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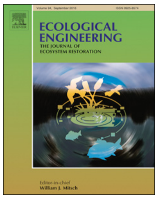

Woodchip denitrification wall technology trialled in a shallow alluvial gravel aquifer

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ABSTRACT

Woodchip denitrification walls are a tried and tested groundwater nitrate remediation concept in shallow sandy aquifer conditions. There are however no published case studies of them having been applied in heterogeneous, fast-flowing gravel aquifers. Such a pilot study is being made in a shallow alluvial gravel aquifer on the Canterbury Plains, New Zealand, as part of an assessment of whether denitrification walls represent a viable edge-of-field nitrate mitigation option for the New Zealand hydrological landscape. Hydrogeological conditions at the field study site were characterised using a suite of investigative methods, the results from which informed design and placement of an experimental woodchip denitrification wall that was installed in November 2018. The average specific flux in the target gravel aquifer is estimated at 2.7 m/d, and 3.1 m/d through the woodchip wall itself, owing to its hydraulic efficiency. These groundwater fluxes are significantly higher than conditions reported for pre-existing denitrification wall case-studies. Monitoring of the groundwater chemistry over the first year of the denitrification woodchip wall's operational life has shown how the woodchip initially leached labile dissolved organic carbon and created a redox plume in which methanogenic conditions existed. Even though dissolved organic carbon concentrations have restored to background levels, the woodchip wall remains effective at nitrate reduction. The measured nitrate removal rate of between 4.2 and 5.4 g N removed/m^3 wall/d is higher than what had previously been predicted from controlled lab-scale studies of the wall media and ranks towards the higher end of published removal rates for denitrification walls. Whilst there is direct evidence that heterotrophic denitrification is contributing to the observed nitrate removal, on the basis of chemical indicators, it is assumed other reactive process, such as dissimilatory reduction to ammonia, anammox, and possibly nitrate-reducing Fe(II)-oxidising reduction reactions may also be contributing to the overall removal of nitrogen in the system. Indications are the woodchip wall is enhancing emission of methane gas, albeit at rates less than what is typically reported for constructed wetlands that are an alternative nitrate-remediation option. Emission of the more potent greenhouse gas nitrous oxide from the woodchip denitrification wall has so far been immeasurably low. Longer-term study of the woodchip denitrification wall is continuing.

1. Introduction

Progressive land-use intensification to support the growing global demand for food production and enabled by use of nitrogenous fertilisers has led to nitrate becoming the most common groundwater contaminant in the world (United Nations, 2011). In New Zealand in particular, the problems associated with nitrate contamination of groundwater and freshwater ecosystems are escalating, partly a consequence of massive expansion of the dairy-farming industry that started in the 1990's (Howard-Williams et al., 2010; Joy, 2015). To address this situation of degrading water quality, legislative reforms are being made to land and freshwater resource management in New Zealand with nutrient load limits to be imposed in freshwater catchments (MfE, 2017; 2019). This action has prompted exploration of methods by which nitrogen load limits might be reduced in sensitive catchments. Part of that exploration is testing the viability of woodchip denitrifying bioreactor systems described by Schipper et al. (2010) and Gold et al. (2013), as edge-of-field N-mitigation practices. Within this scope is evaluation of woodchip denitrification walls, targeting removal of shallow groundwater nitrate.

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Denitrification walls constructed using wood particles, be it sawdust or chip, are a tried and tested groundwater nitrate remediation concept (e.g. Robertson and Cherry, 1995; Schipper and Vojvodić-Vuković, 1998; Jaynes et al., 2008; Vallino and Foreman, 2008; Schmidt and Clark, 2012a). Evidence from the earliest field trials made in Canada and New Zealand show that long after soluble organic compounds have been leached from the wood, such systems can continue to provide steady, passive removal of nitrate from groundwater for several decades (Robertson et al., 2008; Robertson, 2010; Long et al., 2011). Demonstration of the practice however has so far been limited to sandy aquifer settings, where groundwater fluxes are relatively small. As far as we are aware, there are no reports in the scientific literature of woodchip denitrification walls having been applied in gravel aquifer settings, such as constitute the most common and important groundwater systems in New Zealand (Rosen and White, 2001; White et al., 2004). In New Zealand at least, unconfined alluvial gravel aquifer systems are particularly vulnerable to nitrate pollution, as they represent flat-lying land that is intensively used for agriculture, and often overlain by thin, poorly developed soils that are prone to nitrate leaching. Furthermore, they naturally lack electron donors that might otherwise attenuate nitrate through denitrification reactions (Burbery, 2018). In contrast to the sandy aquifer systems in which denitrification walls have so far been trialled, gravel outwash aquifers are inherently heterogeneous, highly transmissive systems that are prone to preferential flow phenomena (e.g. Dann et al., 2008; Burbery et al., 2017). These traits, together with high mass fluxes of water, oxygen and nitrate pose challenges to the design and performance of a denitrification wall that have never been tested in practice.

In this paper we provide details of a woodchip denitrification wall pilot study we are conducting in a shallow alluvial gravel aquifer setting that constitutes a practical assessment of the above. To the best of our knowledge, this work represents the first case study of woodchip denitrifying bioreactor technology being applied under such hydrogeological conditions. Aspects of the site investigation and how findings from this were used to inform design of the denitrification wall are described, as are the reasons for why in practice, the final as-built structure differed from the optimal design. Results from intensive monitoring of the groundwater chemical condition affected by the woodchip wall over the first year of its operation, and its effectiveness at removing nitrate are presented. Included in this is an evaluation of emissions of greenhouse gases (GHGs) N_2O, CH_4 and CO_2 from the nitrate remediation system, as a pollution-swapping phenomenon that has only once before been examined for a field-scale denitrification wall (Gibert et al., 2019). We compare our findings to those of other woodchip denitrification wall studies made in sandy aquifer settings and discuss what implications these may have on the long-term performance and viability of the technology as an edge-of-field N-mitigation practice for gravel aquifer settings.

