of more rapid depletion of carbon and more rapid reduction in hydraulic conductivity in the less robust physical structure of the cobs.

The nitrate removal rate of hardwood (eucalyptus) was similar to softwood indicating hardwood was also suitable for use in denitrification beds. However, hardwood resulted in a lower pH of effluent leaving the barrel than other tested media for the first four months which may not be appropriate for discharge into some environments. Maize cobs had higher BOD and ammonia leaching into effluent than wood media during the first six months which may require management practices to reduce these losses. The management practices could include: commissioning beds during the winter when leaching rates are reduced due to slower decomposition of the carbon media at lower bed temperatures; reducing HRT at start-up to decrease the dissolution concentrations of carbon from the media; pre-leaching of media; or recirculation. To date, these practices have not been employed and their effectiveness is yet to be tested.

6.2.2 Temperature sensitivity of nitrate removal for different substrates

Objective 2 – Determine the temperature sensitivity of nitrate removal for different substrates.

Generally, long-term nitrate removal rates increased with increasing temperature in the barrel trial. Long-term nitrate removal rates were on average 1.5 times higher at 23.5°C than at 14°C (Chapter 3, Cameron and Schipper, 2010; Table 2). This equates to a mean Q_{10} of 1.6 for all tested media. Nitrate removal rates increased in all media with increasing temperature, with the exception of maize cobs. The lack of increase in removal rate in the maize cobs was attributed to more rapid depletion of carbon in the higher temperature maize cob barrels during the first 10 months and/or a lower temperature sensitivity of maize cobs compared to other tested media. Maize cobs had a lower Q_{10} (1.3 and 0.8) than softwood media (1.9 and 1.7) during the first 10 months and 10 to 23 month periods of the trial.

6.2.3 Hydraulic performance and nitrate removal of different woodchip size

Objective 3 – Determine whether hydraulic performance and nitrate removal rate were dependent on woodchip size.

The hydraulic efficiency of fragmented wood decreased with increasing grain-size (Chapter 4, Fig. 4.3). However, the rate of nitrate removal was not dependent on the hydraulic efficiency of the media under non-nitrate limiting conditions (Chapter 4, Table 4.1). The decrease in hydraulic efficiency of softwood media with increasing grain-size was attributed to more short circuit flow within the higher primary porosity of the larger grain-size media. The nitrate removal rate did not decrease with grain-size but rather was similar between grain-size treatments. The absence of correlation between hydraulic efficiency and nitrate removal rate was likely due to the significant secondary porosity of the wood media, allowing the denitrification reaction to occur both on the surface and within the wood particle. Canadian researchers also measured similar removal rates between different grain-sizes of sawdust in a shorter-term batch experiment (Carmichael, 1994) and between sawdust and woodchips in a denitrification bed trial (van Driel et al., 2006a), which they attributed to the dual porosity characteristics of the wood media (Robertson et al., 2000).

These findings imply that for wood-based denitrification beds, it is better to use larger grain-sizes of fragmented wood as they have higher hydraulic conductivity (K) with no loss in removal rate. Higher K allows for higher hydraulic loading rates, reduced risk of hydraulic failure and likely cope better with long-term accumulation of suspended solids. However, the largest grain-size of wood tested in this study was 61 mm, so the removal rate of grain-sizes greater than this size is unknown.

Primary porosity of wood media increased by 10% while secondary porosity decreased by 12% with an increase in temperature in the barrel trial. The change in porosity with temperature was attributed to contraction of the wood particles due to movement of water from the cellulose into the liquid phase (Westman and

Lindström, 1981). The change in porosity had no discernable effect on nitrate removal rate.

6.2.4 Effect of passive solar heating on bed temperature and nitrate removal

Objective 4 – Determine if bed temperature and nitrate removal could be increased by passive solar heating of operational beds.

Increasing temperature was shown to increase nitrate removal rate in the barrel trial. The temperature of pilot scale denitrification beds was increased by 3.4°C on average by passive solar heating (Chapter 5, Cameron and Schipper, 2011; Fig. 5). The increase in bed temperature due to solar heating increased with increasing air temperature. The effectiveness of solar heating was also dependent on flow regime and the highest temperature increase occurred in downflow beds. However, the increase in bed temperature due to solar heating did not result in a measureable increase in nitrate removal rate (Chapter 5, Cameron and Schipper, 2011; Fig. 3). This was attributed to the variability in nitrate removal rates (1 SD = 6.7–8.9 g N m^{-3} d^{-1}) exceeding the expected increase in removal rate (4 g N m^{-3} d^{-1}) due to the temperature increase from solar heating, based on a Q_{10} of 1.6. Also maize cobs demonstrated a low temperature responsiveness for nitrate removal in the barrel trial, suggesting the absence of increase in nitrate removal rate due to solar heating may in part be due to carbon substrate.

6.2.5 Effect of inlet/outlet structure on hydraulic efficiency and nitrate removal

Objective 5 – Determine if different inlet/outlet structures coupled to solar heating, alter hydraulic efficiency and nitrate removal rate in denitrification beds.

Inlet/outlet structures and location affected the hydraulic efficiency of denitrification beds. Nitrate removal rate was lower in flow regimes with poor hydraulic efficiency

The hydraulic efficiency and nitrate removal rate of the following four flow regimes were compared: horizontal-point, horizontal-diffuse, downflow and upflow.

Horizontal-diffuse flow had better hydraulic efficiency than horizontal-point, which was attributed to short circuit flow between the single inlet and outlet pipes of horizontal-point (Chapter 5, Cameron and Schipper, 2011; Fig. 6). Vertical flow regimes were more hydraulically efficient than horizontal, which was attributed to short-circuit flow near the surface of the horizontal flow regimes.

Solar heating decreased hydraulic efficiency in the horizontal and upflow beds due to increase in short-circuit flow of the warmer and more buoyant influent water (Chapter 5, Cameron and Schipper, 2011; Figs. 6 and 8). Conversely, solar heating did not affect the hydraulic efficiency of the downflow beds, which maintained more plug-like flow characteristics. The poor hydraulic efficiency of the solar-heated, horizontal-diffuse flow regime likely contributed to the lower nitrate removal rate (10.8 g N m^{-3} d^{-1}) of this flow regime in the latter period of the trial (Chapter 5, Cameron and Schipper, 2011; Fig. 3).

Generally, downflow was found to be the most effective flow regime as it provided moderate hydraulic efficiency, high nitrate removal rate and was the most effective flow regime for raising bed temperature due to solar heating. There was also indication that short-circuiting increased in solar-heated horizontal flow beds and that perhaps this combination should be avoided or design measures, such as baffles, be incorporated to reduce short-circuiting.

6.3 Summary of findings

This thesis demonstrated that carbon availability of the media, temperature and hydraulic efficiency of the bed flow regime were more important than variation in hydraulic efficiency of the media due to grain-size for influencing nitrate removal rate.

While hydraulic efficiency of the softwood media decreased with increasing grain-size it did not cause a reduction in nitrate removal rate. This was likely due to the large secondary porosity of the softwood media allowing denitrification to occur within the wood particle.

Maize cobs can provide higher nitrate removal rates than fragmented wood for at least 2 years. Solar heating raised denitrification bed temperature by about 3–4^{o}C which theoretically should increase nitrate removal rate by about 12%, based on a Q_{10} of 1.6. Maize cobs had a lower Q_{10} than other tested media. The downflow system was the most effective flow regime when hydraulic efficiency, temperature increase due to solar heating and nitrate removal were considered. For wood-based denitrification beds, it was better to use larger grain-size media as these had higher hydraulic conductivity with no loss in nitrate removal rate.

The size of a denitrification bed could be reduced about 4-fold by using maize cobs as the carbon media and solar heating the bed, compared to an unheated bed using wood fragments. The nitrate removal rate of a denitrification bed using maize cobs is expected to be about 19.6 g N m^{-3} d^{-1}, when results from both the barrel and the pilot scale bed trials are considered. Solar heating the bed is expected to increase nitrate removal rate by 4 g N m^{-3} d^{-1} to 23.6 g N m^{-3} d^{-1}, which is about 4-fold greater than the assumed mean nitrate removal rate for a wood based bed of about 6 g N m^{-3} d^{-1}.

6.4 Future Research

This thesis showed that generally carbon availability of organic media and temperature were more important than hydraulic efficiency of both the media and bed flow regime for increasing nitrate removal rate in denitrification beds under non-nitrate limiting conditions. However, hydraulic efficiency of media and bed flow regime may be more important for increasing nitrate removal rate under nitrate limiting conditions. Furthermore, continued improvement of denitrification bed performance will assist in the uptake of the technology. Aspects of future research for improving nitrate removal rate of denitrification beds under both nitrate non-limiting and limiting conditions are discussed below;

as are approaches for increasing the effectiveness of passive solar heating of denitrification beds, longevity, and minimising adverse effects.

6.4.1 Carbon availability of media

One way to increase the nitrate removal rate of a denitrification bed would be by increasing the carbon availability of a media for denitrification. The nitrate removal rate of a bed is constrained by carbon availability under non-nitrate limiting conditions (Warneke et al., 2011). Under anaerobic conditions, carbon availability is dictated by the rate of decomposition of the organic media by fermentative processes (Tiedje, 1988). Future research on enhancing the decomposition of organic media (e.g., by manipulating fermentative processes) within a denitrification bed could therefore increase nitrate removal rate. Similarly, methods to restore start-up nitrate removal rates of a denitrification bed would increase long-term nitrate removal rate. The nitrate removal rate of organic media is higher at start-up and declines over the first 6–10 months due to depletion of more readily available carbon (Cameron and Schipper, 2010). Draining a denitrification bed every 6 to 10 months to increase the labile fraction of carbon by oxidation of the media is one technique that could be investigated. However, while increasing carbon availability of a media may increase nitrate removal rate it would likely decrease the longevity of the media and require more frequent media replacement.

6.4.2 Media particle size

Results of this thesis suggest that future research on improving the nitrate removal rate of a denitrification bed should focus on carbon availability and temperature, but there are also aspects of media hydraulics that would be useful for advancing denitrification bed technology. For example, this thesis and work of other researchers (Carmichael, 1994; van Driel et al., 2006a) showed that nitrate removal rate was not constrained by the grain-size of wood fragments over the range of particle size investigated (<61 mm). However, the maximum grain-size of wood fragments for which there is no reduction in nitrate removal rate is unknown. Establishing the maximum grain-size would allow for higher hydraulic loading rates of denitrification beds and reduced risk of hydraulic failure without loss of nitrate removal performance.

This thesis found that hydraulic efficiency decreased with increasing wood media grain-size but that hydraulic efficiency did not influence nitrate removal rate under non-nitrate-limiting conditions. However, hydraulic efficiency of wood media, and thus grain-size, may affect nitrate removal rate under nitrate-limiting conditions due to reduction in nitrate-carbon contact. Therefore, optimum media grain-size for nitrate-limiting conditions still needs to be established.

6.4.3 Increasing bed temperature by passive solar heating

This thesis showed that a rudimentary passive solar heating technique increased denitrification bed temperature by about 3–4°C. However, an associated increase in nitrate removal was not measured due to variability in removal rates and possibly low temperature responsiveness of maize cobs. Therefore, increase in nitrate removal rate by solar heating a denitrification bed still needs to be demonstrated.

Greater increase in temperature may be achieved by improving the passive solar heating design. For example:

- insulating the walls and base of the beds, with polystyrene, to reduce heat loss; and
- increasing the HRT of influent in the inlet coil, by increasing coil length, to increase the temperature of influent flowing into the bed.

This thesis also indicated that solar heating of horizontal flow beds caused short-circuit flow near the top of the bed, which caused a reduction in nitrate removal rate. Future research could also include investigating the use of baffles in horizontal flow beds that forces water to flow towards the bottom of the beds. The use of baffles in treatment ponds has been shown to improve hydraulic efficiency and nutrient treatment (Shilton and Sweeney, 2005).

6.4.4 Longevity

The longevity of nitrate removal rate and K of carbon media is fundamental for the viability of denitrification bed technology. To date, both mass balance approach (Blowes et al., 1994; Robertson and Cherry, 1995; Robertson and Anderson, 1999; Robertson et al., 2000; van Driel et al., 2006a) and measurement of total carbon loss (Warneke et al., 2011; Moorman et al., 2010; Long et al., 2011) have been used to estimate potential longevity of carbon availability to support denitrification in reactors using wood media. These techniques generally indicate that there is enough carbon within the reactors to support denitrification for decades. However, ongoing monitoring of long-running denitrification beds under different nitrate loads are required to confirm these predictions. Also, long-term monitoring of nitrate removal rate in reactors using more labile carbon media than wood is required.

To date, no denitrification beds have suffered hydraulic failure due to decrease in K of the carbon media by breakdown of the carbon media structure. Ongoing monitoring of the K of media in long-running denitrification bed is required to establish the longevity of the media hydraulic performance. This is particularly important for beds that use more labile carbon media than wood fragments, such as maize cobs, as the longevity of K for these media are likely to be less than wood media. More labile media are also more likely to be affected by biofilm and gas bubble accumulation, which would also reduce K.

