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Determining the hydraulic properties of wood/gravel mixtures for use in denitrifying walls

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Abstract

New Zealand's alluvial gravel aquifers are particularly vulnerable to nitrate impacts from intensified land-use because they are ineffective at naturally attenuating nitrate. The general limiting factor is a lack of available organic carbon to stimulate nitrate-reducing microbial-catalysed reactions in the groundwater system. Denitrifying walls are engineered permeable reactive barrier systems designed to overcome this carbon-limitation problem and enhance natural attenuation of nitrate in situ, in shallow groundwater settings. These reactive barriers operate as passive groundwater treatment systems and offer a potential nitrate mitigation measure for managing nitrate impacts, in particular those in New Zealand alluvial gravel aquifers.

Successful design of a permeable reactive barrier requires an understanding of the hydraulic and chemical properties of the aquifer target, and the hydraulic properties of the barrier medium, together with some estimate of its capacity to denitrify. A set of permeameter tests were conducted to determine the hydraulic conductivity and porosity of potential reactive barrier fill material consisting of mixtures of wood-chip and gravel. The study used aggregate with a broad particle size distribution, characteristic of alluvial gravel outwash, and which is procurable in bulk during the excavation works for any reactive barrier installed in an alluvial gravel aquifer. The limitations of using conventional mathematical models based on fractional packing concepts to predict the hydraulic properties of wood-chip/gravel mixtures are examined.

A wood-chip/gravel mixture with hydraulic characteristics well suited to a New Zealand alluvial gravel aquifer and which can promote denitrification reactions at an effective rate (estimated to be about 3.2-3.6 mg N/L/d) was identified. When combined, wood-chip and gravel follow a largely occupational packing arrangement and hydraulic conductivity was found to correlate negatively with the porosity of the mixture. Because of the complex shape and rough surface characteristics of wood particles, the hydraulic conductivity of the mixed media could not be predicted using a modified version of the Kozeny-Carmen equation.

This work has established some useful initial permeable reactive barrier design parameters that are applicable to New Zealand alluvial gravel aquifers. Investigation of how the hydraulic and reactive properties of the barrier media degenerate with time under field conditions would best be achieved through an in situ field trial, and an assessment needs to be made of the civil engineering requirements and economics

of constructing denitrifying walls in such a challenging environment.

Keywords

Groundwater; nitrate; denitrifying wall; alluvial gravel aquifers

Introduction

Nitrate pollution of New Zealand's freshwater resources is a growing national concern because it presents both a public and environmental health risk. Nitrate levels in both surface water and groundwater environments continue to increase as a direct consequence of land-use intensification (Daughney and Randall, 2009; Ballantine and Davies-Colley, 2010). The nation's most productive and valuable groundwater systems are composed of sand and gravel alluvium and these important freshwater reservoirs are commonly overlain by thin and poorly developed soils that increase their vulnerability to nitrate leaching. Alluvial sand and gravel aquifers also tend to be fast-flowing, aerobic, and contain negligible carbon. As a consequence, they have limited natural ability to attenuate nitrate pollution (e.g., Burbery *et al.*, 2013). In many catchments, groundwater is a major pathway via which nitrate leached from the land enters surface waters.

The recent national water and environmental management reforms promote nitrate mitigation strategies to enable farmers to operate within freshwater quality limits (e.g., Ministry for the Environment, 2013). Denitrifying bioreactors are such a mitigation measure and provide a pragmatic, cost-effective technology for treating nitrate in agricultural drainage water and shallow groundwater (e.g., Schipper *et al.*, 2010; Christianson *et al.*, 2012). Denitrifying walls are a particular class of bioreactor that target shallow groundwater, as opposed to artificial drainage water, and have a proven history of effective passive treatment of nitrate pollution (Long *et al.*, 2011; Robertson *et al.*, 2008; Schmidt and Clark, 2012). Denitrifying walls offer a promising potential practical solution to the mitigation of nitrate impacts in New Zealand hydrological catchments sensitive to nitrate contamination, most importantly shallow alluvial gravel aquifers, which have limited capacity to assimilate nitrate.

The concept of a denitrifying wall is to emplace a permeable reactive barrier (PRB) across the path of nitrate-contaminated groundwater flow. The 'wall' is typically constructed using sand or gravel aggregate to which some solid organic material has been added. The role of the aggregate is to enhance and maintain the permeability of the barrier; act as a weighting material for wall emplacement, and reduce the amount of compaction after installation (USAF, 2008). The organic fraction promotes anoxic conditions and acts as both a substrate and support matrix for denitrifying organisms which metabolise any nitrate in the groundwater, converting it to gaseous nitrogen products. Denitrifying walls have successfully been trialled in a variety of aquifer settings around the world, albeit examples to date tend to be relatively small-scale structures emplaced in aquifers of relatively low transmissivity (e.g., Robertson and Cherry, 1995; Schipper and Vojvodic-Vukovic, 2000; Kalin *et al.*, 2009). So far there are no examples in the literature of denitrifying walls having been installed or designed for an alluvial gravel aquifer setting, probably because of the technical challenges, which are largely attributed to the high transmissivities of these groundwater systems. In particular, outwash gravel aquifers consist of clast-supported gravel sedimentary features (sometimes referred to as open-framework gravels) along which fast groundwater flow is concentrated. The hydraulic conductivity of open-framework gravel hydrofacies is typically in the range of 10^3-10^4 m/d (e.g., Dann *et al.*, 2008; Zappa *et al.*, 2006), which is orders of magnitude higher than aquifer media into which existing PRBs have been installed. The work we present in this paper is targeted at the topic of denitrifying wall hydraulics; we do not address the civil engineering and cost implications of installing PRBs in alluvial gravel environments.

To function properly, the permeability of a denitrifying wall must equal or exceed the permeability of the aquifer, to ensure good flow capture and reduce the risk that groundwater will by-pass the structure (Robertson *et al.*, 2005). The latter aspect is a particular problem for walls that only partially penetrate an aquifer, which would likely be the common scenario for any wall emplaced in a New Zealand alluvial gravel aquifer. For example, Schipper *et al.* (2004) report on a denitrifying wall that was emplaced across the top of a sandy aquifer at Cambridge, New Zealand, and prepared by mixing sawdust (approximately 30% v/v) with native aquifer material in situ. The resulting permeability of the wall was two-orders of magnitude lower than the undisturbed aquifer, which compromised its treatment efficiency, since most of the groundwater flux deviated under the base of the reactor. The work we present here addresses some of the technical issues about denitrifying wall design discussed by Schipper *et al.* (2004). The purpose is to conduct a technical evaluation of bioreactor fill material with the aim of accruing sufficient knowledge to enable the hydraulic efficiency problem experienced by Schipper *et al.* (2004) to be mitigated in the case where a PRB is to be installed in an alluvial gravel aquifer. The information gathered should be useful in any future assessments of the viability of constructing denitrifying walls at the field-scale.