2. Materials and methods

2.1. Study site setting

The experimental woodchip denitrification wall has been installed on the site of a 3.5 ha public reserve, within the Silverstream catchment, located at the northern-end and along the coastal margin of the Canterbury Plains, South Island, New Zealand (43.4122°S,172.6016°E) (inset Fig. 1). The Silverstream catchment itself represents a lowland spring-fed stream system with flows sustained by groundwater discharging from the Waimakariri-Eyre River fan complex. Land at the site and its surrounds was developed post-1867, before which it represented an active part of the Waimakariri River fan – one of four major alpine braided rivers from which the Canterbury Plains is formed. Nitrate concentrations in the groundwater-fed Silverstream consistently range between 6 and 7 mg/L NO_3-N and diffuse pollution from the predominantly agricultural land-use is assumed to be the nitrogen source (Dodson et al., 2012; Scott et al., 2016).

2.2. Characterisation of subsurface conditions

Baseline hydrogeological conditions at the study site were characterised over the 18 months preceding installation of the denitrification wall that was in November 2018. Ground-penetrating radar (200 MHz antenna coupled to an SIR3000 acquisition unit (Geophysical Survey Systems, Inc., USA)) was initially used to examine subsurface conditions. The resulting radargrams showed 5 m surficial coverage of scour and fill features, confirming the alluvial nature of the surficial geology. A total of 50 investigative bores subsequently drilled across the site using sonic-drilling methods verified a shallow unconfined aquifer composed of a heterogeneous mix of mainly sandy gravel, interbedded with open gravel and sand, typical of outwash deposits (e.g. Dann et al., 2008, 2009; Burbery et al., 2017). From borelog profiles, we estimate sand facies make up approximately 18% of the local aquifer architecture. The bulk (at least 70%) of the aquifer is composed of sandy gravel facies with open framework gravels (OFG) constituting less than 12%. These relative proportions are within the range of values previously reported for alluvium of the Canterbury Plains (Dann et al., 2008, 2009; Burbery et al., 2017). In 10 bores, occasional fragments of woody plant material were detected within the alluvium at discrete depths. The presence of such organic material tended to be focussed to the north and east of the study site. An extensive aquitard layer, marking estuarine deposits from the mid-Holocene sea-level highstand (Brown and Weeber, 1992) defines the base of the phreatic aquifer. The water at the site rests within 0.5 m of the ground surface and the amplitude of seasonal fluctuation is typically less than 0.5 m, owing to the proximity of Silverstream, which acts as a discharge boundary of the local groundwater system. A profile of the shallow aquifer and sample borelogs are presented in Fig. 2.

Bores were completed with 50 mm diameter PVC monitoring wells. Most (39) of the wells screen across the full saturated thickness of the aquifer. A few (6) wells are completed with 0.2 m screen lengths set at 4.0 m below ground level. These short-screened wells include 4 mm diameter multi-level sampling tubes that are set at shallower depths and from which pore water samples can be syringe-sampled from discrete hydro-facies. Repeated surveys of the water table at the site have revealed a constant piezometric gradient of 0.002 and general SW-NE groundwater flow direction, aligned with the regional topography and flow direction of the nearby Silverstream (Fig. 1). To obtain an in situ measurement of the bulk effective hydraulic properties of the shallow aquifer, a 24-hour constant rate pumping test was performed at the site, from centrally located well PW1 (marked on Fig. 1). The transient groundwater level responses at 34 observation wells were simulated with a 3-D numerical flow model, using MODFLOW-NWT (Niswonger et al., 2011). The flow domain was discretised by a 2 m by 2 m regular grid horizontally and five layers vertically. The transient flow model was inverted using PEST (Doherty, 2015) to obtain the calibrated (minimum error variance) specific yield (assumed uniform across the site) and spatially distributed hydraulic conductivity field.

The complex heterogeneity of the aquifer is further demonstrated in the groundwater chemistry. Baseline groundwater nitrate concentrations in the shallow aquifer generally measured from 5 to 7 mg/L NO_3-N, although in three of the wells instrumented with multi-level sampler ports, consistently lower concentrations were detected. The lower nitrate samples corresponded to pore water extracted from discrete sand or sandy gravel facies and below depths of 2.5 m.

As a measure of any background denitrification activity, sediments retrieved from drill cores were tested for denitrifying enzyme activity (DEA), using a modified version of the acetylene-block bioassay developed by Tiedje (1982) and following the methods described by Peterson et al. (2013). The aim was to examine material representative of the major facies of the aquifer system that we classed as sand, sandy gravel and open gravel, consistent with previous hydrogeological