6.4.5 Adverse effects

Adverse effects of denitrification beds have been identified, including: leaching of BOD, NH_4 and organic-nitrogen; and production of greenhouse gases (GHG), methyl mercury, and H_2S.

The leaching of BOD, NH_4 and organic-nitrogen into bed effluent can be problematic depending on the discharge environment. This thesis proposed management practices that could be employed to reduce leaching. For example: commissioning beds during the winter when leaching rates are reduced due to slower decomposition of the carbon media at lower bed temperatures; reducing

HRT at start-up to decrease the dissolution concentrations of carbon from the media; pre-leaching of media; or recirculation. However, the effectiveness of these practices has not been tested. Trials are required to quantify effectiveness of these practices.

Future research on techniques to reduce the production of GHG and H_2S are required. Incomplete denitrification process can lead to production of N_2O. Techniques to maintain gases in solution are needed to encourage complete denitrification to N_2 to resolve this issue. Integration of bed covers to maintain gas emissions in solution with the solar heating of beds is one possible technique that could be explored. Bioreactors are currently being developed to reduce H_2S emissions from geothermal power plant discharges (Bacon, 2011; Rattanapan et al., 2009). Adaptation of this technology could potentially be used to reduce H_2S emissions from denitrification beds discharge.

Sulfate reducing environments in natural wetlands and lakes are known to promote the methylation of inorganic mercury (Gilmour et al., 1992; Eckley and Hintelmann, 2006; Todorova et al., 2009). Methylation allows Hg to bio-accumulate in the food chain with potentially detrimental consequences. Sulfate reducing conditions occur in denitrification beds when nitrate removal is complete (Robertson and Merkley, 2009; Elgood et al., 2010). Studies examining the production of methyl mercury (MeHg) in an organic carbon bioreactor are required. Bed management practices to reduce MeHg production in a denitrification bed may need to be established.

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Appendix 1

Denitrifying Bioreactors – An Approach for Reducing Nitrate Loads to Receiving Waters

This appendix contains the following two journal papers on denitrification bioreactors for which Stewart Cameron was a contributing author. The papers were produced at the same time as work on this thesis was undertaken. While the information presented in these papers is not part of the main objectives of this thesis (to test methods of improving nitrate removal performance of denitrification beds), both papers are directly relevant to application of denitricification bed technology for reducing nitrate discharge to the environment. Schipper et al. (2010a) is review paper of passive technologies for overcoming the carbon limitation of denitrification for enhanced nitrate removal. Schipper et al. (2010b) presents performance results of three large denitrification beds used to remove nitrate from municipal, dairy-shed and hydroponic glasshouse effluents.

Appendix 1a: Schipper et al. (2010a)

Schipper, L.A., Robertson, W.D., Gold, A.J., Jaynes, D.B., Cameron, S.G., 2010a. Denitrifying bioreactors – An approach for reducing nitrate loads to receiving waters. Ecol. Eng. 36 (11):1532–1543.

Stewart Cameron's contribution to the above paper was writing of the section on alternative carbon source, contribution to writing the section on nitrate removal rate and general review of the manuscript.

Appendix 1b: Schipper et al. (2010b)

Schipper, L.A., Cameron, S.G., Warneke, S., 2010b. Nitrate removal from three different effluents using large-scale denitrification beds. Ecol. Eng. 36 (11):1552–1557.

Stewart Cameron's contribution to the above paper was denitrification bed design (dairy-shed and hothouse), installation (dairy-shed), contribution to writing and review of the paper.

Appendix 1a

Denitrifying bioreactors – An approach for reducing nitrate loads to receiving waters

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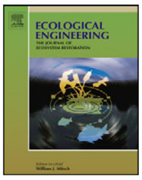

Review

Denitrifying bioreactors—An approach for reducing nitrate loads to receiving waters

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ABSTRACT

Low-cost and simple technologies are needed to reduce watershed export of excess nitrogen to sensitive aquatic ecosystems. Denitrifying bioreactors are an approach where solid carbon substrates are added into the flow path of contaminated water. These carbon (C) substrates (often fragmented wood-products) act as a C and energy source to support denitrification; the conversion of nitrate (NO_3^-) to nitrogen gases. Here, we summarize the different designs of denitrifying bioreactors that use a solid C substrate, their hydrological connections, effectiveness, and factors that limit their performance. The main denitrifying bioreactors are: denitrification walls (intercepting shallow groundwater), denitrifying beds (intercepting concentrated discharges) and denitrifying layers (intercepting soil leachate). Both denitrifcation walls and beds have proven successful in appropriate field settings with NO_3^- removal rates generally ranging from 0.01 to 3.6 g N m^{-3} day^{-1} for walls and 2–22 g N m^{-3} day^{-1} for beds, with the lower rates often associated with nitrate-limitations. Nitrate removal is also limited by the rate of C supply from degrading substrate and removal is operationally zero-order with respect to NO_3^- concentration primarily because the inputs of NO_3^- into studied bioreactors have been generally high. In bioreactors where NO_3^- is not fully depleted, removal rates generally increase with increasing temperature. Nitrate removal has been supported for up to 15 years without further maintenance or C supplementation because wood chips degrade sufficiently slowly under anoxic conditions. There have been few field-based comparisons of alternative C substrates to increase NO_3^- removal rates but laboratory trials suggest that some alternatives could support greater rates of NO_3^- removal (e.g., corn cobs and wheat straw). Denitrifying bioreactors may have a number of adverse effects, such as production of nitrous oxide and leaching of dissolved organic matter (usually only for the first few months after construction and start-up). The relatively small amount of field data suggests that these problems can be adequately managed or minimized. An initial cost/benefit analysis demonstrates that denitrifying bioreactors are cost effective and complementary to other agricultural management practices aimed at decreasing nitrogen loads to surface waters. We conclude with recommendations for further research to enhance performance of denitrifying bioreactors.

1. Introduction

The nitrogen (N) cascade is an increasingly important global issue as N flowing through ecosystems has multiple impacts on terrestrial, aquatic and atmospheric environments (Galloway et al., 2003, 2008). In agricultural systems, N in excess of plant and animal needs can leach to shallow groundwater and ultimately enter surface waters through concentrated or diffuse discharges. Concentrated discharges in agricultural systems occur through under-field tile drainage and ditches (Duda and Johnson, 1985; Dinnes et al., 2002) while diffuse sources are typically through the discharge of shallow groundwater to surface waters. Nitrogen that is captured in biomass passes through the food chain and ends up in wastewater streams, which are ultimately discharged to surface waters.

A number of strategies are being implemented to reduce the N load to aquatic ecosystems. Sophisticated technologies have been developed to remove N from wastewater and are employed in municipal treatment plants and septic tank systems (Oakley et al., 2010). In agricultural ecosystems, many land management approaches have been proposed to reduce N losses, such as

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improved N use efficiency in crops, managing N inputs through soil tests, land management plans and controlled drainage (Sims et al., 1995; Drury et al., 1996; Dinnes et al., 2002; Jaynes et al., 2004). Integrating wetland and riparian buffers into the agricultural landscape have also been demonstrated as a potentially useful way to reduce N losses to surface waters (Hill, 1996; Kadlec, 2005).

The most widely understood process of permanent N removal from terrestrial and aquatic ecosystems is heterotrophic denitrification, which converts nitrate (NO_3^-) to N gases using a carbon (C) source as the electron donor and for growth (Seitzinger et al., 2006; Coyne, 2008; Rivett et al., 2008). In this review, we focus on heterotrophic denitrification but we recognise that other microbial processes such as anaerobic ammonium oxidation (Anammox) and chemo-autotrophic denitrification can also produce N gases (Burgin and Hamilton, 2007). The rates and controlling factors of these microbial processes deserve further attention, but are not covered in this review.

At the microbial scale, the rate of heterotrophic denitrification is controlled by concentrations of oxygen (O_2), NO_3^- and C (Seitzinger et al., 2006). The availability of a degradable C source to drive denitrification becomes critical where NO_3^- is present in excess, such as in many wastewater plants and agricultural settings. Aerobic microorganisms obtain energy through the oxidation of organic compounds, using O_2 as the electron acceptor, until the environment becomes energetically favourable for the use of NO_3^- as an electron acceptor. As such, organic C plays two key roles in promoting denitrification; firstly, to provide an anoxic environment and, secondly, to act as an electron donor for denitrification. In wastewater treatment systems, this C is part of the waste stream, but can also be supplemented with liquid C sources such as methanol (Oakley et al., 2010; Henze et al., 2008). In agricultural soils, denitrification can be limited by sufficient labile C to create an anoxic environment and provide energy for denitrification.

Here, we review passive technologies that have been recently developed to overcome the C limitation of denitrification for enhanced NO_3^- removal. A variety of carbonaceous solids and immiscible liquids have been successfully tested in denitrifying bioreactors (Hunter, 2005; Gibert et al., 2008), although many of C sources have only been tested in laboratory trials. To date, wood-particle media in particular, has been the most widely used material in field trials and has shown an ability to deliver consistent longer term (5–15 years) NO_3^- removal, while requiring minimum maintenance (Robertson et al., 2000, 2008, 2009; Schipper and Vojvodic-Vukovic, 2001; Fahrner, 2002; Schipper et al., 2005; Jaynes et al., 2008). Consequently, this review has a strong focus on the use of wood-particle media, although other carbonaceous solids, including some with higher reaction rates, could also play an important role as additional experience is gained. Our focus is on field trials of solid C substrates that have been used in agricultural and rural settings to enhance denitrification and decrease discharges of NO_3^- from either diffuse discharges (e.g., shallow groundwater) or concentrated discharges (e.g., effluents, tile drainage, small streams and ditches). Because these approaches are intended to be applied throughout the landscape at the scale of individual fields, septic systems and tributary streams it is important that the technologies are simple, passive and that maintenance requirements are minimal.

2. Terminology

There are multiple designs that use solid C sources for enhancing denitrification and are collectively referred to as denitrifying bioreactors (Figs. 1 and 2; Tables 1 and 2). Designs differ primarily in the hydrologic connection between water containing NO_3^- and C source and the ratio of source area:treatment area. Broadly, we use terminology first used by Robertson and Cherry (1995).

"Denitrification walls" are where solid C material is incorporated vertically into shallow groundwater perpendicular to the flow. Darcian flow, saturated hydraulic conductivity, hydraulic gradient and the flow paths intercepted by the walls controls the flux of NO_3^- into the walls. Walls may intercept natural groundwater flow paths, or groundwater flow paths that have been altered by subsurface tile drainage systems or by the morphometry and relatively higher saturated hydraulic conductivity of C additions within the wall. The source area is roughly limited to the boundaries of the wall orthogonal to the flow direction. While the term "wall" suggests a barrier to flow, these walls are designed to sustain elevated hydraulic conductivities (i.e. >10 m day^{-1}) conducive to substantial rates of shallow groundwater flow. Denitrification walls can be 100% wood chips (Farhner, 2002; Jaynes et al., 2008) or sawdust mixed with soil (Robertson and Cherry, 1995; Schipper and Vojvodic-Vukovic, 1998).

"Denitrification beds" are containers (sometimes lined) that are filled with wood chips and receive NO_3^- in concentrated discharges either from a range of wastewaters (Robertson et al., 2005a; Schipper et al., 2010) or tile/drain discharge (Blowes et al., 1994; Robertson et al., 2009; Robertson and Merkley, 2009). Denitrification beds have also been installed into existing stream beds or drainage ditches and are specifically referred to as "stream bed bioreactors" (Robertson and Merkley, 2009). The source area:treatment area ratio for beds is usually much greater than in wall designs, due to either natural or artificial drainage networks that intercept and funnel groundwater inputs to the bioreactor. Beds, referred to as "upflow bioreactors" have also been adapted for use along streambanks (van Driel et al., 2006a,b). These upflow bioreactors do not receive input from a specific point source, but have design features and placement requirements that induce focused flowpaths that resemble the high flux conditions associated with point sources. Upflow bed reactors rely on wood chips with high saturated hydraulic conductivity and create a favourable hydraulic gradient by lowering the water table within the bed through the placement of a drainage pipe near the top of the wall that discharges directly to the adjacent stream.

Finally, "denitrification layers" are horizontal layers of solid C material that have been installed under weeping tiles from septic tank drainage fields (Robertson and Cherry, 1995) or under effluent-irrigated topsoils (Schipper and McGill, 2008).

The key to selecting an appropriate bioreactors design depends on the hydrologic conditions and site constraints of the system of interest (Table 2, and see Section 4).

3. Removal rates and controlling factors

3.1. Removal rates

Nitrate removal rates have been reported for a wide range of denitrifying bioreactors (Table 3) using different units. For consistency, in this synthesis paper, NO_3^- removal rates are expressed as g NO_3-N removed per m^{-3} reactor volume per day (g NO_3-N m^{-3} day^{-1}). Where conversion of rate units was required for study comparisons (Table 3), an effective porosity value of 0.7 (van Driel et al., 2006a) was used in most cases. It is also possible to express NO_3^- removal rates based on surface area of the bioreactor; this can be useful when wanting to compare the performance of bioreactors to NO_3^- removal in wetlands or other terrestrial ecosystems (for example, where effluent is applied to land).