The main study objective was to determine the hydraulic properties, namely the porosity and hydraulic conductivity, of mixtures of wood and gravel, targeted as denitrifying wall fill in an alluvial gravel aquifer. The goal was to identify a binary mixture that at least matches the permeability of open-framework gravels. Wood-chips formed the solid carbon media used in the study because they are a cost-effective carbon substrate and have proven longevity in PRB applications (e.g., Schipper *et al.*, 2010). The wood-chips examined were purposely chosen because they can easily be processed on-site in forest felling areas, conceivably making use of wood residues that are typically treated as a waste product (EECA, 2010). Previous studies that have reported on the hydraulic properties of wood/gravel mixtures for bioreactor fill (Painter, 2005; Christianson *et al.*, 2010) have utilised 'pea gravel', which is a well sorted gravel product, but which cannot be procured in sufficient quantities for denitrifying wall construction without incurring excessive cost. Unlike those studies, we focussed our research on using a gravel base with a broader particle size distribution and that is representative of bulk quantities of aggregate that could be procured on-site during the trenching works for a PRB emplaced in an alluvial gravel aquifer. To the best of our knowledge it is the first time the hydraulic characteristics of such coarse-grade binary mixtures have ever been measured.

As there are no published examples of predictive mathematical models for calculating the hydraulic properties of complex wood-chip/gravel mixtures, we included an assessment of how effective conventional mathematical models that have historically been developed for modelling binary sedimentary mixtures are at this task. In particular, we focus on application of the mixing coefficient and fractional packing models developed by Zhang *et al.* (2011) and Koltermann and Gorelick (1995) respectively. We also examined the solute transport properties of the binary mixture we identified as being best-suited for denitrifying wall fill material, as well as its ability to reduce nitrate.

Materials and methods

Gravel and wood-chip media

Alluvial gravel

The gravel was manually prepared by blending five processed fractions (4-8 mm, 8-10 mm, 10-20 mm, 20-40 mm, and 40-65 mm) of aggregate quarried from Crossbank on the Waimakariri River. The particle size distribution was closely modelled on the natural parent material distribution over this truncated range (e.g., Measures, 2012) (Fig. 1). Particles within the size range 4 mm-65 mm account for approximately 75% of bulk Waimakariri River aggregate, by mass, and Dann *et al.* (2009) previously determined that coarse-grained material (>2 mm diameter) made up 75-87% of bulk sediments sampled from three locations on the Canterbury Plains aquifer. We therefore assume that the particle size distribution of the Waimakariri River gravels provide a reasonable analogue for aquifer sediments of the Canterbury Plains and a useful proxy for other Quaternary gravel outwash systems in New Zealand. The nominal smallest grain size diameter was selected as 4 mm due to both permeability concerns and because aggregate smaller than this fraction holds greatest commercial value (pers. comm. Chris Newcombe, Road Metals, Christchurch).

Wood-chip

The hydraulic properties of four grades of wood-chips were examined: 20 mm 'hogged' wood; 40 mm 'hogged' wood; 100 mm 'hogged' wood, and; wood 'chipped' from branches and logs <45 mm diameter from a mixed forest containing *Pinus radiata* and *Cupressus macrocarpa* species (Fig. 2). Readers are referred to EECA (2010) for a useful description of the different methods used to produce wood-chip. The dimensions of the wood fragments from each product are listed in Table 1. The 20 mm and 40 mm hog-wood had been processed from dry, milled *Pinus radiata*, hence were free of bark, whereas the 100 mm hog-wood was processed from wet wood and included bark. Dry-processed hog-wood was used because it was easily available for examination, not because we perceived that it had any significantly different hydraulic characteristics from wet-processed wood. All the materials that we obtained had been processed using mobile plant operations, hence could conceivably

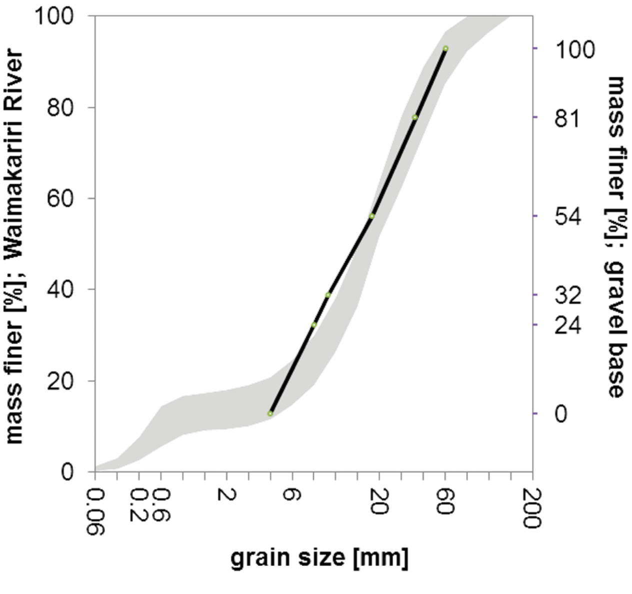

Figure 1 – Particle size distribution of alluvial gravel material. Grey shading highlights range of measured particle size distribution for Waimakariri River alluvium (left hand y-axis) (Appendix B in Measures, 2012); black line marks particle size distribution of composite gravel base used in this work (right-hand y-axis) (d_{10} = 6 mm; d_{50} = 18 mm, d_{90} = 52 mm).

Figure 2 – Various media for which hydraulic properties were examined. Top row L-R: 20 mm 'chipped' wood; 20 mm 'hogged' wood; 40 mm 'hogged' wood; 100 mm 'hogged' wood. Bottom row L-R: 100% gravel; 75% gravel/25% chip; 50% gravel/50% chip; 25% gravel/75% chip. Ruler markings are 10 mm.

Table 1: General dimensions of wood-chip media examined in this study (all units expressed in mm). Statistics determined from measuring major axes of 100 fragments. 'Used' chip is that reclaimed from the bioreactor fill after a permeability measurement.

		'Chipped' wood		'Hogged' wood			
Nominal processed size		**20**	**20 (used)**	**20**	**20 (used)**	**40**	**100**
Average± standard deviation	Length	17±9	16±9	17±10	11±7	31±16	77±31
	Width	7±7	6±4	5±4	4±3	8±5	7±4
	Thickness	3±1	2±2	3±2	2±2	4±4	3±2
d_{10}	L:W:T	9:2:1	8:2:1	8:2:1	6:2:1	15:3:1	43:3:1
d_{50}; median		16:6:3	14:5:2	15:4:2	10:3:2	26:6:4	72:6:3
d_{90}		25:12:5	25:11:4	30:10:5	19:7:3	50:16:8	124:11:5

d_x = particle size of x %-ile.

be prepared at the local site of a denitrifying wall. The dimensions of the 20 mm wood chip products were re-evaluated after they had been hydraulically tested, as a measure of their physical decomposition.

Measurement of hydraulic properties

The hydraulic conductivity of the gravel and wood media was measured using a 0.3 m diameter, 1.5 m long permeameter through which water flowed in an upwards direction at varying rates. Corresponding head differentials were read manually from manometers set 1.3 m apart. A set of multiple flow/head measurements was made for each permeameter test.

In the early stages of experimentation, the 20 mm wood-chip was identified as being the least permeable of the timber products we tested (Table 2) and of the two types,

Table 2: Physical and hydraulic properties of gravel and wood-chip media examined. Dark border outlines media used in binary mixture assessment. Average value ± one standard deviation.