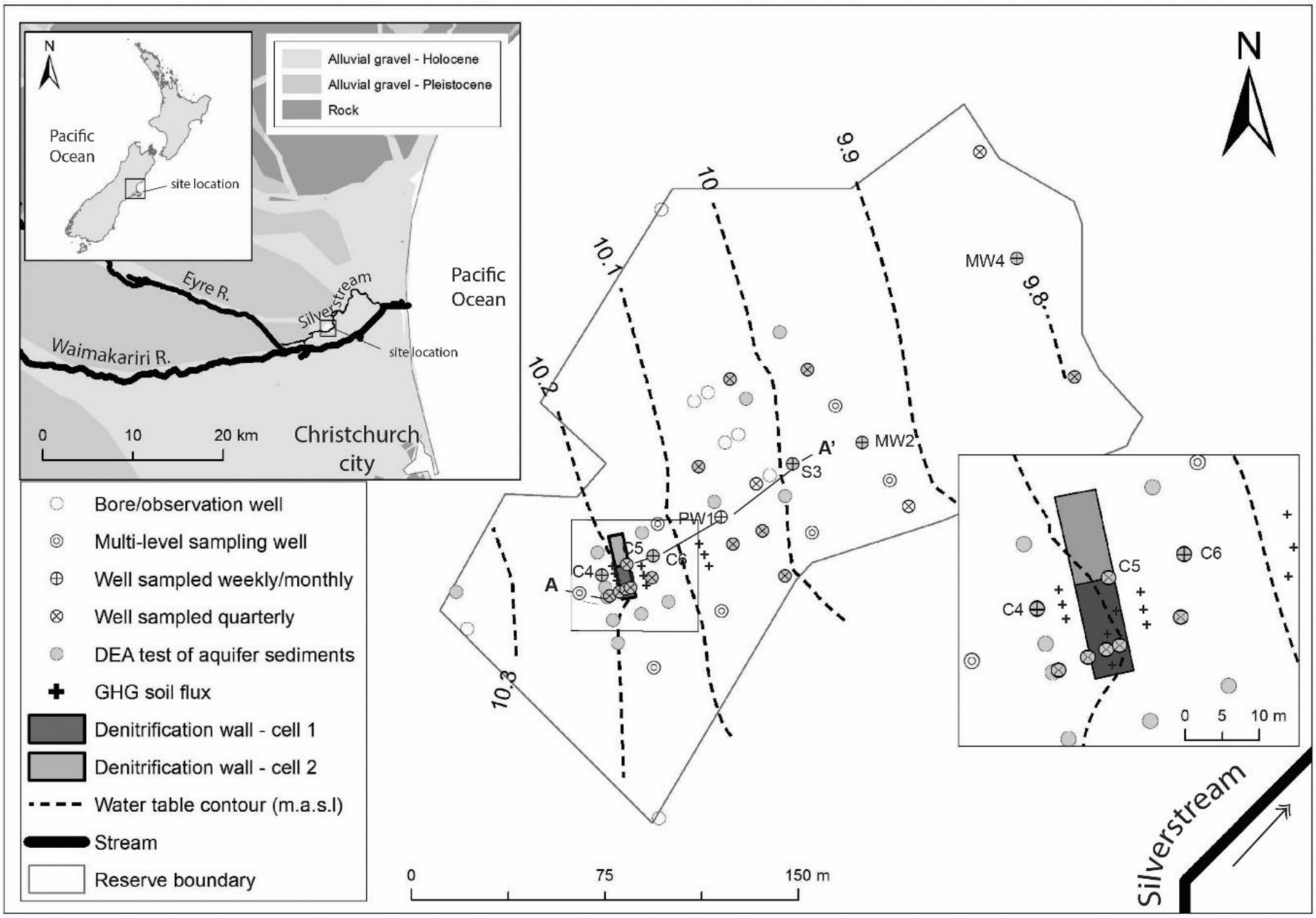

Fig. 1. Site location plan, showing the position of the denitrification wall, monitoring wells and plots where greenhouse gas emissions were measured. The seven wells that were sampled on a monthly basis, data from which are presented in Figs. 4 & 5, and Table 2, are labelled. Piezometric contours are plotted from water table elevations measured 6 months after installation of the woodchip wall.

characterisations made of the Canterbury Plains aquifer system (Dann et al., 2009; Burbery et al., 2017). Silt from the underlying aquitard was also tested. Sediments were stored at 4 °C and held no longer than 36 h prior to assaying. Eleven weeks following installation of the denitrification wall, sonic drilling was again used to obtain two samples of the wall fill media that were also assayed for DEA.

To verify the local direction of groundwater flow and determine the true groundwater velocity, such as required to optimise the design of the denitrification wall, we performed two saline tracer tests about where the denitrification wall was planned and carried out in conjunction with time-lapse electrical resistivity tomography (ERT). In each test, saline tracer was prepared by adding NaCl to 3000 L of native groundwater to achieve a concentration of 1 g NaCl/L with a resulting electrical conductivity of 10,500 μS/cm. This solution was injected down a well screening the full saturated thickness of the unconfined aquifer at a rate of 3.5 L/min, at which no measurable change in the water table was detected. To determine the precise flow direction, we ran three ERT lines perpendicular to the perceived flow direction, as we had inferred it to be from the piezometric data. The tests comprised between 32 and 86 stainless steel electrodes pegged into the ground at 1 m intervals with lines positioned 1 m, 5 m and 15 m downgradient from the injection well. During velocity testing, only a 32-electrode array at 5 m distance was used. With this set-up, time-lapse ground electrical resistivity measurements were made using a 128 channel Allied Tigre multiplexor configured with a standard Wenner Alpha scheme (Allied Associates Geophysical Ltd., UK). Limitations on data acquisition speed, constrained the frequency of measurement to every 20 min from the start time of tracer injection. Resistivity data were normalised against background measures and automatically processed using the RES2DINV software package, from which apparent resistivity pseudosections were obtained. An estimate of the groundwater pore velocity was obtained from the time of peak arrival of the electrically conductive saline tracer, as measured from the pseudosections. In both tests, preferential flow and solute transport was detected from the injection wells, focused at a depth of approximately 1.5 m below ground, through what we interpreted from borelogs and our conceptualisation of the aquifer, to be gravel beds of between 0.3 and 0.5 m thickness. The transport velocity through the open gravel facies was estimated to be in the order of 40–50 m/d. Detection of solute transport through the remainder of the aquifer was below the sensitivity of the ERT measurements, from which we determine it to be minor. The general findings were consistent with preferential flow phenomena observed in other tracer tests conducted in outwash on the Canterbury Plains (e.g. Dann et al., 2008; Burbery et al., 2017; Sarris et al., 2018).

2.3. Denitrification wall design and construction

2.3.1. Wall design

The required size of a denitrification wall is governed by the nitrate flux requiring treatment and the denitrifying reactivity of the woodchip media. Since carbon is rarely limiting in woodchip bioreactor systems, for design purposes it is commonly accepted that a zero-order reaction can be assumed (e.g. Schipper et al., 2010). Assuming uniform horizontal flow, for a unit-wide strip of aquifer into which a denitrification