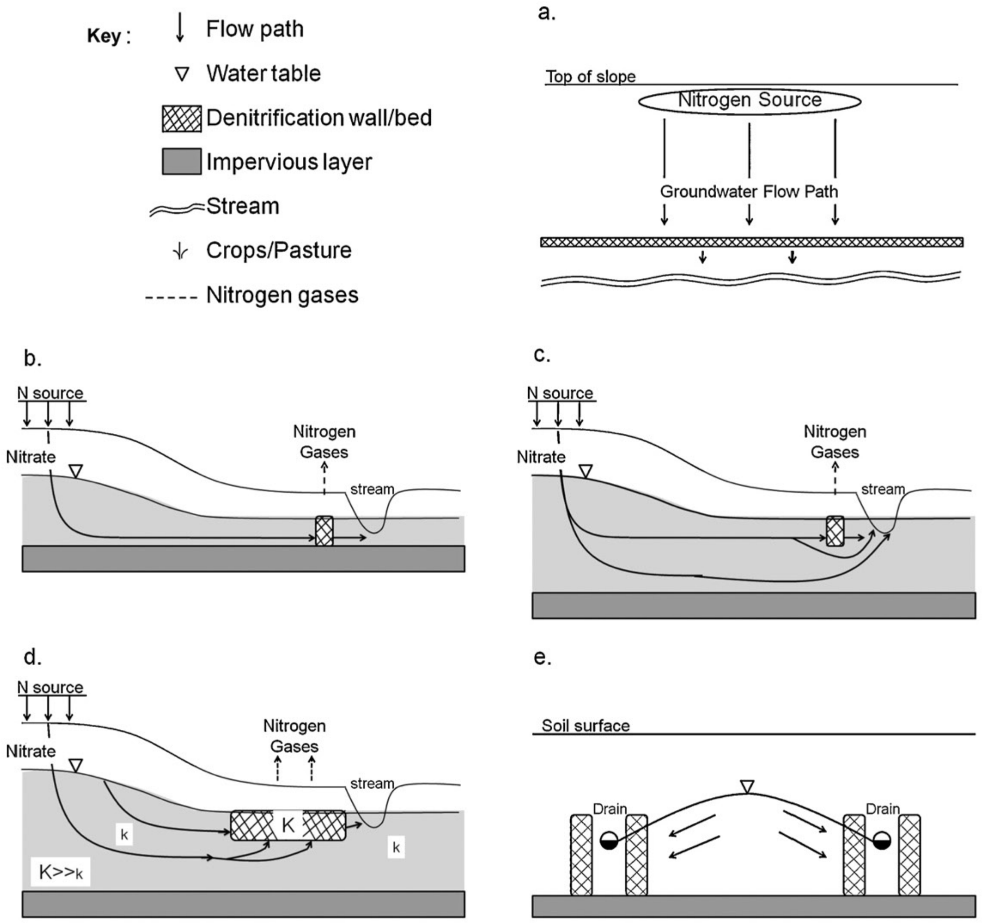

Fig. 1. Schematic of different designs of denitrification walls: (A) plan view of a wall intercepting NO_3^- plume, (B) side view of wall installed to impervious layer forcing shallow groundwater through wall, (C) wall not installed to full depth to impervious layer allowing flow paths under, (D) high permeability layer installed in upper part of aquifer causing upwelling of groundwater containing NO_3^-, and (E) denitrification walls installed on either side of a subsurface tile drain.

Sustained NO_3^- removal rates for denitrification beds incorporating wood, range from about 2 to 22 g N m^{-3} day^{-1}. Variation in rate is predominantly attributed to bed operating temperatures (typically from 2 to 20 °C) and/or influent NO_3^- concentrations (see fuller discussion below). The highest sustained NO_3^- removal rates were measured by Blowes et al. (1994) and Robertson et al. (2000) in a denitrification bed (North Campus, Canada) using woodchips. Removal rates for this trial varied between 4 and 22 g N m^{-3} day^{-1} depending on temperature (2–20 °C). Other denitrification bed studies (van Driel et al., 2006a,b; Schipper et al., 2010) utilizing a combination of sawdust and woodchip media report a slightly lower rate of NO_3^- removal, varying between 2 and 20 g N m^{-3} day^{-1}. Robertson et al. (2005a) measured lower removal rates (2–5 g N m^{-3} day^{-1}), during evaluation of the commercially available Nitrex™ filter which contains a mixture of sawdust and woodchips; however, removal rates were nitrate-limited at these sites.

Nitrate removal rates for denitrification walls (Robertson et al., 2000; Schipper et al., 2005; Jaynes et al., 2008) containing wood media are generally an order of magnitude lower (0.014–3.6 g N m^{-3} day^{-1}) than denitrification beds. Nitrogen removal rates within walls may be limited by low rates of NO_3^- loading, as most walls removed virtually all the NO_3^- but also because walls can have wood mixed with inert material such as soil or sand. The highest reported removal rate (15 g N m^{-3} day^{-1}) was for a 100% sawdust wall constructed in Western Australia (Fahrner, 2002), which received very high NO_3^- concentrations and had relatively high soil temperatures (Table 3); all of which would promote relatively high denitrification rates.

We have not addressed the importance of the dominant denitrifying organisms in the denitrifying bioreactors but these organisms are very wide-spread (Coyne, 2008), and bioreactors studied to date have not required inoculation as the denitrifiers respond rapidly to environmental drivers. However, microbial population diversity and dynamics deserve further attention as appropriate molecular tools are developed (Wallenstein et al., 2006).

3.2. Nitrate concentration

While denitrification is likely to obey Michelis–Menton kinetics with regard to NO_3^- concentration, most denitrifying bioreactors receive NO_3^- concentrations higher than Km of denitrifying bacteria (see Barton et al., 1999). Consequently, when considering whether NO_3^- removal follows either zero-order and first-order kinetics, the situation may be viewed as functionally similar to zero-order kinetics in many cases (Robertson et al., 2000; Schipper

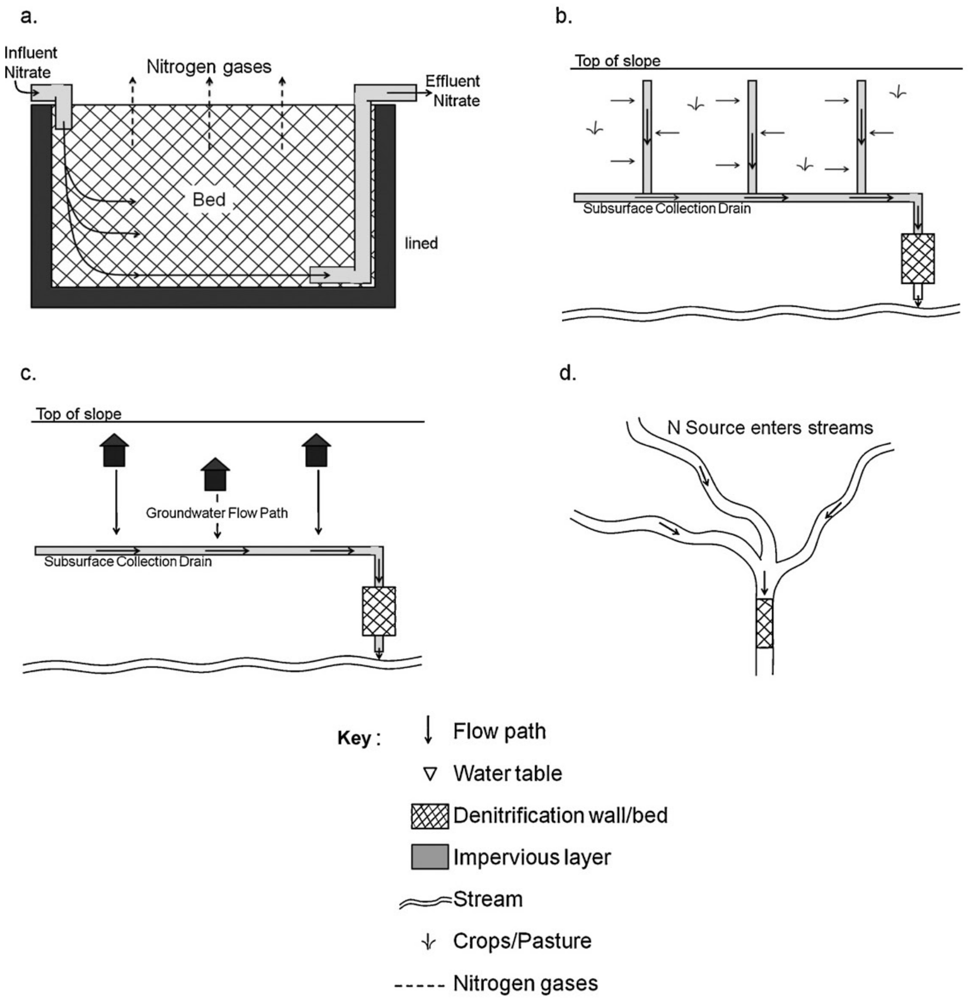

Fig. 2. Schematic of different designs of denitrification beds: (A) side view of bed treating concentrated discharges of effluent or drainage water, (B) plan view of bed installed to intercept drainage water from agricultural land, (C) plan view of bed installed to intercept drainage water leaching from septic tank drainage fields, and (D) bed installed into base of stream.

et al., 2005), although first order approaches have also been used in some studies (Chun et al., 2009; Leverenz et al., 2010). There is experimental evidence to support the notion that NO_3^- removal in denitrifying bioreactors is operationally zero-order. In a series of column tests using aged woodchip media (fresh to 7 years old), successive runs at increasing influent NO_3-N concentrations (3.1–49 mg L^{-1}) did not result in increased NO_3^- removal (Robertson, 2010). This indicated that the reaction was controlled by an independent parameter (presumably the release rate of degradable C from the carbonaceous media) and thus zero-order reaction kinetics would apply over this concentration range. A transition to first-order kinetics may occur at lower NO_3^- concentrations (such as might be found in stormwater), but in most settings, zero-order kinetics likely represents much of the NO_3^- transformation, and could be used for most design purposes.

3.3. Alternative C sources

Field-scale denitrification bed and wall studies have mainly used wood products (sawdust and wood chips) as a C source, generally because wood is commonly available at low cost, supports high permeability, has a high C:N ratio (ranging from 30:1 to 300:1 depending on source and type of wood material; Gibert et al., 2008; Vogan, 1993) and long durability (Robertson et al., 2009). There have been a number of smaller-scale laboratory experiments, which have examined the NO_3^- removal rates in a range of other C substrates (Table 4 and see also Gibert et al., 2008). Some of the highest reported NO_3^- removal rates (19–105 g N m^{-3} d^{-1}) are from the column studies of Vogan (1993) and Shao et al. (2009) using cellulose, alfalfa, wheat straw, and rice husk as the C substrate.

While more labile C sources (e.g., cracked corn, corn stalks, straw, etc.) may support higher removal rates than wood media, these may require more frequent replenishment because of rapid C depletion. For example, Stewart et al. (1979) found that humus rich soil was ineffective for long-term NO_3^- removal from septic tank effluent due to relatively rapid depletion of available C. Decreases in the saturated hydraulic conductivity of the more labile C sources may also occur as the C structure breaks down. Cameron and Schipper (this issue) found that while maize cob media sup-

Table 1
Physical description and potential settings for different denitrifying bioreactor designs.

Nomenclature	Physical description	Objective	Potential settings	Field examples
Denitrification wall	(i) C substrate placed into the upper 1–2 m of shallow groundwater in a trench perpendicular to groundwater flow path towards surface water.	Removal of NO_3^- from ground water prior to surface water recharge	Down gradient of localized sources of nitrate-enriched groundwater; at focal points of groundwater flow.	Canada (Robertson et al., 2000), New Zealand (Schipper et al., 2005), Australia (Fahrner, 2002)
	(ii) C substrate placed into the upper 1–2 m of shallow groundwater in a trench on either side of a tile drain	Removal of NO_3^- from groundwater before entering drainage network	In subsurface drained agricultural land	Jaynes et al. (2008)
Denitrification bed	Container (varied length and breadth dimensions but typically 1–2 m deep) filled with solid C substrate. Effluent or drainage water enters and exits in pipes. Beds may be lined.	Removal of NO_3^- from wastewaters or tile drainage from agricultural fields.	Concentrated discharges that have high NO_3^- concentrations such as from tiles or treated wastewater	van Driel et al. (2006a) and Schipper et al. (this issue)
Upflow bioreactors (subset of denitrification beds)	C substrate in container with lined sides, open to groundwater flow at bottom. Groundwater flows towards C substrate with elevated saturated hydraulic conductivity and is discharged to adjacent stream via pipe.	Removal of NO_3^- from ground water prior to surface water recharge	Adjacent to surface water where groundwater is shallow and aquifers have lower conductivities than added C substrate	van Driel et al. (2006b)
Stream-bed bioreactor (subset of denitrification beds)	Container (varied length and breadth dimensions but typically 1–2 m deep) filled with solid C substrate installed in the base of a stream	Reducing NO_3^- concentrations in streams	Streams and drainage ditches	Robertson and Merkley (2009)
Denitrification layer	A horizontal layer of woodchips that receives nitrified effluent from above.	Reduce NO_3^- leaching vertically to groundwater	Below septic wastewater drainage field that passed through a sand/gravel filter or other land-based effluent treatment system	Canada (Robertson et al., 2000) New Zealand (Schipper and McGill, 2008)

ported a 6.5-fold higher NO_3^- removal rate than wood media over a 24-month period, the decline in saturated hydraulic conductivity was generally greater in the maize cob media.