Porous medium	**Gravel**			**'Hogged' wood**		
Gravel content f_g (% v/v)	100	100	100	0	0	0
Wood-chip content f_w (% v/v)	0	0	0	100	100	100
Nominal grain size (mm)	4-8	8-10	10-20	20	40	100
Hydraulic conductivity K (m/d)	11129	30415	66138	8718±1550	21976±6228	26973±4393
Primary porosity θ^1 (%)	36.6	35.5	36.4	45.2±3.9	51.7±8.5	47.2±6.9
Secondary porosity θ^2 (%)	n/a	n/a	n/a	33.2±4.5	33.5±9.5	31.4±8.1
Total porosity θ (%)	n/a	n/a	n/a	78.4±0.5	85.2±1.0	78.6±1.2
Bulk density ρ_b (10^3 kg/m^3)	1.56	1.64	1.64	0.48±0.13	0.43±0.08	0.44±0.04

n/a not applicable

the green 'chipped' wood showed evidence of being a physically more stable product than the aged 'hogged' wood (e.g., Table 1). For this reason 20 mm 'chipped' wood was the wood media used in all the gravel/wood binary mixture assessments. Gravel/wood mixtures were assessed at ratios of 75/25, 50/50 and 25/75 by percentage volume.

For completeness, the hydraulic conductivities of the well-sorted minor gravel fractions from which the model gravel base was composed were also measured. 10-20 mm was the threshold grain size fraction for which hydraulic conductivity could be evaluated using the permeameter apparatus, since head differentials were unmeasurable for coarser materials. We estimate that the hydraulic conductivities for the coarser grained fractions (i.e., 20-40 mm and above) were in excess of 116,000 m/d.

To ensure consistency in weight measurements and to mitigate the risk of the timber changing its size during examinations due to potential swelling effects, wood-chips were soaked for at least 3 days before use. To ensure complete mixing, gravel/wood mixtures were prepared on a volumetric basis in 10 L batches, which were used to fill the (103 L) permeameter. The total mass of material used to pack the permeameter was recorded, from which bulk density was determined. Following each 10 L addition, the permeameter was vibrated and the contents tamped down in a consistent manner, using a 100 mm diameter, 25 kg steel tamper. To account for variance in packing configurations, each medium was tested in quadruplicate, using a freshly prepared bulk sample in every other test. An exception to this was examination of the 75/25 gravel/wood mixture, for which duplicate tests were made of four independently prepared mixtures (i.e., 8 examinations). No repeated measures were made in the case of the three well-sorted, minor gravel fractions examined.

Measured hydraulic conductivity (K) values were determined from Darcy's Law:

$$K = -\frac{Q}{A}\frac{\Delta L}{\Delta h} \tag{1}$$

where Q is the measured flow rate; A is the cross-sectional area of the permeameter (0.071 m^2); ΔL is the length between manometers (1.3 m in all tests) and Δh is the

Table 2

Gravel	Gravel/Wood-chip			'Chipped' wood
100	75	50	25	0
0	25	50	75	100
4-65	4-65/20	4-65/20	4-65/20	20
14796±3872	13562±2917	13800±1456	11958±2285	10535±2951
26.7±1.9	29.5±1.0	33.6±0.5	37.8±1.7	43.0±1.0
n/a	n/a	n/a	n/a	37.9+1.9
n/a	n/a	n/a	n/a	80.9+0.9
1.88±0.05	1.63±0.04	1.36±0.01	1.01±0.05	0.61±0.04

measured hydraulic head differential. The linearity between Q and Δh was inspected in each observation dataset, as a check that measurements were not corrupted by turbulent flow effects. Generally, data obtained under conditions corresponding to a Reynolds number value of ≥ 30 (assuming the median grain size as the characteristic length) (e.g., Bouwer, 1978) were identified as exhibiting non-Darcian behaviour and were omitted from analysis. No fewer than 12 reliable head measures made under a range of flows were in any single permeameter dataset.

At the end of each test, the pemeameter was left to drain overnight, under gravity. The drainable porosities of the media were assumed to be representative of their primary porosities. For the various wood-chip media, total porosity (as the sum of both primary and secondary porosity) was also determined. To do this, a known weight of kiln-dried wood sample was packed in to a 480 mL sealable container to achieve a bulk density similar to that used in the larger-scale permeameter experiments. The container was subsequently maintained full of water and after 10-days soaking the total porosity was determined gravimetrically by measuring both the drainable fraction of water plus the amount of water absorbed in the wood. Such measurements were conducted in triplicate for each wood-chip type.

Assessment of predictive models of hydraulic properties

Mixing efficiency and porosity

The mixing efficiency of a binary mixture is a reference to how much of the pore space of the coarser-grained material is occupied by the finer-grained material. For using gravel and wood as building blocks for a denitrifying wall, the mixing efficiency provides some indication of how the wall storage volume – and therefore the hydraulic residence time of the bioreactor – correlates with the mixture composition. Furthermore, porosity is a variable in some hydraulic conductivity models, and so is a useful property to be able to predict. It is important to note that porosity referred to throughout this section relates to primary (drainable) porosity.

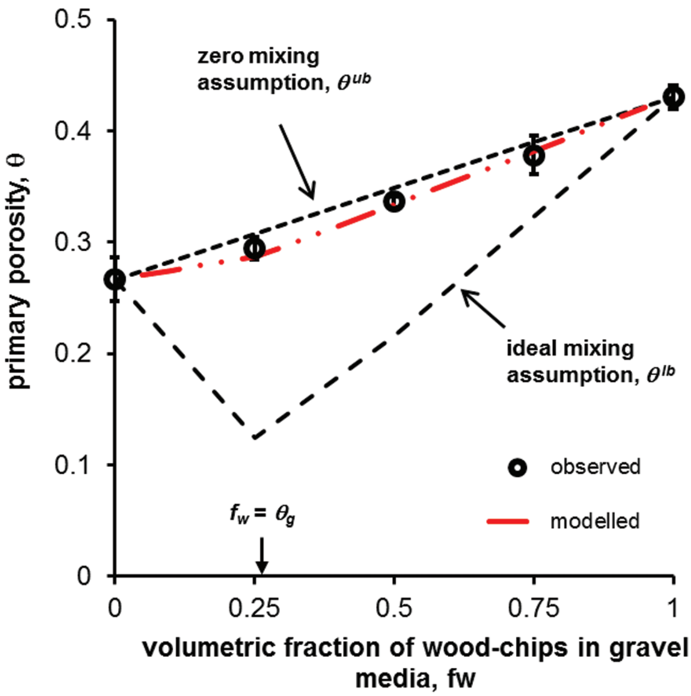

Figure 3 – Porosities determined for gravel/wood-chip mixtures. Error bars on observed porosity data represent one standard deviation. Modelled porosity based on mixing coefficient model of Zhang *et al.* (2011) (Eq. 3), assuming $\lambda = 0.11$.