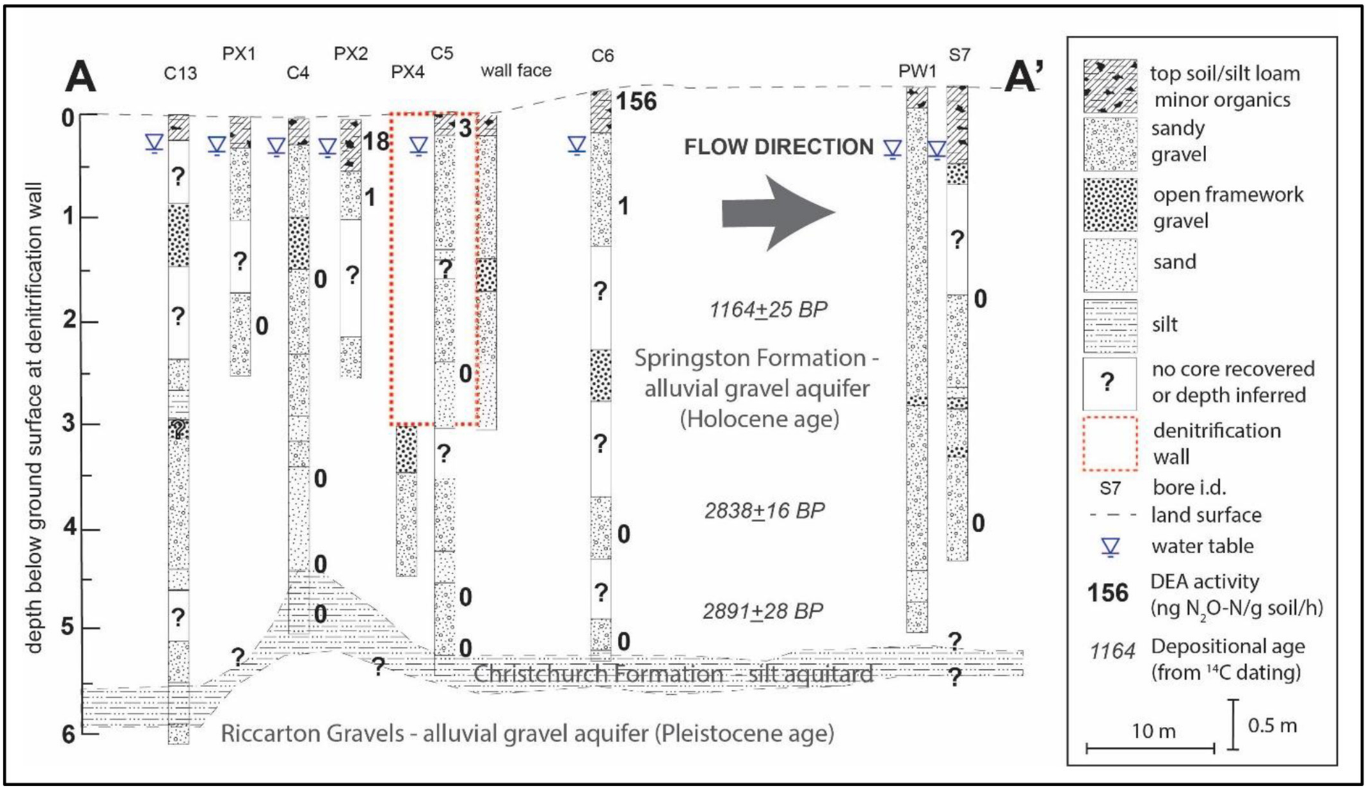

Fig. 2. Geological profile of the shallow groundwater system at Silverstream Reserve, as recorded from drill core logs along transect A-A', marked on Fig. 1. Denitrifying enzyme activity results are labelled for discrete facies samples that were assayed. The position of the woodchip denitrification wall that partially penetrates the unconfined aquifer is marked. Depositional ages were determined from radiocarbon dating of wood fragments sampled from core material across the site.

wall is to be entrenched, a simple estimate of the necessary wall width w required to achieve complete nitrate removal can be estimated from Darcy's Law and consideration of the residence time for complete denitrification reaction:

$$\overline{w} = \overline{q}\bullet t_{res} = \overline{K}\bullet i\bullet t_{res} \tag{1}$$

$$t_{res} = \frac{C}{k_{NO3}} \tag{2}$$

where q, K and i are the specific discharge [L/T], hydraulic conductivity [L/T] and hydraulic gradient [−] of the aquifer, respectively. We use the macron in eq. (1) to denote bulk aquifer properties. t_{res} is the hydraulic residence time in the denitrification wall [T], evaluated from both the groundwater nitrate concentration requiring treatment C [M/L^3] and the zero-order denitrification rate constant k_{NO3} as applies per unit volume of denitrification wall [M/L^3/T]. In a prior study we made of potential woodchip/gravel mixtures suitable for application in gravel aquifers of the Canterbury region (Burbery et al., 2014), we predicted a long-term denitrification rate of 1.3–1.5 g N/m^3 wall/d or 3.2–3.6 mg N/L/d for a mixture similar to that used in this study. This falls within the range of in situ rates Long et al. (2011) report for aged denitrification wall examples in Canada and New Zealand built using sawdust (15–30% v/v).

Our ERT tests support the findings of Dann et al. (2008) who demonstrated that in alluvial gravel aquifers, like the one at our study site, mass transport is dominated by flow through the OFG. Ignoring mass transport through the other facies, eq. (1) can be rewritten as a flow-weighted mass transport expression through the OFG according to:

$$w = \frac{b_g\bullet v_g\bullet \theta_g}{(b_g + b_s)}\bullet t_{res} \tag{3}$$

Where b_g and b_s are the respective effective thicknesses of open gravel and any sandy matrix that make up the saturated aquifer thickness, and v_g and θ_g are the OFG effective pore (i.e. transport) velocity and effective porosity respectively. Informed by both hydrogeophysical and geological bore data, we assumed that OFG, effectively constitute somewhere between 0.3 and 0.5 m of the total sedimentological profile of the shallow aquifer.

Given our prior knowledge of both the hydraulic and effective transport properties at the study site, we made independent predictions of an optimal denitrification wall size considering both eqs. (1) and (3). The wall depth and length were optimised using the site calibrated flow model, with an aim to maximize the intercepted flow. The predefined total excavation volume was fixed for this analysis and was informed by budgeting constraints. The optimal cross section was found to be 25 m long and 3 m deep. Table 1 lists the parameter values assumed in the design optimisation problem when it is assumed the wall will penetrate the top 3 m of aquifer. From those, an optimal wall thickness in the realm of 8–12 m was predicted.

2.3.2. Wall construction

Across the Canterbury Plains there is a history - associated with construction of irrigation galleries - of excavations having been made below the water table without need of implementing any trench stabilisation methods. At the start of our pilot study we were optimistic this would be the case at our study site. However, that proved not to be the case and geotechnical conditions required for us to employ sheet-piling to shore up the walls of any open excavation to prevent wall collapse and mitigate the risk of compromising the hydraulic function of the aquifer. The unplanned expense of sheet-piling ultimately impacted on the final design of the wall that in practice we limited to a sub-optimal width of 5 m. Sheet-piles were toed into the top of the silt aquitard circa 5 m, which enabled dewatering of the excavation and dry deposition of the woodchip/gravel mixtures, as is the emplacement

Table 1
Parameter values assumed in denitrification wall width design optimisation problem when aquifer function is inferred from observed hydraulic data (eq. 1) or observed effective transport properties (eq. 3).