The effect of media particle size on reaction rates has also been considered. Several studies have found no significant difference in the NO_3^- removal rates in wood-particle media of different particle sizes (Carmichael, 1994; van Driel et al., 2006a,b; Robertson et al., 2000; Cameron and Schipper, 2010), although Greenan et al. (2006) measured initially greater NO_3^- removal for both wood chips and cardboard when ground to <2 mm. In comparing two denitrification beds, one constructed with predominantly coarse-grained wood particles (woodchips, 1–50 mm) and the other constructed with fine grained wood particles (sawdust, 1–5 mm), van Driel et al. (2006a) measured NO_3^- removal rates of 5.9 g N m^{-3} day^{-1} for coarse grained media and a similar rate of 5.5 g N m^{-3} day^{-1} for fine grained media. Robertson et al. (2000) speculated that denitrification is associated with reaction rims that penetrate, by diffusion, into the carbonaceous solids, rather than being restricted to the grain surfaces. This was supported by examination of a denitrification bed after 4 years of operation, which revealed that the larger centimeter-sized wood particles exhibited dark coloured rims that extended several millimetres into the particles, while the centre of the particles remained light coloured and appeared unaltered from their original condition. They interpreted this to indicate that the dark rims represented the denitrification zone. The smaller woodchips were dark coloured throughout.

There is no evidence of a difference in the NO_3^- removal rate achieved by hardwood in comparison to softer, faster growing tree species (Gibert et al., 2008; Cameron and Schipper, 2010). It is possible that hardwood may maintain physical properties for longer due to greater density. However, hardwood is not as readily available in some areas and may be more expensive. Both hardwood and softwood species have been used successfully in field trials (Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 1998; van Driel et al., 2006a,b; Jaynes et al., 2008) with little advantage indicated of one over the other.

While laboratory-scale experiments provide opportunity for relative comparison of the NO_3^- removal potential and hydraulic performance of different C substrates, these studies may not be a reliable indication of removal rates or hydraulic performance achievable in larger-scale field installations. This is due in part to the effect of dissolved O_2 (DO) content of the influent water on removal rates in small scale trials. Also laboratory trials tend to be of short duration, typically less than 6 months and NO_3^- removal rates tend to decline with time as labile C is reduced (Schipper and Vojvodic-Vukovic, 1998). The results of short-term experiments may not be reliable for assessing longer term sustainablity of removal rates (Cameron and Schipper, 2010). Multiyear field testing of wood media in bioreactors has shown that rates measured after about 1 year of operation are generally representative on long-term operation (Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 2001; Jaynes et al., 2008). Recommended best practice would be field testing of favourable substrates identified from laboratory studies for a minimum of a year. Ultimately the selection of an appropriate C media is a balance between availability, cost and reaction rate.

3.4. Temperature

In general, biological reactions rates increase with increasing temperature. Examination of reaction rates from a variety of studies where NO_3^- was non-limiting (Table 3) support a general positive

Table 2
Hydrological connections, limitation and potential approaches to overcoming limitations in denitrifying bioreactors.

Nomenclature	Hydrological connections	Limitations	Potential for overcoming limitations
Denitrification wall	(i) Down-gradient of NO_3^- source. Flow into wall is governed by Darcian principles of groundwater flow. Pore water velocities are likely to be low (0.05–0.5 m day^{-1}) and retention times within the wall are expected to be 3–10 days. Retention time within the wall is governed by incoming flow rate (passive). Hydrologic properties are likely to display high spatial (i.e., *K*) and temporal (i.e., hydraulic gradient) variability.	Requires site-specific analyses of hydraulic gradient, the depth and extent of NO_3^- plumes. Removal of NO_3^- limited to up-gradient source areas and within the upper 1–2 m of groundwater. If wall has lower saturated hydraulic conductivity than surrounding aquifer, NO_3^- plumes may flow under or around the wall.	In aquifers > 2 m deep, upwelling of NO_3^- laden groundwater into the interceptor wall may be enhanced by increasing the width (parallel to flow path) of the interceptor wall.
	(ii) For walls adjacent to tile drains, groundwater flow moves through bioreactors following drainage flow lines. Retention times are limited when water tables are highest and flow is greatest.	For walls adjacent to tile drains, high flows with high NO_3^- concentrations lead to short retention times resulting in large losses of NO_3^-.	
Denitrification bed	*For tile drains*: Flow rate is governed by properties of subsurface drainage network including: area of drained land, pattern and extent of excess rainfall or irrigation, designed depth of water table decrease due to drainage system, and intensity of drainage network. Retention time within the bed is governed by incoming flow rate. *For wastewater*: flows controlled by upstream waste generation and wastewater plant management.	Seasonality of flow rates can create high flow situations with limited retention rates within the bed, limiting NO_3^- removal.	High flow bypass can be incorporated into design to minimize flooding and overflow within the ditch. Cellular designs can be coupled with flow diverters to optimize retention times at different flow regimes.
Upflow bioreactor	Groundwater upwells into open bottom of reactor: (i) C substrate has higher conductivity than the aquifer. (ii) Drainage pipes installed at upper portion of reactor discharges to adjacent stream, lowers water table within reactor and enhances hydraulic gradient to upflow reactor.	Very site specific applications. Stream side location may be prone to erosion; flow rate is effected by stream stage	'Rip-rap' can be used to control erosion
Stream-bed bioreactor	A bioreactor installed in bottom of stream with a down-gradient riffle creates a pressure gradient and stream water flows down through lower conductivity C substrate and through an exit pipe back into the lower reach of the stream	Seasonal flows over the top of the riffle resulting in partial treatment. Potential for siltation of surface inlet requiring cleaning	Rip rap cover and channel narrowing can minimize siltation
Denitrification layer	Loading is determined by the design of the septic system.	Extent of nitrification in preceding sand/gravel filter can limit N removal. Difficult to replace C substrate because underneath discharge.	Ensure appropriate pre-treatment, e.g., sand filter

Table 3
Rates of NO_3^- removal for a range denitrifying bioreactors in the field. In general average rates of NO_3^- removal are presented. Many of the systems recorded here had complete NO_3^- removal which would limit the rate of denitrification and consequently are likely underestimates of potential removal rate. Units are $g\,N\,m^{-3}\,d^{-1}$ where m^{-3} refers to volume of bioreactor.

System design	Study	Size of bioreactor (m^3)	Typical NO_3^- inputs ($g\,N\,m^{-3}$)	Temperature annual average (°C)	Average rate of N removal ($g\,N\,m^{-3}\,d^{-1}$)
Walls	Robertson et al. (2000)	1	50	14	1.7
	Schipper et al. (2005)	78	5–15	12	1.4[a]
	Jaynes et al. (2008)	79	87	10	0.62
	Fahrner (2002)	160	>60	19	12.7
Beds	Robertson et al. (2000)	2	5	10	10
	Robertson et al. (2005a,b)	9	17	15	1.8[a]
		108	38	15	2.4[a]
		120	35	15	2.5[a]
		360	14	15	5.1[a]
	van Driel et al. (2006a) upflow reactors	0.7	9	9	2.1
		0.2	13	13	3.7
	Robertson and Merkley (2009)	40	5	8	3.2
	Robertson et al., 2009	17	10	7.7	3.4
	Schipper et al. (this issue)	83	53	15–25	1.4[a]
		294	5.5		0–11[a]
		1320	250	20	9.7
Layer	Robertson et al. (2000)	1	57	10	1.8

[a] Nitrate removal rate limited by NO_3^- concentrations.

Table 4
Laboratory-scale experiments (column and batch) that have tested a range of C sources for NO_3^- removal.

Carbon media	Reference
Wood	Vogan (1993), Carmichael (1994), Healy et al. (2006), Greenan et al. (2006), Gibert et al. (2008) and Cameron and Schipper (this issue)
Cardboard	Greenan et al. (2006)
Newspaper	Volokita et al. (1996a,b)
Wheat straw	Vogan (1993), Soares and Abeliovich (1998) and Cameron and Schipper (this issue)
Alfalfa	Vogan (1993)
Corn	Fay (1982)
Maize cobs	Cameron and Schipper (this issue)
Soil	Stewart et al. (1979) and Gibert et al. (2008)
Soil and sawdust	Healy et al. (2006)
Soil and jute pellets	Wakatsuki et al. (1993)
Cotton	Volokita et al. (1996b), Della Rocca et al. (2005, 2006), Su and Puls (2007)
Compost, mulch or greenwaste	Gibert et al. (2008) Cameron and Schipper (this issue)
Seaweed	Ovez et al. (2006)

Table 5
Theoretical percent of dissolved organic C (DOC) that is utilized for denitrification when dissolved O_2 (DO) reduction occurs first. Calculation uses the stoichiometry of Robertson and Merkley (2009) for the denitrification and aerobic respiration reactions, and assumes initial DO of 8 mg L^{-1} (saturation value at 25 °C).

NO_3-N removed (g m^{-3})	DOC utilized for denitrification (%)
1	22
3	46
10	74
30	90

relationship between NO_3^- removal and average annual temperature (Robertson et al., 2008, 2009; Cameron and Schipper, 2010). Field testing of near-surface reactors in Canada has shown that these continue to remove NO_3^- at a modest rate (~2 g N m^{-3} day^{-1}) even at effluent temperatures as low as 1–5 °C (Robertson and Merkley, 2009; Robertson et al., 2009; Elgood et al., 2010). In the latter study, the stream-bed bioreactor continued to operate and provided NO_3^- removal throughout the winter season even though the stream surface was periodically frozen. These studies were conducted using a range of wood-particle materials and it is likely that other factors also influenced the temperature response such as the degradability of different C substrates. For example, in a 23-month barrel study, Cameron and Schipper (this issue) found that Q_{10} (the increase in rate for a 10 °C increase in temperature) for NO_3^- removal differed between C substrates ranging from less than 0.8 to 2.3, between 14 and 24 °C. In the case of maize cobs, Cameron and Schipper (this issue) found that in the longer term NO_3^- removal was less at the higher temperature, presumably because labile C had been depleted more rapidly at higher temperature. While NO_3^- removal rate generally increases with increasing temperature, further information is needed for different substrates for design purposes.

3.5. Processes competing for available C

A key determinant for NO_3^- removal is the availability of C to denitrifiers and any microbial process that out-competes denitrifiers for this C will reduce NO_3^- removal in denitrifying bioreactors. Dissolved O_2 in either groundwater or in point source discharges may allow aerobes to out-compete denitrifiers for available C (Rivett et al., 2008). This is most likely an issue when retention times are short but less likely of concern in large bioreactors with long retention. Laboratory column tests have shown that the time required to deplete the dissolved O_2 in DO saturated water is approximately 1 h in aged, 2-year-old woodchip media (Robertson, 2010) and field trials have indicated similar rates of DO removal in wood particle reactors (Down, 2001; Robertson et al., 2009). Data in Table 5 shows the percent of dissolved organic C (DOC) that would theoretically be consumed by denitrification and aerobic respiration in DO saturated water, for a range of NO_3^- removal amounts. In bioreactors where NO_3-N removal is less than about 3 g N m^{-3}, either because of short retention times (less than several hours) or because of low NO_3^- concentrations, consumption of available C by aerobes can exceed that by denitrifying bacteria. Initially poor NO_3^- removal in the denitrification bed field trial of Healy et al. (2006) was attributed to high DO concentration (3.7–7.3 mg L^{-1}) and the relatively short retention time.

Sulfate can also be present in wastewaters and groundwaters and act as an alternative electron acceptor when more reducing conditions develop. However, denitrifying organisms generally out-compete sulfate reducers for available C (Appelo and Postma, 1994), consequently sulfate reduction normally only occurs when NO_3^- concentrations have been substantially depleted (Vogan, 1993; Robertson and Merkley, 2009; Robertson et al., 2009; Robertson, 2010; Woli et al., 2010; Elgood et al., 2010). Sulfate-reducing conditions are often also accompanied by increasing DOC concentrations (Vogan, 1993; Robertson, 2010). Thus, reactors that have excessively long retention times, beyond that required to fully deplete NO_3^-, risk generating high levels of DOC and undesirable reaction by-products such as hydrogen sulfide. If sulfate reduction is significant there is the possibility of production of toxic methyl mercury (Woli et al., this issue) by sulfate reducing bacteria; however, this production has yet to be measured.

4. Hydrology

The application of denitrifying bioreactors requires an understanding of the specific hydrologic settings and the spatial and temporal patterns of NO_3^- flux at the site (Table 2). Consequently, site investigations differ between walls, beds and layers and are site-specific.