The mixing efficiency of the wood-chip/gravel was assessed by comparing the measured drainable porosities for the three examined binary compositions (25/75; 50/50; 75/25) against the theoretical upper and lower bounding porosities that relate to a zero-mixing and ideal-mixing model assumption, respectively (Koltermann and Gorelick, 1995; Zhang *et al.*, 2011). For an index we used the mixing coefficient term λ proposed by Zhang *et al.* (2011):

$$\lambda = \frac{\theta^{ub} - \theta_m}{\theta^{ub} - \theta^{lb}} \tag{2}$$

where θ_m is the measured porosity of a specific gravel/wood mixture and θ^{ub} and θ^{lb} are the respective upper and lower bounding porosity values for the same mixture, i.e., if it were assumed the wood/gravel either did not mix at all or ideally mixed, respectively. Mathematical definitions for θ^{ub} and θ^{lb} can be found in Zhang *et al.* (2011) and they are plotted as continuous functions in Figure 3. The coefficient λ has limits of 0 and 1; 1 being ideal mixing and 0 implying zero-mixing. In total we determined three independent values for λ – one for each wood/gravel composition examined.

With knowledge of the porosities of the pure gravel and wood phase end members: θ_g and θ_w, and using the averaged value of λ, we applied the mixing-coefficient model for evaluating the porosity of binary mixtures to our problem (Zhang *et al.*, 2011):

$$\begin{aligned} \hat{\theta}_m &= \left(f_g - \lambda f_g + \lambda\right)\theta_g + f_w\theta_w - \lambda f_w \quad if \quad f_w < \theta_g \\ &= (1-\lambda) f_g \theta_g + f_w \theta_w \qquad\qquad\quad if \quad f_w \geq \theta_g \end{aligned} \tag{3}$$

where we use the circumflex on the θ_m term to denote an estimated porosity for the binary mixture, as opposed to a measured value as was used in derivation of λ. Terms f_g and f_w refer to the respective volumetric fractions of gravel and wood.

Hydraulic conductivity model

In assessing whether the properties for wood-chip/gravel mixtures might have a generalised solution that could allow hydraulic conductivities to be predicted for any mixture, measured *K*-values were compared against theoretical values (K_m) derived using a Kozeny-Carmen equation modified for binary mixtures (Koltermann and Gorelick, 1995):

$$K_m = \left(\frac{\rho_w g}{\mu}\right)\left[\frac{d_m^2 \hat{\theta}_m^3}{180(1-\hat{\theta}_m)^2}\right] \tag{4}$$

where ρ_w is the density of water (999.8 kg/m^3; 10°C), g is the gravitational constant (9.806 m/s^2), μ is the viscosity of water (0.00131 kg/m/s; 10°C), $\hat{\theta}_m$ is the porosity of the mixture (estimated from Eq. 3) and d_m is the effective grain size diameter for the mixed media. The effective grain sizes for the pure phase end members, i.e., 100% gravel (d_g) and 100% wood-chip (d_w), were determined from matching Eq. 4 with measured hydraulic conductivity and primary porosity values for these media. The power-averaging method described by Zhang *et al.* (2011) was subsequently applied to calculate a representative grain size diameter for the binary mixtures.

Measurement of transport properties and nitrate reactivity

To examine the general groundwater transport properties of the wood/gravel fill, a flow-through column tracer experiment using a pulse injection was carried out in the permeameter apparatus for 50/50 gravel/wood PRB fill. Under a constant upward flow regime of 0.5 L/min, a 50 mg/L bromide solution was injected for a period of 30 minutes and the concentrations eluted from the permeameter column were monitored for a period equivalent to 10 flushed pore volumes. Bromide concentrations were analysed using an ion selective electrode (Thermo Scientific Orion 9635BNWP). The resulting bromide breakthrough curve was interpreted using the 1-dimensional advection dispersion model encoded within the CXTFIT software package (Tang *et al.*, 2010).

Despite their limitations as a consequence of not simulating groundwater flow dynamics, batch tests provide a quick and inexpensive screening method for evaluating potential reaction rates (Gavaskar *et al.*, 1998). As a crude estimation of the denitrifying potential of the 50/50 gravel/wood mixture, we completed a static batch reactor test, similar in design to the static column tests Trois *et al.* (2010) conducted to measure the denitrification potential of pine bark media. The packed permeameter column was filled with a 30 mg N-NO_3/L solution that had been prepared by dissolving KNO_3 salt in unchlorinated Christchurch City tap water. The saturated column was stored in a static condition for a period of one week, over the course of which dissolved oxygen (DO) levels and temperature were continuously monitored using an optical DO sensor with in-built thermistor (HACH IntelliCal™ LDO101). Aliquots of the nitrate solution were drawn periodically from the centre of the reactor for chemical analysis of nitrate, nitrite, ammonium, dissolved organic carbon (DOC), pH and alkalinity.

pH was measured at the time of sampling using a Thermo Scientific Orion 8102BN ROSS™ combination pH electrode. Likewise, alkalinity was determined immediately, following the APHA (1999) standard titration method (2320), using phenolphthalein indicator. Total inorganic carbon (TIC) was calculated from pH and alkalinity measures (method 4500D in APHA (1999)). Nitrogenous species were analysed by an IANZ-accredited lab using flow injection analyser technology, and the same lab analysed for DOC using a Shimadzu TOC analyser. The water samples submitted to the lab were preserved in a frozen condition pending chemical analysis.

Results

Porosity and mixing efficiency

All the wood media examined had high primary and secondary porosities, averages for which lay in the range of 43-52% and 32-38%, respectively (Table 2). We found that the bulk density of 'chipped' wood was approximately 30% greater than that of 'hogged' wood product, even though the two products were handled in a consistent manner.

From Figure 3, it is clear that the gravel and wood-chips did not mix efficiently, since they plot close to the line of a zero-mixing assumption. There is however a small amount of fractional packing, as can be witnessed in the slight non-linearity of the measured porosity values and maximum deviation from the zero-mixing model (θ^{ub} line) at the critical fractional volume of the gravel, that is: $f_g = 1-\theta_g = 0.73$; $f_w = \theta_g = 0.27$. The porosity of the binary mixture is well represented by the mixing coefficient model of Zhang *et al.* (2011) (Eq. 3; Fig. 3), assuming a mixing coefficient λ value of 0.11, which was the average value determined from the three binary compositions examined.

Hydraulic conductivity

The hydraulic conductivity of the different wood-chip types that were examined ranged between 8,718 to 26,973 m/d, and for the 'hogged' wood, conductivity correlated positively with nominal chip-size (Table 2). Applying a *t*-test assuming unequal variances, the measured difference between the hydraulic conductivity of the 20 mm 'hogged' wood and 'chipped' wood of the same nominal size was significant ($p<0.05$). As a pure product and being the wood material used in the binary mixture assessments, the 20 mm 'chipped' wood had an average saturated hydraulic conductivity of 10,535 m/d (sd = $\pm$28%).

With an average hydraulic conductivity of 14,796 m/d, the alluvial gravels were more permeable than the 20 mm wood-chip media, but less permeable than the wood-chip graded above 40 mm. However, when the large variation of $\pm$26% observed in the gravel permeability measurement data are factored against the similarly large variance in the 20 mm wood-chip data, then the difference in measured hydraulic conductivity between the two end-members is not statistically significant ($p>0.05$).