	Parameter	Units	Assumed value(s)	Comments/data source
Eq. (2)	C	g NO_3-N/m^3	6	Average field measurement 2017–2018
	k_{NO3}	g NO_3-N/m^3/d	1.3–1.5	Burbery et al. (2014)
	t_{res}	d	4.0–4.6	Calculated from eq. (2)
Eq. (1)	K	m/d	1332	Bulk aquifer property, inferred from constant rate pump test
	i	–	0.002	From piezometric surveys
	q	m/d	2.66	Calculated from eq. (1)
	w	m	10.6–12.3	Calculated from eqs. (1) & (2)
Eq. (3)	v_g	m/d	40–50	Inferred from time-lapse ERT salt tracer tests
	θ_g	–	0.3	Dann et al. (2009)
	b_g	m	0.3-0.5	Borelogs and ERT observations
	b_s	m	2.5–2.7	Borelogs and ERT observations
	w	m	8.0–11.5	Calculated from eqs. (1) & (3)

method recommended by Barkle et al. (2008) to ensure uniformity. The open excavation was made to 3 m below ground level, meaning the wall structure partially-penetrated the shallow aquifer (e.g. Fig. 2).

The experimental wall was divided into two separate, but contiguous 12.5 m-long cells, as are shown in Figs. 1 and 3. Each cell contained different woodchip/gravel media, albeit in both cases, a 50/50 (*v/v*) ratio of wood/gravel was used, since in a preliminary, lab-based study, we found this to offer a good compromise between hydraulic performance and reactivity (Burbery et al., 2014). In cell 1, the binary mixture comprised 'chipped' wood of nominal 20 mm diameter, mixed with 20–40 mm gravel rounds. We have previously speculated such a uniform mixture containing 'chipped' wood offered superior functional properties than a less uniform mixture or one made up using 'hogged' wood, which is cheaper to prepare (Burbery et al., 2014). To examine this in practice and on a larger scale, the contents of cell 2 were filled with 'hogged' wood (i.e. splintered wood, broken up using hammers) mixed with coarse gravel material (20+ mm diameter), screened from the diggings. Virgin wood from *Pinus radiata* was used throughout. The binary mixtures for each cell were prepared by filling a 17 m^3 dump truck with sequential (2 m^3) scoop-loads of wood and gravel material, the contents from which were emptied into the open shored-trench, where a long-arm excavator then spread and agitated the fill material to achieve a uniform mixture. The final dimensions of the denitrification wall were 25 m long x 5 m wide x 3 m deep (Fig. 3).

The permeabilities and porosities of the fill material were measured from lab-based permeameter tests, following the method described in Burbery et al. (2014). The respective hydraulic conductivities (*K*-values) of the woodchip/gravel media used in cell 1 and hogged wood/gravel media used in cell 2 were K_{cell1} ~ 30,000 m/d; K_{cell2} ~ 20,000 m/d. The porosities were 50% and 43%, respectively. It is worthy to note that these hydraulic conductivities are higher than that typically associated with OFG facies (Klingbeil et al., 1999; Ferreira et al., 2010) and significantly higher than the average hydraulic conductivity of 1322 m/d we inferred for the shallow aquifer from the constant rate pumping test.

2.4. Groundwater monitoring and analysis

Groundwater chemistry at the site was regularly monitored for aqueous nitrogen species, pH, alkalinity, electrical conductivity, dissolved organic carbon (DOC) and redox indicator variables: dissolved oxygen (DO), oxidation-reduction potential (ORP), dissolved iron, dissolved manganese and sulphate. A set of nine wells on a transect following the general direction of groundwater flow and passing through cell 1 were sampled on a weekly basis for a period of six months, after which sampling frequency was reduced to monthly. Every quarter, the groundwater chemistry survey was extended to include an additional 14 wells with a broader site coverage. Sampled wells are marked on Fig. 1.

Groundwater samples were collected using a GP1002 downhole centrifugal pump (Whale, UK) set at a level 1.5 m below ground surface, i.e. half the depth of the denitrification wall. Samples were collected after field parameters - pH, temperature, EC, ORP and DO (measured using a YSI Pro Series field meter) - stabilised. Water sampled for dissolved metals, DOC, nitrate, nitrite, ammonium and sulphate analyses was filtered at the well-head using 0.45 µm polypropylene filters. The samples for metal analyses were also preserved using nitric acid. All water samples were stored and transported chilled, pending chemical analyses done by a commercial lab following standard methods (AWWA, 2017). Alkalinity measurement was made following standard method APHA 2320 B. Metal species were analysed by ICP-MS following method APHA 3125 B. Nitrate, nitrite and ammonium were measured by FIA following standard method APHA 4500, although on occasion nitrate and nitrite were analysed using a UV-spectrophotometer (TriOS-OPUS, Germany). Sulphate was analysed by IC, following method APHA 4500 B, and DOC analysis followed standard method APHA 5310C. For each sampling event, the redox condition of the groundwater was classified according to the framework devised by McMahon and Chapelle (2008) and using the threshold criteria that Close et al. (2016) applied to redox maps of New Zealand groundwaters. These were: DO 0.1 mg/L; NO_3-N 1.0 mg/L; Mn 0.05 mg/L; Fe (II) 0.1 mg/L; SO_4 0.5 mg/L.

Being both products of the denitrification process and greenhouse gases, dissolved N_2O and CO_2 were measured in the broader survey.