For denitrification walls, the NO_3^- flux relies on both Darcian principles and the extent of groundwater NO_3^- contamination. If a denitrification wall is located in an area with either low NO_3^- concentrations or low groundwater flow rates, the removal rates will be quite low due to NO_3^- limitations. Hence, a number of aquifer characteristics must be investigated to determine site suitability and design parameters, including:

- Depth to the water table. Low cost wall construction usually precludes placing C material deeper than 4–5 m depth, therefore the water table needs to be within 2–3 m of the ground surface in most cases.
- Pattern and values of saturated hydraulic conductivity. The wall should be placed in media that is conducive to groundwater flow ($K > 1$ m day^{-1}).
- Depth to a restrictive layer with low saturated hydraulic conductivity.
- Direction and gradient of groundwater flow. In many areas, hydraulic gradient undergoes marked seasonal changes, thus site investigations should target both high and low water table conditions.
- Spatial pattern of shallow groundwater NO_3^- concentrations. Where walls are to be placed near localized sources of NO_3^- input, such as septic systems or animal waste disposal sites, the

potential for narrow plumes warrants field investigations with multiple monitoring wells to optimize site location.

Bioreactor designs that treat concentrated flows (e.g., tile drains or wastewater) or surface flows, avoid the necessity for site specific studies of shallow groundwater flow conditions, and therefore can have a considerable cost advantage in many cases.

Differences between the saturated hydraulic conductivity of the denitrifying bioreactor and the surrounding aquifer can either diminish or enhance NO_3^- flux into the wall. Schipper et al. (2004) found that in situ mixing of sawdust into saturated sands substantially lowered the saturated hydraulic conductivity of the wall compared to the coarse sand media that composed the shallow aquifer. Consequently, some shallow groundwater bypassed below the wall, substantially decreasing overall NO_3^- removal. Barkle et al. (2008) demonstrated that mixing of sands that were saturated while constructing a denitrification wall caused a decline in saturated hydraulic conductivity, presumably because of particle resorting. Furthermore, they showed that the addition of larger particles of organic material (garden mulch) did not improve saturated hydraulic conductivity when mixed with sand. However, walls composed entirely of wood chips can have very high hydraulic conductivities in excess of 100 m day^{-1} and can induce groundwater flow convergence and upwelling particularly as the width of the wall in the direction of flow is increased (Robertson et al., 2005b). Several studies have used model simulations to provide insight into the nature of groundwater flow in and around reactive barriers considering a variety of geometries and permeability characteristics (Benner et al., 2001; Robertson et al., 2005b, 2007). These studies were also accompanied by field tests with detailed monitoring in order to validate model simulations. Nitrate flux into walls can also be enhanced by their placement at locations where ambient hydraulic gradients have been enhanced. For example Jaynes et al. (2008), placed denitrification walls parallel to tile drains in artificially drained fields. Current studies have been mostly small scale and more work is required to better understand the nature of groundwater flow in and around reactive barriers particularly as they are scaled up in size and a wider range of configurations and media types are tested.

Design of denitrification beds requires information on the seasonal variability in flow rate and NO_3^- flux. Bypass systems that divert flows around a denitrification bed can be installed where flow rates vary greatly or are flashy with rainfall.

In many cases it may be useful to adopt a mass removal approach when considering bioreactor use. If the selected bioreactor design can provide adequate flows and NO_3^- levels to avoid NO_3^--limiting conditions, then the amount of nitrate removal can be easily estimated simply by considering the volume of media utilized and the published reaction rates (Section 3.1). This approach could become very attractive if (when) programs of nutrient trading are adopted. With trading incentives, bioreactors would be preferentially deployed at the most efficient, lowest cost locations, for example in shallow sand and gravel aquifers with high groundwater fluxes in intensively cultivated landscapes with high groundwater NO_3 concentrations.

5. Mechanism for nitrate removal

In most studies of denitrifying bioreactors, it is assumed that conventional heterotrophic denitrification is the dominant mechanism of NO_3^- removal. Other possible fates for NO_3^- include N immobilisation into organic matter, dissimilatory nitrate reduction to ammonium (DNRA), and Anammox (Burgin and Hamilton, 2007). There is evidence in both laboratory and field studies that denitrification is the dominant mechanism of NO_3^- removal in denitrifying bioreactors. Greenan et al. (2006) added ^{15}N-labelled NO_3^- into wood chip columns and laboratory incubations and found that immobilisation and DNRA accounted for less than 4% of total NO_3^- removed. Similarly, Gibert et al. (2008) concluded that less than 10% of NO_3^- removed was attributable to DNRA (and generally this was less than 5%). Further evidence against the occurrence of DNRA is the lack of significant ammonium (NH_4^+) production observed in most denitrification walls and beds (Schipper and Vojvodic-Vukovic, 1998; Robertson et al., 2000, 2005a, 2007; Schipper et al., 2010). Although, there is little evidence for DNRA occurring in wood particle barriers, it could be more important when considering other more labile carbonaceous substrates. Vogan (1993) observed an NH_4^+ increase of 5 mg N L^{-1} in a laboratory column test utilizing alfalfa straw as a C source. Because the NH_4^+ increase occurred in the same column zone where NO_3^- was being depleted and not further along the column where NO_3^- was fully depleted and DOC was still increasing, it was concluded that the NH_4^+ increase was probably the result of DNRA, rather than from mineralization of organic N from the media. Long-term accumulation of N into organic matter is difficult to assess because even large amounts of N accumulation in added C source would only result in small (and likely undetectable) declines in C:N ratio.

In support of active denitrification in bioreactors, elevated levels of denitrifying enzyme activity (DEA) have commonly been measured in denitrification walls and layers (Schipper et al., 2004, 2005; Schipper and McGill, 2008; Barkle et al., 2008; Moorman et al., 2010). However, elevated DEA does not always mean that significant denitrification is occurring, Schipper and McGill (2008) did not measure much NO_3^- removal in a denitrification layer despite increased DEA. In this case, leaching rates were very high and residence times short (<1 day). Further evidence to support denitrification as a major mechanism for NO_3^- removal comes from a field study conducted by Schipper and Vojvodic-Vukovic (2000) who calculated NO_3^- removal in a denitrification wall using hydraulic gradients, saturated conductivity and NO_3^- concentrations and compared these calculations to laboratory measures of denitrification rate. Schipper and Vojvodic-Vukovic (2000) found that denitrification rates (0.6–18.1 ng N cm^{-3} h^{-1}) were sufficiently high to account for NO_3^- removal from shallow groundwater (0.8–12.8 ng N cm^{-3} h^{-1}); however, error bars for both measurement approaches were large. A subsequent study at the same site, where NO_3^- was injected into the denitrification wall, measured greater rates of NO_3^- removal than could be accounted for by laboratory measurements of denitrification (Schipper et al., 2005). Moorman et al. (this issue) measured denitrifcation potential in bioreactors to be comparable to activity in the surface 15 cm of an organic rich field soil. In contrast to the soil, enrichment with glucose did not increase denitrification potential in the bioreactor indicating that the woodchips provided sufficient C substrate for the denitrifiers.

Another line of evidence supporting denitrification activity is enrichment of ^{15}N in the residual NO_3^-, because denitrifying bacteria preferentially consume the lighter isotope (^{14}N). In contrast, immobilisation of NO_3^- into organic pools does not discriminate between isotopes (Mariotti et al., 1982). In laboratory studies using woodchips of varying age (fresh to 7-year-old), Robertson (this issue) observed progressive enrichment of NO_3^--^{15}N as depletion proceeded. Enrichment was similar in all four woodchip types and was consistent with a Rayleigh-type distillation process with isotopic fractionation factor of −13 per mil. Similar fractionation has been reported for denitrification in groundwater (Robertson, 2010). Enrichment of NO_3^--^{15}N has also been observed in field bioreactors (Down, 2001; Robertson et al., 2000) In each of these studies NH_4^+

concentrations remained low (<1 mg N L^{-1}) making it unlikely that DNRA or Anammox caused the enrichments.

6. Potential adverse effects of using denitrifying bioreactors

A general concern associated with enhancing denitrification is that nitrous oxide (N_2O), a greenhouse gas, can also be produced as a by-product, but so far there are only a few studies of N_2O fluxes from denitrifying bioreactors. In column studies, Greenan et al. (2009) measured N_2O emissions that were between 0.003 and 0.028% of the total NO_3^- removed. This was much less than IPCC default value for production of N_2O assumed to ultimately arise from NO_3^- leaching from soil (0.75%; Mosier et al., 1998). N_2O fluxes were also measured from a denitrification wall and adjacent pasture using closed chamber techniques for 2-year period and fluxes were significantly greater ($P < 0.05$) from the wall (average 0.31 g N ha^{-1} h^{-1}) than the adjacent pasture (average 0.05 g N ha^{-1} h^{-1}) (Schipper and Vojvodic-Vukovic, unpublished data). It is likely that N_2O emissions will be lowest from denitrifying bioreactors with complete or near-complete NO_3^- removal. This was the case for N_2O flux from a stream-bed reactor (Avon site, Canada, Elgood et al., 2010) where dissolved N_2O was found to be much lower when NO_3^- removal was complete (0–5 μg N L^{-1}) compared to when NO_3^- removal was incomplete (10–35 μg N L^{-1}). Overall dissolved N_2O production amounted to 0.5% of NO_3^- removed over a 1-year period. Similarly, Moorman et al. (this issue) estimated N_2O production at 0.62% of NO_3^- removed in denitrification walls on either side of a tile drain.

Other gases will also be released from the denitrifying bioreactors including CO_2 and potentially CH_4 both derived from decaying organic matter. The emission of CO_2 does not result in a net increase in CO_2 emissions as the C substrate used in the bioreactor would have decayed if used for other purposes. Elgood et al. (this issue) collected gas bubbles erupting from the surface of the Avon streambed reactor, and found these to contain substantial amounts of CH_4 (25–45%). Methane was also detected during early operation of the bioreactors described by Jaynes et al. (2008), but disappeared after a few months presumably as highly labile C in the wood chips was consumed. Theoretically, the fluxes of CH_4 from bioreactors should be low when NO_3^- concentrations remain sufficiently high to suppress methanogens; however, this concept requires validation.

During start-up of denitrifying bioreactors there is also the potential for the release of soluble C compounds (measured as biochemical oxygen demand, BOD) associated with fresh wood material or other solid C sources. Release of BOD can reduce DO in receiving waters and adversely affect biota. Fresh wood contains 1–2 wt% soluble organic constituents such as tannic acids (Vogan, 1993), which can rapidly leach from wood-particle media during start-up. Initial reactor effluent is normally dark coloured and can have DOC concentrations of hundreds of mg L^{-1}. This is similar to the leachate that occurs at sawmills and in log storage yards where control measures focus on high DOC, trace metals and phenolic compound levels (Taylor et al., 1996). In wood particle reactors, the duration and magnitude of soluble DOC leaching during start-up is dependant upon the reactor retention time. Several field studies have observed dissipation of the initial DOC spike over the first 3–6 months of reactor operation (Robertson and Cherry, 1995; Robertson et al., 2005b; Leverenz et al., 2010; Schipper et al., 2010). In other reactor studies with shorter retention times, more rapid dissipation of the initial DOC spike has been observed. In column tests with sand and sawdust media and one day retention time, Vogan (1993) observed that the initial effluent DOC of 33 mg L^{-1} declined to <10 mg L^{-1} after 10 days of column operation. However, substantial NO_3-N concentrations (>10 mg L^{-1}) remained in the column effluent which may have assisted with DOC consumption. Likewise, Carmichael (1994) observed DOC depletion to <15 mg L^{-1} after 25 pore volumes in a laboratory column utilizing 100% woodchips with a 2-day retention time. Interesting, DOC declined from 43 mg L^{-1} at pore volume 22 down to 11 mg L^{-1} at pore volume 26, coincident with the breakthrough of NO_3^- in the column effluent. Thus, at sites where high initial DOC concentrations may be unacceptable, control measures might include maintaining high flow rates during start-up, installing post-bioreactor treatment (e.g., sandfilter) or collection of the initial effluent for disposal elsewhere. In agricultural terrain, a practical solution may be to use the initial effluent water for irrigating adjacent fields. Another option is to pre-leach the media prior to use, but this is likely to be logistically difficult adding to costs and has not, as yet, been attempted. Robertson and Merkley (2009) observed that slightly elevated concentrations of total phenolic compounds (4 μg L^{-1}) persisted in the Avon streambed reactor into its second year of operation. Similarly, water passing through a denitrifying bioreactor will have DO removed by microbes and this deoxygenated water could have adverse effects on biota of receiving waters. Currently, there is little information on this potential impact, but presumably this would depend on the relative flow rates of the reactor and the receiving waters and the nature of the receiving waters.

7. Longevity of nitrate removal and maintenance of saturated hydraulic conductivity

The longevity of NO_3^- removal in denitrifying bioreactors is not fully known because currently there appear to be no examples of reactors that have failed due to C depletion (Robertson et al., 2008). Two factors will affect longevity—the continued supply of C to denitrifiers and the maintenance of adequate saturated hydraulic conductivity. Decomposition of solid C sources (e.g., woodchips, sawdust) are greatly slowed when water saturated conditions are maintained and, in most cases, only slow rates of C decomposition are needed to support NO_3^- removal because there is generally a large amount of C relative to NO_3^- inputs.