From the Kozeny-Carmen equation (Eq. 4), the effective grain size diameters for the 100% gravel and 100% wood-chip media were estimated to be 9 mm and 3 mm, respectively. 9 mm corresponds to approximately d_{30} in the actual gravel distribution used in the study. Applying the same measurement logic to the timber product, less than 1% of the wood-chips were 3 mm in physical length. Ultimately, the modified Kozeny-Carmen equation proved to be a wholly inadequate model for the distribution of hydraulic conductivities measured for the mixtures of gravel/wood-chip, as our data suggest an inverse relationship between primary porosity and hydraulic conductivity in the mixed media.

Despite a high level of noise in the hydraulic conductivity measurements, the data display a distinct negative trend between the gravel and wood end-member fractions (Fig. 4). Of the various compositions tested, the 50/50 mix of gravel and wood-chip exhibited the least variation in measured hydraulic properties (Table 2; Figs. 3 and 4). Although the result is tempered by the large variances exhibited in the collective K-dataset, the average hydraulic conductivity of the same mixture also appears to plot above the value that might be predicted from a simple linear interpolation between the gravel and wood end-members (Fig. 4). This apparent local hydraulic conductivity maxima phenomenon is the complete inverse of K_m patterns

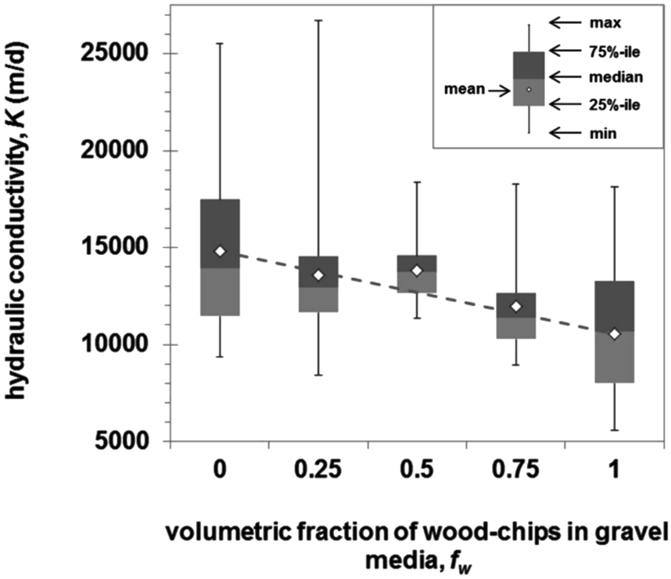

Figure 4 – Measured saturated hydraulic conductivity of wood/gravel mixtures. Dashed line marks a linear interpolation between average *K*-values of gravel and wood-chip end member fractions.

generally associated with fractional packing models such as Equation 4.

Solute transport and nitrate reactivity

The bromide tracer breakthrough curve data from the flow-through column tracer experiment conducted using the 50/50 gravel/wood mixture were well described by the 1-D advection dispersion transport equation (Fig. 5). The Gaussian behaviour of the data and absence of a long tailing effect are characteristic of equilibrium transport, implying solute transport through the binary mixture was not subject to dual porosity or preferential flow effects. Bromide transport was conservative, with complete mass recovery achieved. The effective porosity of 0.41 estimated in the process of matching the advection dispersion transport equation to the observation data was somewhat larger

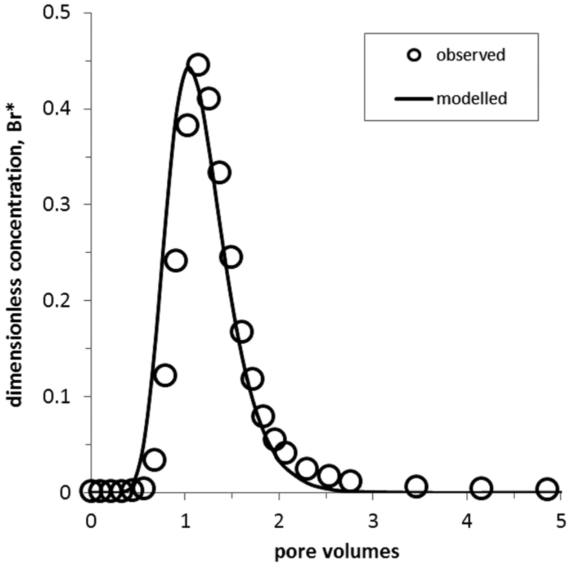

Figure 5 – Bromide tracer breakthrough curve from the solute transport experiment conducted on the 50/50 gravel/wood-chip mixture. Solid line is the 1-D advection dispersion transport equation fit to the problem, assuming an effective dispersivity value of 6.0% and effective porosity of 0.41.

than the primary porosity determined from the hydraulic experiments (listed in Table 2).

The nitrate batch reactor experiment conducted with the same 50/50 gravel/wood was subject to fluctuating temperatures as it was performed outdoors over 96 hours. At the beginning of the nitrate reaction test, the temperature of the bioreactor was 10.2°C. Within 18 hours temperatures had steadily fallen to approximately 5°C and then fluctuated between 2.6 and 8.4°C (average 5.2°C) over the remainder of the test (Fig. 6A). DO was scavenged to below detection levels within 7 hours of incubation (data not shown), over which time temperatures averaged approximately 10°C.

The nitrate concentration data showed a bi-linear temporal trend: nitrate levels dropped by 38% within the first 24 hours of incubation, after which they declined at a relatively constant rate that we interpreted as an effective zero-order decay rate of 5.0 mg N/L/d (Fig. 6B). A concomitant increase in total inorganic carbon was recorded (Fig. 6A), equivalent to 1.6 moles CO_2:NO_3. No major increase in nitrite or ammonium levels was detected, with concentrations of both species maintained below 0.03 mg N/L (data not shown). The pH of the initial nitrate solution was 7.4. Although pH in the bioreactor dropped to 6.2 during the first 20 hours, a small but steady increasing trend is evident in the pH values after this time – levels rose to 6.5 by the end of the incubation period (Fig. 6A). All of the above hydrochemical parameters support the notion that denitrification was the primary reaction pathway by which nitrate was reduced in the bioreactor.

Discussion

Hydraulic properties of wood-chips

The porosity values we determined for the various wood-chip types are consistent with values typically reported for wood-chip media applied as bioreactor fill (e.g., Cameron, 2011; Robertson, 2010). With regards to measured hydraulic conductivities of wood-chips, K-values for a hardwood wood-chip