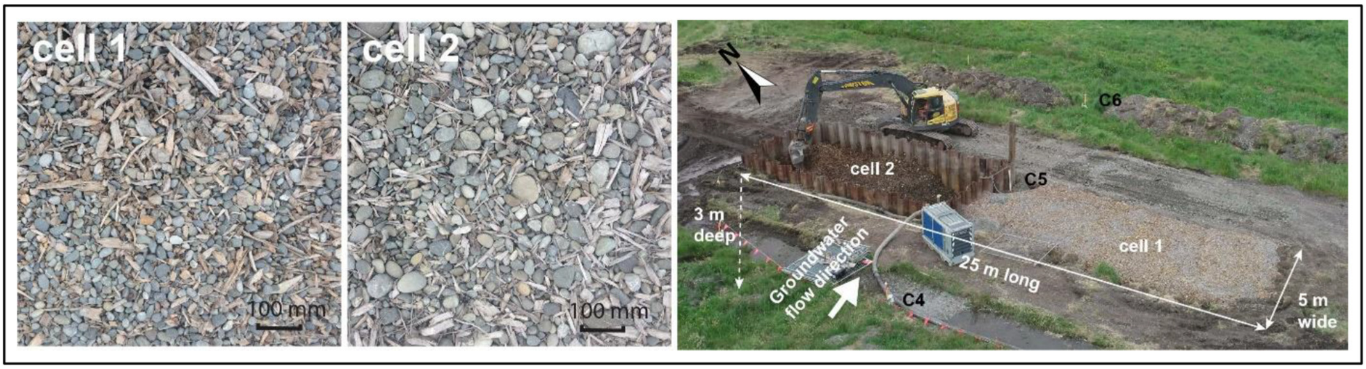

Fig. 3. Pictures of the 50/50 woodchip/gravel mixtures that make up the denitrification wall, and a photo showing installation works. Cell 1: chipped wood mixed with 20–40 mm gravel rounds. Cell 2: hogged wood mixed with parent aquifer material, screened of material under 20 mm diameter. The positions of monitoring wells C4:C6 are marked on the photo.

Whilst not a product of denitrification, the greenhouse gas CH_4 was included for completeness, since conceivably there is potential for methanogenesis to occur from biodegradation of the woodchip. Aqueous concentrations of N_2O and CH_4 were measured using the headspace equilibration technique (e.g. Clough et al., 2007; Magen et al., 2014). As groundwater was being pumped from a monitoring well, a 50 mL sample was collected using a plastic syringe, via an in-line 3-way sampling port. The syringe was pre-flushed with sample water and samples were drawn under water, using an improvised water bath, so at to minimise risk of any contamination by air. The syringed water sample was immediately injected into an evacuated 100 mL serum bottle of known weight containing 500 μL of 50% *w/v* $ZnCl_2$ solution as a biocide preservative. Using a gas syringe, helium gas was introduced to the headspace so that the pressure equilibrated with atmospheric pressure. Serum bottles were stored underwater and transferred back to the laboratory where they were reweighed to determine the precise volume of water sampled, shaken vigorously for one minute, then left to stand overnight to reach room temperature. Using a gas syringe that had been pre-flushed with helium, approximately 7 mL of gas headspace from the serum bottle was transferred to a pre-evacuated 6 mL Exetainer, the contents of which were analysed by GC-FID at the [New Zealand] National Centre for Nitrous Oxide Measurement. Dissolved gas concentrations were evaluated using the calculation-steps described in Magen et al. (2014), referencing the CH_4 and N_2O gas solubilities reported by Weisenburg and Guinasso (1979), and Weiss and Price (1980), respectively. Method detection limits varied between individual testing events, but at worst were 0.6 μg N_2O-N/L and 16 μg CH_4-C/L. Being a weak acid, the use of $ZnCl_2$ compromised analysis of CO_2 using the headspace-equilibriation method. Consequently, free- and total-CO_2 concentrations in groundwater were calculated from sample alkalinity and pH measurements (standard method APHA 4500 D).

Whilst indicative of potential, aqueous GHG concentrations do not necessarily translate to GHG emission to the atmosphere. To reconcile this and to assess whether the woodchip wall promoted GHG emission, a one-off survey of N_2O, CH_4 and CO_2 emissions from the land surface about the woodchip wall was conducted, exactly one year after the installation date. Gas flux measures were made using static soil flux chambers and following international guidelines (Klein and Harvey, 2015). Measurement targeted three sub-plots of the study site: i) upstream of the wall; ii) atop of the wall (cell 1), and iii) downstream of the wall yet above the plume of treated groundwater, both 5 m and 25 m distant from the wall. Triplicate tests were made within each of the sub-plots (mapped on Fig. 1). Soil gas chambers were constructed from white PVC and measured 260 mm in diameter with a headspace volume of 1.4 L. The soil gas survey was conducted between the hours of 10:00 and midday, on a day when meteorological conditions were stable. Gas fluxes were calculated using the linear regression scheme, applied to three observation datapoints spanning a 20-min monitoring period. Following the calculation steps described by Parkin et al. (2012), flux detection limits were determined to be 2.2 μg N_2O-N/m^2/h, 3214 μg CO_2-C/m^2/h and 88 μg CH_4-C/m^2/h.

3. Results

For conciseness, we limit presentation of water quality monitoring data from the study to only nitrogen-species and redox indicator variables for seven wells positioned along a conceptualised streamline transecting the woodchip wall that were sampled most frequently (Fig. 1).

3.1. Development of a redox plume and effectiveness at nitrate removal

Fig. 4 plots the water chemistry monitored for the seven wells. The results show that entrenchment of woodchip into the aquifer fuelled reactions leading to immediate changes in the groundwater redox state. The data demonstrate a pulse release of DOC from the woodchip wall, promoting a decline in DO and nitrate, increase in dissolved iron and manganese, and decline in sulphate, as the mass of reactive DOC migrated from the wall. Within the wall itself, a peak DOC concentration of 35 mg/L was detected 33 days after installation. After this, concentrations in the downgradient groundwater receded rapidly and effectively restored to ambient background values of the range 1.5 ± 0.7 mg/L after 28 weeks. In wells C6 and PW1, located 10 m and 40 m down-gradient of the wall, respectively, peak DOC concentrations of 22 and 24 mg/L occurred between 14 and 26 days of the wall being commissioned. No significant change in DOC concentration was detected in groundwater 190 m down-stream of the wall, although small responses in some other chemical parameters such as nitrate, sulphate and alkalinity (not shown) were.

Table 2 records the spatio-temporal changes of redox processes, as determined using the redox classification framework of McMahon and Chapelle (2008). For the first 34 weeks of operation the woodchip promoted a zone of sulphate-reduction in the aquifer that extended at least 40 m down-stream from the wall. ORP values measured in the groundwater of this zone were close to -200 mV (Fig. 4). Whilst not monitored as frequently as other analytes, dissolved methane was detected at elevated levels in the same zone, which indicates redox conditions were also supportive of methanogenesis (Fig. 5). We determine nitrate-reduction to have been the Terminal Electron Acceptor Process (TEAP) within the treated groundwater system since at least week 48 (Table 2), yet there is evidence of some reduction of alternative electron acceptors: manganese, iron and sulphate (Fig. 4).