Currently, the most long-lived bioreactor is the denitrification wall of Robertson and Cherry (1995), constructed in 1992 to treat a septic system plume. In a recent re-examination of this wall in 2007 (year 15, Robertson et al., 2008), core samples of the reactive media provided a NO_3^- removal rate in laboratory tests, of ~4 g N m^{-3} day^{-1}, which was only about 50% lower than the rate measured in year 1 (7 g N m^{-3} day^{-1}). Schipper et al. (2005) reported ongoing NO_3^- removal in a denitrification wall over 7 years of operation, and found that denitrification continued to be nitrate-limited, rather than C-limited, throughout this period. In the denitrification walls constructed by Jaynes et al. (2008), more than 60% of the NO_3^- was removed during the first 2 years of operation while removal was slightly more than 50% on average in the following 6 years (Moorman et al., 2010). Moorman et al. (this issue) measured an exponential decrease in the C content over the first 8 years for wood chips located at the saturated/unsaturated interface of the bioreactor. After 8 years, only about 25% of the C content of these woodchips remained with an estimated half life of 4.6 years. However, for woodchips that were deeper in the bioreactor and below the water table for a greater fraction of the year, more than 80% of the C still remained (estimated half life of 36.6 years), which accounted for the continued NO_3^- removal efficacy of the bioreactor. In a comparative study of woodchip media of varying age, Robertson (this issue) measured reaction rates in core samples from two reactors that were 2 and 7 years old, and found that NO_3^-

Table 6
Cost/benefit analysis of N removal of a denitrifying bioreactor (Robertson et al., 2009) installed for treatment of tile drainage in comparison to other agricultural approaches for reducing N.

Practice	US\$ (kg-N^{-1})	Source
Bioreactor	2.39–15.17	This paper
Soil testing and side dressing N fertilizer	1.15	Saleh et al. (2007)
Drainage water management	2.71	Jaynes and Thorp (2008)
Wetlands	3.26	Hyberg (2007)
Fall cover crops	11.06	Saleh et al. (2007)

removal rates remained within 50–75% of rates measured in fresh woodchips.

With such slow degradation rates, woodchip bioreactors have demonstrated an ability to remain highly permeable over a number of years with no deterioration in saturated hydraulic conductivity (~100 m day^{-1}) evident (Robertson et al., 2009). However, the bioreactor in the latter study was a surface installation that was subject to minimal overburden pressures. Subsurface bioreactors that experience greater overburden pressures could potentially be prone to greater deterioration in saturated hydraulic conductivity with time. However, little long-term saturated hydraulic conductivity data is currently available for subsurface bioreactors.

8. Cost–benefit analysis

While it is clear that denitrifying bioreactors can remove NO_3^- from concentrated or diffuse discharges, there are other technologies/approaches that are also effective. To be applied in the “real world”, denitrifying bioreactors need to be cost effective when compared to these other approaches for managing NO_3^-, e.g., installing wetland and riparian buffers, or more intensive management of N application.

To estimate the cost effectiveness of bioreactors, the bed reactor described in Robertson et al. (2009) will be used as an example. This bioreactor was 13 m long × 1.2 m wide × 1.1 m deep for a total volume of 17.2 m^3. It removed an average of 11.3 kg N year^{-1} from an agricultural field drain. Assuming a conservative 20-year life expectancy for this bioreactor, a total of 226 kg N will be removed. In the central US, woodchips can be purchased for US\$ 26.50 m^{-3}. Hauling to a site within 35 km would cost an additional US\$ 65. Rental of a backhoe for installation would range from US\$ 500 to 1000 and incidental expenses would add another US\$ 50. Assuming 4% annual interest for the “time value of money” for the installation costs gives a total cost of installation of US\$ 3249 or a cost per removal of NO_3^- of US\$ 15.17 kg-N^{-1}.

However, many bioreactors might be installed on farms where farmers have access to both a backhoe and wood from wind breaks or other local sources, greatly reducing the cost of installation. In addition, the bioreactor described in Robertson et al. (2009) only removed NO_3^- for about 70% of the year when the field tile was draining. Connecting a bioreactor to a NO_3^- source that flowed year round would increase its efficiency. Thus, for a farmer installing this bioreactor onto a year-round source the cost of NO_3^- removal would be reduced to US\$ 2.39 kg-N^{-1}. This cost of removal range (US\$ 2.39–15.17) compares favourably with estimates of other NO_3^- removal technologies as shown in Table 6. Cost efficiencies for bioreactors of other designs would of course vary, but bioreactors can be cost efficient alternatives for removing NO_3^- when compared against other commonly promoted approaches for managing N. In many cases, denitrifying bioreactors are complementary with these other practices and do not preclude the use of multiple mitigation approaches (Woli et al., 2010).

9. Treatment of other contaminants

The majority of data on the performance of denitrifying bioreactors has logically focused on NO_3^- removal but there are other redox sensitive contaminants in wastewaters and shallow groundwater that might be treated using modified bioreactors. These include pathogens and pharmaceutical compounds in wastewaters, pesticides in agricultural drainage and industrial contaminants such as perchlorate which is associated with explosives and rocket fuel manufacturing. Monitoring of four sawdust beds treating septic tank effluent in Ontario (Robertson et al., 2005a), showed that over several years of operation, *Escherichia coli* levels generally remained below detection in the reactor effluents (<10 cfu 100 mL^{-1}). However, several breakouts did occur, up to ~1000 cfu 100 mL^{-1}, particularly at the site with the highest loading rate. Robertson et al. (2007) reported complete attenuation of trace levels of perchlorate (ClO_4) occurring in agriculturally impacted groundwater in Ontario, during migration through a woodchip layer. In a subsequent experiment, Robertson et al. (2009) immersed a highway safety flare containing ClO_4 in the inlet pipe of a woodchip reactor treating agricultural drainage and the elevated influent ClO_4 concentration (up to 33 μg L^{-1}) was entirely attenuated in the reactor. It was noted that ClO_4 attenuation did not commence until NO_3^- was first depleted, demonstrating that NO_3^- inhibits the degradation of ClO_4.

Of the N forms (NO_3^-, NH_4^+, organic N), only NO_3^- and NO_2^- seem to be removed with little, if any, removal of organic N or ammonium (Robertson et al., 2005a; Schipper et al., 2010). This reinforces the need for a nitrification step of wastewater prior to being loaded into a denitrifying bioreactor.

Phosphate is often at low concentrations in groundwater but can be significant in effluents. To date, there has been little evidence that wood-based bioreactors remove phosphate from effluents (Robertson et al., 2005a; Jaynes et al., 2008; Schipper et al., 2010). However, the addition of other amendments to bioreactors (e.g., iron slag), has resulted in considerable phosphate removal from treated septic tank effluent (Baker et al., 1998; Robertson, 2000) and streams (McDowell et al., 2008).

Emerging contaminants such as pharmaceutical compounds also have the potential to be attenuated in denitrifying bioreactors but monitoring data is, as yet, lacking.

10. Conclusions and future work

To date, field studies have demonstrated that denitrifying bioreactors are capable of substantial NO_3^- removal in a number of watershed settings. Major advantages of denitrifying bioreactors are their simplicity with low maintenance requirements and the ability to tailor designs to fit hydrological site criteria. It is not clear how long these systems will continue to remove NO_3^- because no studied systems has yet been observed to fail—consequently we can only conclude that denitrifying bioreactors could last for a minimum of 15 years (Robertson et al., 2008). Moorman et al. (this issue) suggest that sustainability of wood chips to support NO_3^- removal was dependent on the time that wood chips remained water saturated (and presumably anoxic). Half lives varied between 4.6 and 36.6 years for woodchip either periodically saturated or permanently saturated, respectively.

Where NO_3^- loading is high, NO_3^- removal is dependent on temperature and availability of C. The high loads of NO_3^- entering denitrifying bioreactors mean that often NO_3^- removal rates are zero-order. Organic N and NH_4^+ are not removed in denitrifying bioreactors and a nitrification step may be required before wastewater enters the bioreactor. Development of simple nitrification pre-treatment systems coupled with bioreactors should be encouraged such as those described by Oakley et al. (this issue).

There is some laboratory and field evidence that denitrification is the main mechanism for NO_3^- removal but further work on the microbial ecology of these systems is needed and may lead to approaches for increasing nitrate removals rates and longevity. Field-scale research is needed to determine the effectiveness, costs, and factors controlling the rate of NO_3^- removal and denitrification in different bioreactors, particularly the suitability of alternative C sources. Management approaches still need to be developed for decreasing unwanted side effects, such as the production of N_2O and initial leaching of dissolved organic matter. Design criteria and demonstration sites are warranted to test alternative designs that merge bioreactors with constructed wetlands to provide co-benefits of biodiversity and aesthetics (Leverenz et al., 2010). Integration of bioreactors with other approaches for reducing NO_3^- loads to surface water, such as riparian zones or controlled drainage, would also be beneficial.

While there are unanswered questions about performance of denitrifying bioreactors, there is sufficient information available to utilize bioreactors for reducing NO_3^- fluxes in a variety of settings. Design manuals should be developed that address site evaluation, provide detailed construction approaches that integrate with local hydrology while meeting policy directives and performance goals of different countries and regions. These design manuals might be developed for engineers but, where appropriate, also for farmers and farm advisors. Finally, of particular importance is determining linkages between hydrological flow paths, retention time in the bioreactors and NO_3^- removal efficiency, thus we recommend interdisciplinary research combining the skills of hydrologists, hydrogeologists, engineers, biogeochemists, and land managers.

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Appendix 1b

Nitrate removal from three different effluents using large-scale denitrification beds

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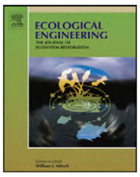

Nitrate removal from three different effluents using large-scale denitrification beds

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ABSTRACT

Simple technologies that remove nitrate from effluents and other point discharges need to be developed to reduce pollution of receiving waters. Denitrification beds are lined containers filled with organic carbon (typically wood chip or coarse sawdust) and are a technology that is proving promising. Water containing NO_3^- (treated effluent or agricultural drainage) is passed through the bed and the wood chips act as an energy source for denitrifying bacteria that convert NO_3^- to N gases. There are few data on the efficiency of NO_3 removal in large-scale beds. We report here NO_3^- removal results from three large denitrification beds with volumes of 83, 294, and 1320 m^3 treating dairy shed effluent, treated domestic effluent and glasshouse effluent, respectively. Nitrate was nearly completely removed from the dairy shed effluent (annual load of 31 kg N) and domestic effluent (annual load 365 kg N). In these beds, NO_3^- removal, presumably by denitrification, was limited by NO_3^- concentration. However, the bed treating glasshouse effluent was overwhelmed by very high NO_3^- concentration (about 250 g N m^{-3}) and high flow rates (about 150 $m^3\,d^{-1}$) but still reduced NO_3^- concentration to about 150 g N m^{-3}. For this bed, long-term NO_3^- removal was between 5 and 10 g N m^{-3} of bed material when NO_3^- was non-limiting and was similar to rates reported for other smaller denitrification beds. As expected, organic N, ammonium and phosphorus were not removed from any of the effluents following passage through the beds. Our results suggest that denitrification beds are a relatively inexpensive system to construct and operate, and are suitable for final treatment of a range of NO_3^--laden effluents.

1. Introduction

Excess nitrogen entering and polluting aquatic environments continues to grow as a global problem (Galloway et al., 2003). This N is predominantly derived from use of fertilizers or through enhanced N fixation, both of which are aimed at increasing food and fiber production. Not all of the applied N is assimilated by crops and animals and once nitrified, excess NO_3^- can leach to groundwater and then to surface waters as a non-point source of pollution. Where agricultural land is drained, N can enter surface waters as point discharges through sub-surface drains. N that is captured in food ultimately ends up in effluent treatment systems designed to remove nutrients. Generally, these treatment systems are not 100% efficient, resulting in discharges of some N and other nutrients to water bodies.

There is a need to develop simple, low-cost treatment systems (both in terms of construction and ongoing maintenance) to remove NO_3^- from effluents and from point source discharges from drained agricultural land. To complete the N cycle, NO_3^- can be converted to dinitrogen gas via denitrification. Nitrate removal of non-point source discharges can occur in wetlands and riparian buffers when these ecosystems contain significant organic matter, which provide an energy source to denitrifying bacteria (Hill, 1996; Dinnes et al., 2002). With increasing land-use intensity and urbanization, the N removal capacity of the remaining, often highly modified, wetlands and riparian buffers can be overwhelmed or bypassed by tile drainage systems (Dinnes et al., 2002). Constructed and natural wetlands have also been used in many parts of the world to remove nutrients from a range of effluents, but denitrification in these systems can be limited by carbon availability to denitrifying bacteria (Kadlec, 2005).

One relatively inexpensive approach to address the issue of carbon limitation of denitrification is to add a commonly available carbon source into the path of the NO_3^- discharge. This approach was trialed by Robertson and Cherry (1995) who added wood chip material into the flow path of groundwater (termed a denitrification wall) and also intercepting a tile drain (denitrification bed). Both these systems passively removed considerable NO_3^- for at

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least 15 years (Robertson et al., 2008). Similarly, Schipper and Vojvodic-Vukovic (1998) and Schipper et al. (2005) demonstrated the ability of sawdust to remove NO_3^- from groundwater for more than 7 years. A major advantage of these systems was the relatively low construction cost and no maintenance for many years. The denitrification beds tested by Robertson et al. (2005) ranged in size from 9 to 360 m^3 treating septic tank effluent volumes of 1–73 $m^3\ d^{-1}$. Often effluent flows can be much greater than these volumes and there is a need to determine whether denitrification beds may also be useful for treating variety of other effluent types with greater influent flows and masses of NO_3^-.