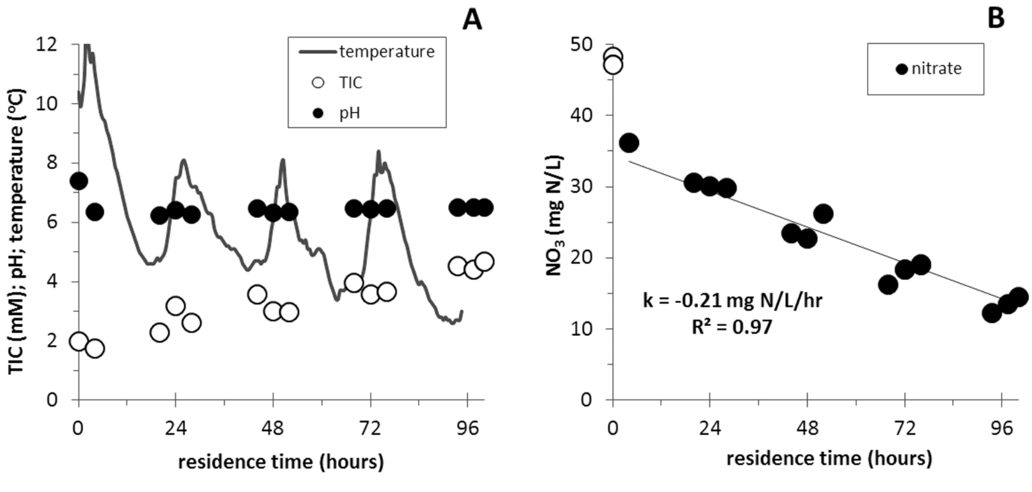

Figure 6 – Measured water chemistry time-series data from the nitrate batch reactor test conducted on the 50/50 gravel/wood mixture. The linear regression applied to nitrate data in Figure 6B ignores observations made in the first 6 hours of incubation, during which time aerobic conditions prevailed. TIC = total inorganic carbon.

tested by Christianson *et al.* (2010) of mean length 13 mm ranged between 6,300 and 9,600 m/d, Chun *et al.* (2009) reported 2,332< K <4,234 m/d for a mixed species of chip of average length 13 mm, but which also contained a considerable number of fines (29.5% <6 mm length). Cameron and Schipper (2010) tested a variety of wood-chip media ranging from sawdust to 61 mm wood-chip, all of which they report had hydraulic conductivities below 10,000 m/d. In our case, 8,718 m/d was the lowest hydraulic conductivity we recorded and this was for the 20 mm 'hogged' wood, the average fragment length of which varied over the course of the experiments but was between 11 and 17 mm. The average K-value of the 20 mm freshly 'chipped' wood used in the binary mixture evaluations was 10,535 m/d, which is close to the conductivity of the 61 mm chip tested by Cameron and Schipper (2010).

The broad ranging hydraulic conductivity values reported for wood-chip examined by different research groups in some ways reflects the organic nature of the product. The large variability in published K-values is mainly related to differences in the particle size distribution of independent wood-chip samples – a property that is generally governed by the mechanical processing methods used in their production, as well as their storage and handling. For example, we observed that the seasoned, 20 mm 'hogged' wood was a very friable product that made it more prone to physical degradation during the experiment than the 20 mm 'chipped' wood, which in contrast was a much fresher product. The relative changes in the particle size distributions of the two different wood-chip media measured before and after hydraulic testing supports this observation (Table 1). We attribute most of the physical breakdown of the wood we witnessed to mechanical erosion rather than any hydraulic or biological action, and in particular pulverization of the wood that occurred during the tamping process we applied when packing the permeameter. Since wood-chips would be susceptible to similar mechanical forces during the construction phase of a PRB, and because the hydraulic characteristics of the wood-chip are directly related to its physical dimensions, we infer from our observations that from a structural preservation perspective, use of fresh timber is favoured over aged and well-seasoned woody material, in denitrifying wall installations.

'Chipped' wood is a higher quality timber product than 'hogged' wood, which is splintered in its manufacture and produces wood spears rather than uniformly shaped and sized chips (see Fig. 2 and EECA (2010)). There are therefore distinct technical advantages in using 'chipped' over 'hogged' wood in a denitrifying wall build, particularly if the wood is to be mixed with gravel aggregate. Further study on the advantages and challenges of using either timber product is warranted.

We emphasise that the wood-chip we used was relatively clean and devoid of green organic material, such as leaves and pine needles, as well as dirt. We would expect that a nominally processed 20 mm sized wood-chip like we used, tainted with such fine contaminative material, would be considerably less permeable than the product we examined. For this reason, we suggest that some post-processing quality control measure, such as secondary screening of wood-chip, would be a useful addition to any field-scale operation trying to replicate the product we described.

Another advantage of fresh timber is that it contains a higher content of labile organic carbon than seasoned timber and as a consequence has potential to promote greater nitrate reduction in the initial stages of PRB operation. Robertson (2010) detected evidence of this when he compared bioreactor fill media of varying age and concluded that wood-chips lose about 50% of their reactivity during the first year of operation, after which he claims biodegradation reactions stabilise. Cameron and Schipper (2010) recorded similar rates of decline in the nitrate-reducing capacity of wood-chip media they examined in a set of model denitrifying bioreactors, operated under controlled conditions. Schmidt and Clark (2010) similarly reported high levels of DOC exported from their denitrifying wall constructed of pine sawdust during its first year of operation, although the net loss in carbon did not appear to affect the denitrification efficacy of the wall. The DOC initially leached from Schmidt and Clark's wall did, however, have a short-term adverse effect on the water quality of a receiving low-order stream situated immediately down-gradient of the PRB (Schimdt and Clark, 2012), which is something to be aware of when designing a field-scale PRB.

Hydraulic properties of gravel/wood-chip mixtures

The primary purpose of this work was to identify the composition of a gravel/wood mixture suitable as fill material in the construction of a PRB for treating nitrate in a New Zealand alluvial gravel aquifer, using natural gravel material procurable in bulk quantities during entrenchment works. Availability of resources determined that hydraulic testing of binary mixtures was limited to a common gravel particle size distribution, amended only with varying volumetric fractions of a single type of wood-chip. All the mixed gravel/wood compositions we examined had hydraulic conductivities in the order of 10^3 m/d and we did not measure the order-of-magnitude differences in hydraulic conductivity reported in similar technical studies conducted with pea gravel and sawdust (e.g., Painter, 2005). Our result was, of course, engineered by our choice of binary end-member components of: i) natural alluvium from the Canterbury Plains aquifer processed to exclude fine sediment less than 4 mm and coarse cobbles larger than 65 mm, and ii) 20 mm 'chipped' wood.

The 50/50 gravel/wood mixture we tested, whose hydraulic conductivity ranged between 11,339 and 18,364 m/d (average 13,800 m/d) is well suited as PRB fill material for an alluvial gravel aquifer. The permeability of this mixture is commensurate with that of open-framework gravel hydrofacies that are responsible for transmitting the bulk of groundwater flow in New Zealand's alluvial gravel aquifers, and which Dann *et al.* (2008) report have typical K-values ranging between 1,498 and 16,000 m/d. Although we suspect the difference would be reasonably small, it is possible that all the hydraulic conductivities we measured using a vertically-oriented permeameter apparatus slightly underestimate the horizontal hydraulic conductivity that would apply to a field setting, because of potential anisotropy effects that we did not examine.

On the basis of the hydraulic conductivity values measured for the larger wood-chip types we examined and the apparently poor degree of mixing between gravel and 20 mm wood-chip media, we would expect substitution of the 20 mm wood-chip with a coarser product to result in more permeable mixed media for the same relative volumetric fraction of gravel/wood. On the other hand, it is evident from the observations of others, most notably Cameron and Schipper (2010), that wood-chip media processed smaller than 20 mm would probably not be useful in the construction of a denitrifying wall emplaced in an alluvial gravel aquifer. Equally, using a gravel base component containing material finer than 4 mm would probably also severely compromise its usefulness as PRB construction material. The single hydraulic conductivity measurement we made on gravel particles of 4-8 mm diameter predicted K = 11,129 m/d, which is substantially lower than the average value for the bulk, well-graded gravel media: K = 14,796 m/d (Table 2).