The data record for well C4 in Fig. 4 provides a reference for the background condition of untreated groundwater at the site entering the wall – the wells location can be seen in Figs. 1 and 3. The intensive monitoring has revealed that over the course of the first year the wall has been operating, ambient groundwater nitrate concentrations in the Silverstream catchment have steadily increased from 6.3 to 7.8 mg N/L. This increase was not foreseen in the preparatory or design stages of the pilot study. Over the first 19 weeks of operation, nitrate concentrations in pore water of the wall (well C5 in Fig. 4) were consistently below 0.2 mg N/L, indicating effectively 100% nitrate removal. Then an almost step-change in concentration and treatment performance occurred, with nitrate concentrations in the wall never dipping below 0.7 mg N/L, and reaching up to 1.2 mg N/L. Nonetheless, for the first 39 weeks this residual nitrate was scavenged in the plume of treated groundwater, as evidenced by the lack of nitrate ($<$ 0.2 mg N/L) in groundwater 10 m downstream from the wall (well C6, Fig. 4). After 39 weeks, the capacity of the system to offer complete removal of all groundwater nitrate passed through the wall appears to have diminished and 10 m down-stream of the wall groundwater nitrate concentrations have consistently been over 0.8 mg N/L. This effect has been accompanied by a noticeable trending increase in the nitrite concentrations (maximum 0.07 mg N/L) that have been measured in both wells C5 and C6. One year after its installation, the woodchip wall appears to be effective at reducing nitrate concentrations to 93% of their influent value – equivalent to a denitrification factor value of 0.07 (Gibert et al., 2019).

3.2. Evidence for denitrification

We were not able to measure excess-N_2 in our study that might otherwise have provided direct evidence of complete denitrification. In lieu of this, we relied on collating anecdotal evidence of denitrification activity and conducted a nitrogen mass balance, assuming all nitrogen in the system is input as nitrate, as measured in well C4, up-stream of the woodchip wall. We assume nitrate assimilation into microbial biomass is insignificant compared to dissimilatory nitrogen-consuming reactions for reasons discussed below.

Fig. 6 plots results from the DEA assays made on sedimentary material, classed by facies. More than half of the (57) samples of aquifer material that were assayed before installation of the woodchip wall

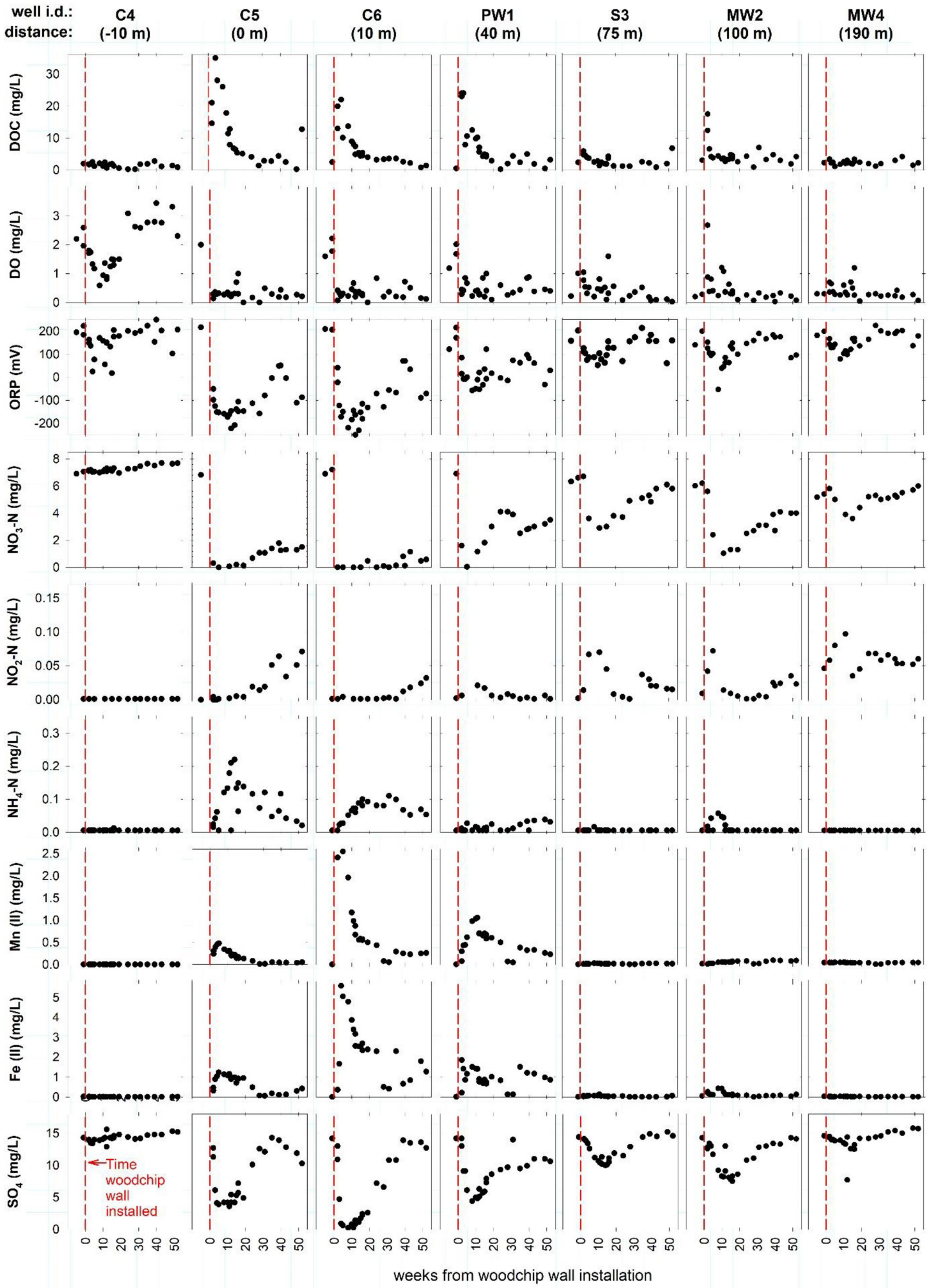

Fig. 4. Time series data for select water chemistry parameters, monitored at seven wells (mapped in Fig. 1) positioned along conceptualised groundwater flowpath, transecting the woodchip denitrification wall. Relative distances are measured from well C5, which is positioned within cell 1 of the wall (see Fig. 3). The vertical dashed line marks the time woodchip was emplaced in the aquifer.