Key questions remain when considering scaling up of denitrification beds and utility for treating different effluents. The main uncertainty is what the upper limit for NO_3^- removal would be for very large denitrification beds where hydraulic flow properties may differ from smaller systems. It is also unclear whether other forms of N (ammonium and organic N) might be removed by denitrification beds via microbial immobilization. This information is critical in order to design future denitrification beds for other applications. However, obtaining such performance information from large denitrification beds can constrain the opportunity for replication at a specific site and effluent type. Here, we report rates of NO_3^- removal in three medium- to large-scale denitrification beds treating effluents derived from a hydroponic glasshouse, wash-water from a farm dairy milking shed and feedlot, and a sewage treatment plant. Even without on-site replication, rates of nitrate removal for a range of systems is valuable for design purposes.

2. Material and methods

We measured the performance of denitrification beds that received effluent from three different treatment systems. Effluent composition, flow rates, and operator objectives of these treatment systems differed and as a consequence the beds were all of different dimensions (Table 1). Bed temperatures were occasionally measured at all beds, but not generally at the same time as water sampling, and therefore only temperature ranges are presented here (Table 1).

2.1. Glasshouse effluent – Karaka

To avoid accumulation of salts and decrease risk of plant diseases some hydroponic glasshouse systems discharge a proportion of their nutrient solutions, which can have quite high N concentrations predominantly as NO_3^- (200–300 g N m^{-3}). In November 2006, a denitrification bed was constructed at Underglass Hothouses in Karaka just south of Auckland, New Zealand. This bed was 136 m long by 1.5 m deep and 7 m wide at the ground level tapering to 3 m wide at the bottom of the bed. For construction, a pit was dug into the soil and lined with plastic silage wrap and then the pit was backfilled with coarse sawdust and wood chip derived from softwood *Pinus radiata* (about a 50:50 mix). In April 2007, the bed was extended a further 40 m. Effluent entered through a single horizontal pipe (150 mm diameter) which discharged onto the top of one end of the bed. The outlet pipes consisted of four (150 mm diameter) vertical pipes 1 m apart linked via t-junctions to a single horizontal pipe at the other end of the bed. Final discharge of effluent was to a small stream on the property or irrigated onto nearby pasture land.

Inlet and outlet water samples were taken periodically by glasshouse operators, stored at 4 °C, couriered to a commercial analytical firm (Hills Laboratories, Hamilton, New Zealand) for analysis for total Kjeldahl N, NO_3^-, NO_2^-, and NH_4^+ using standard methods (APHA, 2005). Effluent flow rates were measured using a water meter (LXLG-80, Water Supply Products Ltd., New Zealand) that was read at the same time as sample collection.

2.2. Domestic effluent – Kinloch

A second bed was installed at Kinloch subdivision on the northern shore of Lake Taupo. This subdivision has large seasonal variations in populations because it is a popular vacation destination. The effluent from the subdivision was reticulated to a sequencing batch reactor (SBR) for secondary treatment and then into the denitrification bed. Two beds were constructed, each being 49 m long by 4 m wide and 1.5 m deep. Carbon material was a 50:50 woodchip (predominantly 10–30 mm diameter) and sawdust (predominantly 1–4 mm diameter) mix derived from *P. radiata*. Effluent from the treatment plant was diverted into both beds by a concrete diversion chamber that had two PVC pipes exiting from the base of the chamber. Final effluent exited the bed via two PVC pipes that were combined and then injected into shallow groundwater.

Inlet and outlet water samples were collected about every 2 weeks by the staff of the Taupo District Council who are responsible for the operation of the effluent treatment plant and analysed in their laboratories for NO_3^- and NH_4^+, total Kjeldahl N, total P and BOD (APHA, 2005). Flow was determined from an inline sonic flow meter (Wastemaster V, ABB, New Zealand).

2.3. Dairy farm effluent – Dargaville

The third bed (13 m long by 4 m wide by 1.5 m deep) was constructed on a dairy farm near Dargaville, Northland. The bed was filled with a 50:50 woodchip (predominantly 10–30 mm diameter) and sawdust (predominantly 1–4 mm diameter) mix derived from *P. radiata*. The bed was installed down stream of a membrane biological reactor (MBR) which received wash-down water from the dairy shed and feed lot. Effluent was pumped into the MBR plant from a storage pond that provided some reduction in suspended sediment load. The MBR plant converted the majority of the effluent N to NO_3^-. Effluent from the denitrification bed was discharged into a surface water drain.

Inlet and outlet samples from the bed were taken weekly for the first 16 months of operation and then at monthly intervals for the remaining 6 months. Total flow into the MBR plant for the sampling interval was measured by an impellor water meter. Flow data were only available for the latter part of the trial, which constrained calculation of N removal rates. Water samples were analysed for NO_3^- and NH_4^+, total Kjeldahl N, and total P using Hach test kits (Hach Company, Colorado).

Table 1
Properties of denitrification beds including size (length by width by depth), effluent type, bed temperature range, typical effluent NO_3^- concentrations and flow rates.

Denitrification bed	Bed dimensions (m)	Effluent type	Temperature (min–max) (°C)	NO_3 concentration (g N m^{-3})	Flow rate ($m^3\ d^{-1}$)
Karaka	176 × 5 × 1.5[a]	Glasshouse	14–25	250	150
Kinloch	49 × 4 × 1.5	2° treated domestic	14–22	5.5	182
Dargaville	13 × 4 × 1.6	2° treated dairy shed	15–26	53	1.6

[a] Surface width is 7 m tapering down to 3 m at bottom of bed.

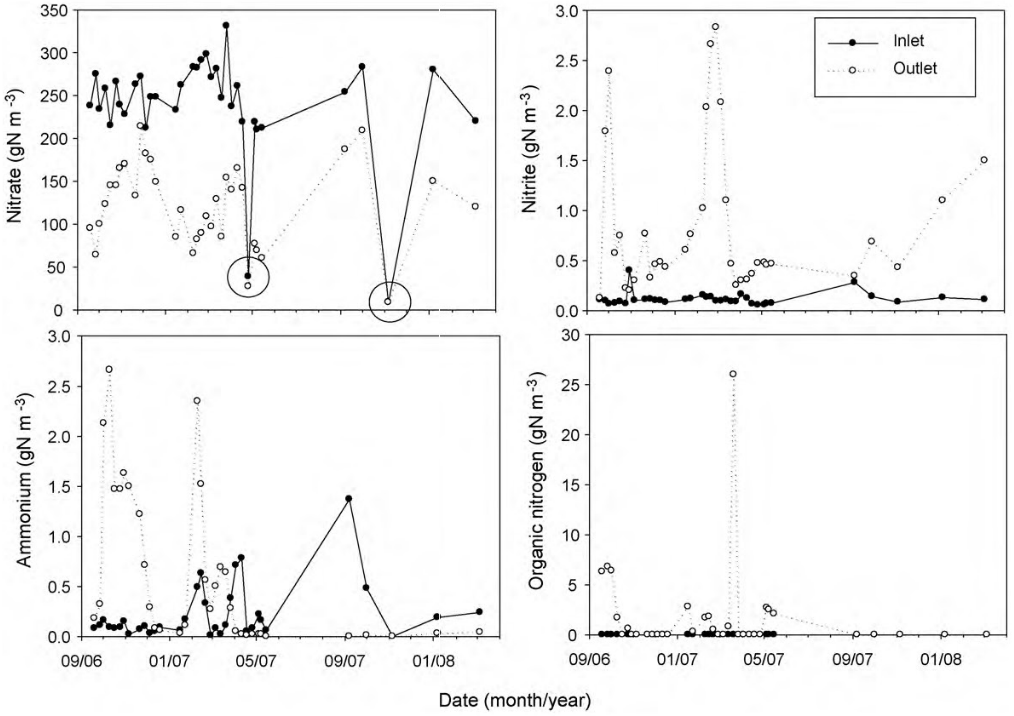

Fig. 1. Karaka denitrification bed: changes in N species as hothouse effluent passed through the denitrification bed. Note two circled points in NO_3^- graph were responsible for the low NO_3^- removal rates in Fig. 4.

3. Results and discussion

3.1. Nitrogen species in inflows and outflows

Total N loads and composition of effluent varied greatly between the three sites and with time. At the Karaka hothouse site, total N concentrations were very high (up to 350 g N m^{-3}) and was predominantly NO_3^- with little organic N or ammonium (Fig. 1). The bed receiving domestic effluent from Kinloch township received lower total N concentrations (up to 20 g N m^{-3}) dominated by NO_3^- with lesser amounts of NH_4^+ and organic N (Fig. 2). The Dargaville site which received effluent from dairy wash-down water had greatly fluctuating total N concentrations (up to 250 g N m^{-3}) that consisted of both NO_3^- and NH_4^+ (Fig. 3).

Nitrate was the major form of N removed from the effluents passing through the beds. At both Kinloch and Dargaville, nearly all the NO_3^- was removed; however, at the Karaka site, the bed was overwhelmed and NO_3^- concentration exiting the bed were often greater than 100 g N m^{-3} (Fig. 1). Nitrite was consistently analysed for at the Karaka bed (Fig. 1) but was generally low (generally less than 3 g N m^{-3}) relative to NO_3^- concentrations (>100 g N m^{-3}). Nitrite was only occasionally measured in the Dargaville bed (data not shown) but was always less than 1 g N m^{-3}. The Dargaville bed was the only bed that received substantial amounts of NH_4^+ and organic N in the inflow and did not display any consistent reduction in concentration of these N species (Fig. 3). Similarly, Robertson et al. (2005) did not measure any reduction in NH_4^+ concentrations through the beds they studied.

3.2. Removal mechanism

Denitrification was the most likely pathway for the removal of N as effluent passed through the beds because NO_3^- was consistently the main form of N removed. Alternative mechanisms for NO_3^- removal would include: immobilization into microbial biomass, dissimilatory NO_3^- reduction to NH_4^+ (DNRA), and anaerobic NH_4^+ oxidation (ANAMMOX).

When beds were initially flooded with effluent, N immobilization into an establishing microbial population might have been important until the biomass reached a steady-state when presumably immobilization would be matched by mineralization with no further net accumulation of N. If immobilization was a major long-term sink for N, then decreases in NH_4^+ and organic N concentrations through the beds would also be expected and these were not observed. DNRA is the anaerobic reduction of NO_3^- to NH_4^+ using a carbon source as an electron donor (Tiedje, 1988). It seems unlikely the DNRA was a major sink for NO_3^- in the denitrification beds as no accumulation of NH_4^+ was observed. The lack of significant NO_3^- removal by immobilization or DNRA was supported by a laboratory study conducted by Greenan et al. (2006). They incubated different carbon sources (including wood chips) with ^{15}N-labelled NO_3 under anaerobic conditions and found less than 4% of removed NO_3^- could be attributed to DNRA and immobilization.

ANAMMOX is the microbial conversion of NO_3^- and NH_4^+ to N_2 gas via an intermediate NO_2^- (Kunen, 2008). There was no consistent decrease in NH_4^+ through the Dargaville and Kinloch beds (where inflow contained ammonium) and so it would seem unlikely that ANAMMOX was a major process for N removal. However, the role of ANAMMOX should be explored further. If ANAMMOX could be enhanced in denitrification beds this would be beneficial because the beds would also reduce incoming NH_4^+. Kunen (2008) argued that the slow growth of ANAMMOX microbes means long start-up periods (more than 2 years in effluent treatment plants) to establish an active population of these organisms. Consequently, it may be that populations of

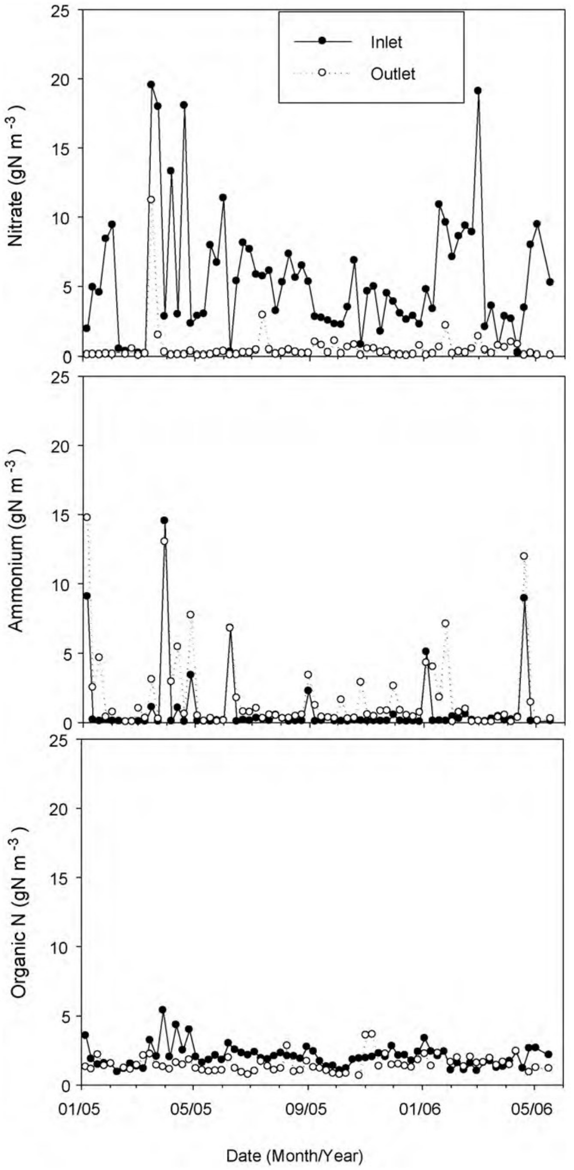

Fig. 2. Kinloch denitrification bed: changes in N species as treated domestic effluent passed through the denitrification bed.