No effort was made in our study to explicitly measure the compacting forces applied in experiments, although we can estimate, based on the measured bulk density of the 50/50 gravel media of 1,400 kg/m^3 and permeameter height, that overburden pressures would have been in the region of 6.3 kN/m^2. Higher stresses than this are to be expected in a PRB installed in the field and will be governed mainly by the additional weight of material making up the unsaturated zone which, for a typical gravel soil, equates to an additional stress of approximately 19 kN/m^2 for every metre the water table is below ground level (e.g., Bolz and Tuve, 1973). A functional role of gravel in the construction of a denitrifying wall is to absorb the overburden pressures, thus provide structural support to the PRB. However for the particle size distribution of the wood and gravel we report on, the low mixing coefficient value we evaluated implies the 20 mm wood-chip adopted a mainly occupational packing mechanism in the well-graded alluvial gravels, as opposed to a filling mechanism (Yu and Standish, 1991). From this observation, we would presume that the 20 mm wood-chip bore some of the weight of the overburden, for which implications on long-term viability of the PRB fill media remain undetermined. As Schipper *et al*. (2010) mentioned in their paper reviewing denitrifying PRB technology, the effect of overburden pressures on long-term hydraulic performance of PRBs remains a topic that is not widely reported and deserves future study.

Despite our best efforts to pack the permeameter in a consistent fashion, we can infer from the large variances in the hydraulic conductivity measures that it is extremely difficult to achieve any consistent structural packing arrangement working with wood-chip and/or well-graded alluvial gravels. This problem could be mitigated if uniform-sized gravel material were used, but this would offset our goal of engineering denitrifying walls using aggregate that can be easily procured in bulk, on site, during PRB excavation works. It is interesting to note that of the binary compositions examined, the 50/50 gravel/wood-chip appeared to exhibit the least variance in measured hydraulic conductivity, which suggests that the packing arrangement in this media between tests was more consistent than was achieved with other compositions.

Ability to predict the hydraulic properties of gravel/wood-chip mixtures

We found that the mixing coefficient model described by Zhang *et al.* (2011) (Eq. 3) fit the drainable porosity data of our gravel/wood media very well. At this stage, however, its practical use is limited to predicting the primary porosity of mixed compositions of gravel and wood-chip media that have the exact particle size distribution of those we examined, i.e., interpolating between observation points we established. To predict the porosity of mixtures of gravel and wood-chip of different grades would require repeat experimentation to obtain independent estimates of the mixing coefficient λ. Also, our subsequent discovery that the effective porosity of a gravel/wood mixture appears to lie somewhere between its primary and secondary porosities evaluated using gravimetric methods, highlights limitations in the methods we applied that focussed on drainable porosity data. Establishing a relationship between effective porosity and the composition of gravel/wood-chip mixtures would provide more meaningful data, but entails conducting numerous tracing experiments.

Knowledge of λ for a binary medium is in itself useful information, as it provides a metric of the packing arrangement. We can infer from the average λ value of 0.11 determined in our tests that the 20 mm wood-chip mainly arranged itself according to an occupational packing mechanism, i.e., rather than fill void spaces in the gravel media, the wood-chip itself provided some skeletal component to the binary structure (e.g., Yu and Standish, 1991). Some of the technical implications of this structural arrangement on PRB design have been discussed above.

Inferences of critical mixing arrangements in binary systems are often assessed from a comparison of the effective particle sizes (Cumberland and Crawford, 1987; Yu and Standish, 1991). In our application of the Kozeny-Carmen equation, we determined effective particle diameters for the wood-chip and gravel media to be d_w = 3 mm and d_g = 9 mm, respectively. These values suggest a fine to coarse-grained ratio (d_w/d_g) value of 0.3, which is greater than the critical ratio of entrance value of 0.154 that marks the threshold above which packing changes from a filling mechanism to an occupational mechanism (Yu and Standish, 1991). It is important to realise, however, that the critical ratio of entrance model is a geometrical model conceived for binary systems comprising mono-sized spherical particles and therefore is only a very crude analogue for non-uniform gravel and wood-chip media. Indeed, Yu and Standish (1991) mention “it is very difficult, if not impossible, to characterise mathematically the packing structure of a particle mixture”, from which we infer that a reliable predictive model for wood-chip and gravel mixtures might never be developed.

The complexity of the packing structure between the flat, angular wood-chips and rounded gravel is further highlighted in the hydraulic conductivity data that the modified Kozeny-Carmen equation failed to model. The inverse relationship exhibited between hydraulic conductivity and porosity of wood-chip/gravel mixtures is the complete opposite of that assumed in Equation 4, whose mathematical foundations lie in the concepts of pipe flow and flow along capillary tubes. Our general observations concur with those reported by Christianson et al. (2010) and Painter (2005), who examined the hydraulic properties of pea gravel mixed with wood-chip and saw-dust, respectively. We presume that the contrast in effective size and shape, combined with differences in plasticity and surface roughness characteristics between the wood-chip and gravel, promote tortuous flow and frictional head-losses that contribute to the curious result.

Although we have failed to identify a suitable physical model to describe the hydraulic conductivity of binary wood/gravel mixtures, we note that the pattern of our data is not unique. Hydraulic conductivity measurements made by Christianson *et al.* (2010) on mixtures of 13 mm wood-chip amended with 8 mm pea-gravel also signify a possible local *K*-maxima phenomenon. Moreover, the local *K*-maxima in both cases appear to coincide with instances where the gravel fraction of the binary mixture was close to the theoretical critical fractional volume of wood-chip: (1 - θ_w). The uncertainty in the hydraulic conductivity data precludes any meaningful interpretation at this stage and further work is required to test the hypothesis that a local *K*-maxima occurs in wood/gravel mixtures where an occupational packing mechanism is active, and that it occurs where the gravel content equals the theoretical fractional volume of the wood-chip.

Transport properties and nitrate reactivity of 50/50 gravel/wood-chip media

The nitrate batch reactor test using the 50/50 gravel/wood medium demonstrated that denitrification was the main nitrogen removal process in the treatment system and that the bioreactor did not adversely alter the water chemistry, such as inducing major changes to pH. The results indicate that conditions within the bioreactor were conducive to the microbial activities of importance to us, since nitrate reduction proceeded unabated over the course of the test. On the basis that ammonium levels in the bioreactor were maintained below 0.03 mg N/L we can infer that dissimilatory nitrate reduction to ammonia (DNRA) (e.g., Tiedje, 1988) was not an active process. As no significant accumulation of nitrite occurred in the bioreactor we can also deduce that the nitrate reaction rate of 5.0 mg N/L/d we determined was a consequence of denitrification, which we assume continued to completion according to the following general reaction stoichiometry (Appelo and Postma, 2005):

$$CH_2O + \frac{4}{5}NO_3^- + \frac{4}{5}H^+ \rightarrow CO_2 + \frac{2}{5}N_2 + \frac{7}{5}H_2O \quad (5)$$

Evidence from published bioreactor studies indicates that incomplete denitrification is generally only likely to be an issue in an operational PRB if its hydraulic residence time is insufficient (Schipper *et al.*, 2010). General indicators of incomplete denitrification are elevated concentrations of meta-stable intermediate nitrogen species in the nitrogen reduction sequence spanning from nitrate to di-nitrogen gas, i.e., nitrite or N_2O gas (Appelo and Postma, 2005). We postulate that since no nitrite accumulated in the reactor, it is highly improbable that N_2O gas did either, since the heterotrophic bacteria capable of metabolising N_2O were never starved of energy.