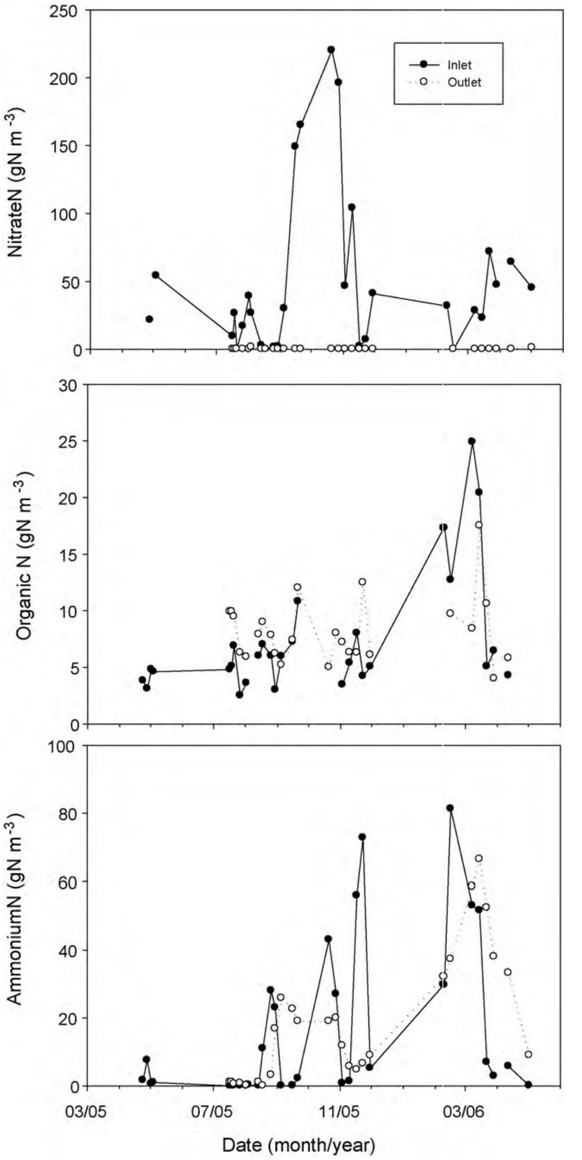

Fig. 3. Dargaville denitrification bed: changes in N species as treated dairy wash-down water passed through the bed.

ANAMMOX bacteria have not yet established in the beds studied here.

3.3. Nitrate removal rates

Nitrate removal rates were calculated as the difference between the mass of NO_3^- in the inlet and outlet (concentration in g N m^{-3} multiplied by flow in m^3) divided by the volume of the bed (Table 1). Nitrate removal rates (Fig. 4) ranged from around 11 g N m^{-3} d^{-1} down to near 0 g N m^{-3} d^{-1} in the Kinloch bed while NO_3^- removal in the Dargaville bed was generally lower (average 1.4 g N m^{-3} d^{-1}). However, the low rates of NO_3^- removal in both Dargaville and Kinloch occurred when there was complete removal of NO_3^- and so denitrification was likely limited by availability of NO_3^-. The same order of magnitude of NO_3^- removal was recorded at Karaka, where rates were initially more than 10 g N m^{-3} d^{-1} but with time decreased to between 5 and 10 g N m^{-3} d^{-1}. On two occasions, there was no apparent NO_3^- removal in the Karaka bed coinciding with large decrease in the concentrations of NO_3^- in the inlet. As with the other beds, low inputs of NO_3^- would result in denitrification being NO_3^--limited.

A few other studies have examined NO_3^- removal in generally smaller denitrification beds. Robertson et al. (2005) measured NO_3^- removal in denitrification beds ranging in size between 9 and 360 m^3, van Driel et al. (2006) tested beds between 0.2 and 0.7 m^3 and finally Robertson and Merkley (2009) investigated a bed 40 m^3 in volume. Despite these large differences in size between these beds and the beds we studied (up to 1320 m^3 at Karaka), rates of

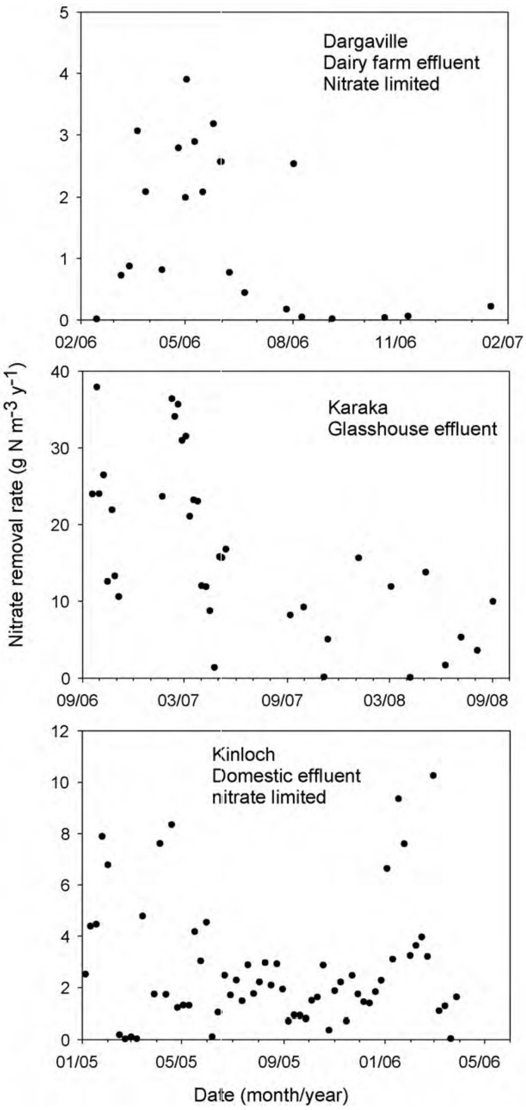

Fig. 4. Nitrate removal rate of all three beds. On many occasions at the Kinloch and Dargaville sites, NO_3^- was completely removed before exiting the bed and denitrification was likely limited by NO_3^- concentration; consequently NO_3^- removal rates were low, see text for full discussion. Note differences in scales of axis.

NO_3^- removal were similar across all beds when not limited by NO_3^- concentration. The previous reports by Robertson and colleagues have presented NO_3^- removal rates on the basis of mobile fluid volume of the beds (cf., effective porosity) rather than on a woodchip volume (Robertson, W.D., pers. comm.). To convert rates of NO_3^- removal based on effective porosity (NR_{ep}) to the rate of NO_3^- removal based on bed volume (NR_{bv}) requires the following adjustment: $NR_{bv} = NR_{ep} \times$ effective porosity, where effective porosity is the ratio of the pore space through which water flow occurs to the total volume of the bed. Effective porosity is generally determined by tracer studies. Applying this adjustment to reported measurements, Schipper et al. (this issue) recalculated NO_3^- removal rates of these studies. Average removal rates in the beds reported by van Driel et al. (2006) ranged between 2.1 and 3.7 g N m^{-3} d^{-1} in upflow denitrification beds installed adjacent to a stream treating groundwater. Adjusted rates of NO_3^- removal reported by Robertson et al. (2005) ranged from 1.8 to 5.1 g N m^{-3} d^{-1} and for the study of Robertson and Merkley (2009) average NO_3^- removal was 3.2 g N m^{-3} d^{-1}. As with our studies at Kinloch and Dargaville, NO_3^- was often completely removed in the beds studied by Robertson and colleagues suggesting that the maximal removal rates of NO_3^- had not always been reached. The rates of NO_3^- removal measured in the denitrification beds were greater than removal rates measured in denitrification walls of about 1 g N m^{-3} d^{-1} (Robertson et al., 2008; Schipper and Vojvodic-Vukovic, 2000; Schipper et al., 2005; Jaynes et al., 2008). The lower removal rates in denitrification walls are most likely because denitrification walls have lower proportion of wood chips or sawdust material.

In summary, across these studies NO_3^- removal rates for wood chips and sawdust are generally less than 10 g N m^{-3} d^{-1}. Removal rates can initially be greater (such as Karaka) most likely due to initial release of soluble carbon which is more biologically degradable. Other solid substrates (e.g., corn stalks) may be able to support greater removal rates (Greenan et al., 2006; Cameron and Schipper, this issue) but have yet to be tested at field scales.

3.4. Total P and BOD changes

Total P was measured in the inlet and outlets of the Kinloch and Dargaville beds and there were no consistent changes in phosphorus concentration as effluent passed through either bed

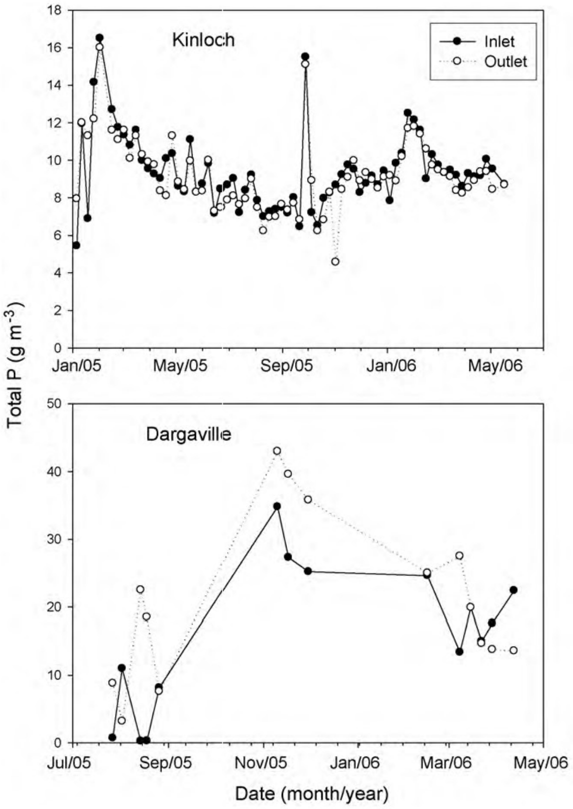

Fig. 5. Changes in total P in inlet and outlet of Kinloch and Dargaville denitrification beds. Note change in axis scales.

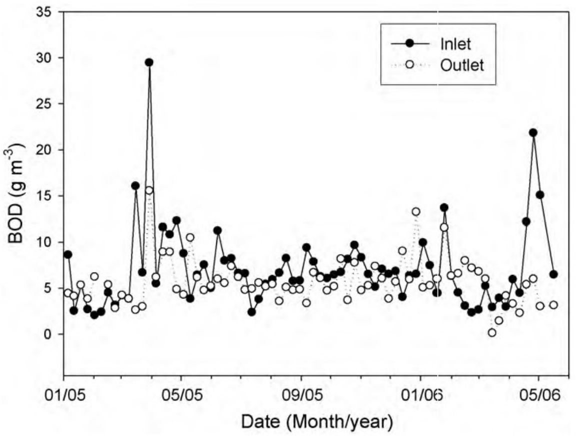

Fig. 6. Changes in BOD between inlet and outlet of the Kinloch bed.

(Fig. 5). Other approaches for removing P have been tested, such as the use of iron compounds (e.g., Robertson, 2000; McDowell et al., 2008) that could be easily incorporated in denitrification beds.

As beds are filled with woodchips there is the potential for the release of soluble carbon compounds through the outlet, which might enhance undesired oxygen consumption in receiving waters. BOD was only continuously measured in the Kinloch bed and generally ranged between 0 and 15 $\mathrm{g\,m^{-3}}$ and there was no obvious difference between concentrations in inlet and outlet (Fig. 6). Further measurements of BOD need to be made during the start-up period of beds to ensure that BOD loss is not a short-term concern (Robertson et al., 2005).

4. Conclusions

Denitrification beds are a relatively simple technology for removing NO_3^- from a variety of effluent streams. We demonstrated that NO_3^- removal rates of large denitrification beds receiving large effluent volumes with high NO_3^- concentrations are similar to smaller beds (van Driel et al., 2006; Robertson et al., 2005). Nitrate removal rates were between 5 and 10 $\mathrm{g\,N\,m^{-3}\,d^{-1}}$ when the beds were not NO_3^- limited and denitrification was the most likely mechanism for NO_3^- removal. Despite good NO_3^- removal, there was no evidence of removal of NH_4^+, organic N, BOD or total P as effluent passed through the bed. For denitrification beds to be effective, effluent needs to be filtered and oxidized to convert N to NO_3^- and remove organic matter; otherwise, N removal is likely to be limited and clogging of the bed might occur.

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