The water used in the nitrate batch reactor test was natural groundwater from the Christchurch City Aquifer, hence we can assume its fundamental chemical properties, including natural buffering capacity, are characteristic of shallow groundwater typically encountered in New Zealand alluvial gravel aquifers (e.g., Rosen and White, 2001). The slight acidification of the water by 1.2 pH units, from pH 7.4 to 6.2, detected in the initial stages of incubation, we mostly attribute to CO_2 production from aerobic respiration, which was exhausted within 7 hours. After this aerobic stage of microbial activity, it appears pH reached a relatively stable condition, despite on-going nitrate reaction. We do not perceive that pH changes of the magnitude we observed would present any significant environmental risk to the natural condition of a typical New Zealand alluvial gravel aquifer.

From the nitrate and TIC concentrations we monitored (Fig. 6), we calculate that 28% more CO_2 was generated in the bioreactor than would theoretically have been produced if denitrification was the only active reaction process (see Eq. 5). We can only speculate on the possible anaerobic microbial processes that could have generated the extra CO_2, but strongly suspect it evolved from fermenting bacteria active in decomposing the wood-chip (e.g., Appelo and Postma, 2005). Nitrate concentrations never approached rate-limiting levels during the test, so we assume nitrate was the terminal electron acceptor process and that redox conditions were insufficient to activate Mn(IV), Fe(III), sulphate reduction or methanogenesis microbial processes (Chapelle, 2001).

The water chemistry data for the nitrate batch reactor test show some response to the fluctuating experimental temperatures (Fig. 6), which were beyond our control. The nitrate reaction rate predicted from the experiment relates to an average bioreactor temperature of 5.2°C. This temperature is lower than the natural groundwater temperature generally encountered in New Zealand alluvial gravel aquifers, which depends on regional climate, but as a rule of thumb is typically equal to the long-term average air temperature. Cameron and Schipper (2010) report on nitrate reactivity of wood-chip increasing ×1.6 for every 10°C increase in temperature. Applying such a correction factor to the denitrification rate we determined in the nitrate batch reactor test for 50/50 gravel/wood media, would suggest the 5.0 mg N/L/d might more realistically be 6.3-7.2 mg N/L/d in a New Zealand aquifer setting where groundwater temperatures are between 10 and 13°C. If however one assumes that nitrate reactivity could realistically halve within the first year of bioreactor operation (Robertson *et al.*, 2008; Cameron and Schipper, 2010), then the long-term denitrification rate for the 50/50 gravel/wood fill, if installed in a field-setting where nitrate concentrations are non-rate limiting, might be a more modest 3.2-3.6 mg N/L/d.

It is important to recognise that this reaction rate estimate stems from a static batch reactor test that examined just 103 L of potential PRB fill that was carefully prepared by hand. We suspect that it is closer to a maximum potential rate than an average reaction rate that might be encountered under real-world field conditions. In the batch experiment we performed, chemical diffusion processes dominated and no provision was made to simulate solute transport and mixing via advection-dispersion, as would occur in the natural world. Furthermore, it is difficult to perceive that at the field-scale, wood-chip and gravel could be mixed and packed quite as effectively as they were in the lab experiments. Implicit to this problem is the risk that preferential flow effects and nitrate reactive hot-spots could occur within the denitrifying wall structure – a problem highlighted by Schipper *et al.* (2005). A philosophical discussion on how representative reaction rates derived from lab experiments are of the real-world is beyond the topic of this paper, and yet it is interesting to note that our predicted rate of 3.2-3.6 mg N/L/d closely matches the maximum nitrate removal rate of 1.4 g N/m^3 of wall/d (3.0 mg N/L/d) Schipper *et al.* (2005) determined from in situ field measurements made at the site of a 7-year-old denitrifying wall located in Cambridge, New Zealand, and constructed with sawdust (30% v/v).

The effective porosity of the 50/50 gravel/wood media predicted from the tracer experiment was significantly greater than the drainable porosity, and highlights limitations in assuming the drainable porosity estimates in reactive transport modelling through wood/gravel media. Other transport studies conducted on PRB fill material have experienced similar results (Ahmed, 2007; Cameron, 2011). Furthermore, Cameron (2011) noted long-tailing in his tracer breakthrough curve data, signifying non-equilibrium solute transport through wood-chips, yet we, like Ahmed (2007), saw no such effect and were able to model solute transport through the gravel/wood mixture assuming equilibrium transport.

Conclusions

Through conducting a number of permeameter tests, supported by a denitrifying batch reactor test and a flow-through column tracer experiment, a binary gravel/wood-chip mixture has been identified that is suitable as fill material in a denitrifying wall for treating nitrate in shallow groundwater of an alluvial gravel aquifer. The mixed media is composed of alluvial gravels with a natural particle size distribution, but filtered of sediment finer than 4 mm diameter and coarser than 65 mm, to which relatively clean 20 mm wood-chip is added. Minimum variability in measured hydraulic conductivity was detected where the mixture comprised 50% gravel and 50% wood-chip (measured by volume). From this we currently suggest that, on the balance of hydraulic performance, perceived long-term structural integrity and nitrate reactivity considerations, the 50/50 composition is a favourable ratio of wood-chip and gravel to use. Further work, including a cost-benefit analysis, would be useful to verify these presumptions.

On the basis of as single solute transport experiment, one can assume that 50% gravel/wood-chip media of the type described has an effective porosity of approximately 41%, which is more than the 34% repeatedly determined from drainable porosity tests. The packing arrangement of the 20 mm wood-chip mixed with non-uniform, well-graded gravels is mainly occupational in its nature. Whether or not this packing arrangement presents implications for the long-term hydraulic performance of a PRB remains to be determined. Although highly variable, the media had an average hydraulic conductivity of 13,800 m/d and promoted denitrification reaction at a rate of 5.0 mg N/L/d. A maximum denitrification rate closer to 3.2-3.6 mg N/L/d is predicted for the likely long-term performance under New Zealand field conditions. A field-scale pilot study would go a long way toward answering many of the outstanding technical questions regarding the operation of a PRB emplaced in an alluvial gravel aquifer.

This collection of experimental values is a first of its kind for such coarse-grained, well-graded media and provides useful design parameters for PRBs for treating shallow groundwater nitrate in alluvial gravel aquifers. Priority however should be given to assessing the civil engineering challenges of installing a PRB in a gravel aquifer, including the likely size requirements and associated costs of construction, to understand whether denitrifying walls present a feasible groundwater nitrate mitigation solution for New Zealand.

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