Table 2
Redox state, as determined from groundwater chemistry along monitoring well transect and using the classification framework devised by McMahon and Chapelle (2008). n/c = not classified. Multiple indicators denote a mixed redox condition.

	well	C4	C5	C6	PW1	S3	MW2	MW4
	distance (m)	-10	0	10	40	75	100	190
weeks from woodchip wall installation	**-2**	O2	n/c	O2	O2	O2	NO3	NO3
	1	O2	Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	O2	NO3-Fe(III)/SO4	NO3
	5	O2	Fe(III)/SO4	Fe(III)/SO4	Fe(III)/SO4	NO3	NO3-Fe(III)/SO4	NO3
	10	O2	Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3-Fe(III)/SO4	O2-Fe(III)/SO4	NO3
	14	O2	Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Fe(III)/SO4	NO3
	18	O2	Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Mn(IV)	NO3
	24	O2	NO3-Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Mn(IV)	NO3
	27	O2	NO3	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3	NO3
	30	O2	NO3	Fe(III)/SO4	NO3-Fe(III)/SO4	n/c	NO3	NO3
	34	O2	NO3-Fe(III)/SO4	Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Mn(IV)	NO3
	38	O2	NO3-Fe(III)/SO4	NO3-Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Mn(IV)	NO3
	42	O2	NO3-Fe(III)/SO4	NO3-Fe(III)/SO4	NO3-Fe(III)/SO4	NO3	NO3-Mn(IV)	NO3
	48	O2	NO3	NO3	NO3	NO3	NO3	NO3
	52	O2	NO3	NO3	NO3	NO3	NO3	NO3

tested negative for any DEA. Moreover, where DEA tests proved positive based on measurable N_2O production, rates were overall very low - less than 5 ng N_2O-N/g soil/h in 72% of samples. Only two sediment samples yielded notably high rates of N_2O production of 156 and 299 ng N_2O-N g soil/h. These corresponded to sandy gravel material sampled from 0.4 m depth (and which included brown humic material from the overlying soil horizon) and a sample of silt aquitard material taken from 4.4 m deep, respectively. The DEA of these two samples was close to the activity (378–653 ng/N_2O-N/g wall/h) measured for woodchip/gravel media, sampled from the wall, 11 weeks after its construction.

Aqueous N_2O concentrations in groundwater sampled from well C4, located immediately up-stream of the woodchip wall were consistently detected at low levels, in the range of 6–8 μg N_2O-N/L (Fig. 5A). Elsewhere, variable N_2O concentrations were detected, reflective of the development of the redox plume extending downstream from the woodchip wall. The data tend to suggest increasing potential for N_2O generation over time, as the woodchip wall ages and its reductive potential drops. Nevertheless, there is no evidence of N_2O accumulating in the plume of treated groundwater and at 23 μg NO_2-N /L, even the peak nitrous oxide concentration in groundwater 40 m down-stream of the wall after one year operation reflects a very small fraction ($< < 1\%$) of the total nitrogen mass in the system, relative to amounts in the form of either nitrate, nitrite and ammonium.

Combining this result with the observed nitrate loss coupled to no significant measurable increase in nitrite or ammonia, but an increase in alkalinity (data not shown) and evidence of enhanced DEA within the woodchip wall, it is apparent the woodchip wall is supporting heterotrophic denitrification with presumably complete reduction to N_2, such as it is intended to do. Whilst evidence is weighted towards denitrification being the main nitrate-reduction process, the presence of detectable amounts of ammonium in the pore water of the wall signify some alternative nitrogen reaction processes that our study was not designed to examine objectively. These alternative processes are discussed below.

3.3. Greenhouse gas emissions

Results of dissolved N_2O were presented above. Immediately up-gradient of the woodchip wall, dissolved methane concentrations have consistently been < 0.5 μg CH_4-C/L and similarly low concentrations have repeatedly been measured 190 m down-gradient of the wall (Fig. 5C). We assume these values are indicative of the natural condition of the shallow aquifer at the study site. Like N_2O, elevated levels of dissolved methane were detected within the woodchip wall and the associated plume of reduced groundwater. A maximum concentration of 1.2 mg CH_4-C/L was detected in pore water of the woodchip wall and groundwater 40 m down-gradient of the wall on the initial survey, made 18 weeks following installation of the wall. This concentration is substantially below the solubility (~21 mg CH_4-C/L) of methane in groundwater at the site (e.g. Weisenburg and Guinasso, 1979), suggesting low potential for methane gas emission. Unlike nitrous oxide, methane concentrations have demonstrated a progressive decline with time, as the chemical reactivity of the system has declined with the ageing of the wall. Evidence is that by the end of year one, dissolved methane levels across the study site have reverted to typical natural background levels of < 1 μg CH_4-C/L.

The pattern in free carbon dioxide concentrations in groundwater shown in Fig. 5B follow that of dissolved methane concentrations (Fig. 5C). CO_2 increased in the initial stages of the wall operation because of enhanced microbial respiration. By week 40 however, signs of significant CO_2 production from the woodchip wall had diminished with no discernible difference in free CO_2 in groundwater detected across the site. A gradual drop in the pH of groundwater by 0.7 pH units, from 6.7 to 6.0 has been detected over the course of the year of study (data not shown), although this drop has been affected in all groundwater sampled at the site, not just that conceivably affected by the woodchip wall. Groundwater at the study site has a background alkalinity within the range of 55–60 mg $CaCO_3$/L, which is typical of values for Canterbury gravel aquifers. Implementation of the woodchip denitrification wall affected an increase in alkalinity that peaked at 102 mg $CaCO_3$/L four weeks after installation, but this has since stabilised at 70–85 mg $CaCO_3$/L for groundwater within and immediately downgradient of the wall (data not shown). Considering the pH condition at the site, effectively all (> 99%) inorganic carbon in the groundwater system resided in bicarbonate form, hence degassing of free CO_2 was unlikely.

GHG flux measurements made at the land surface (Fig. 5D) after a

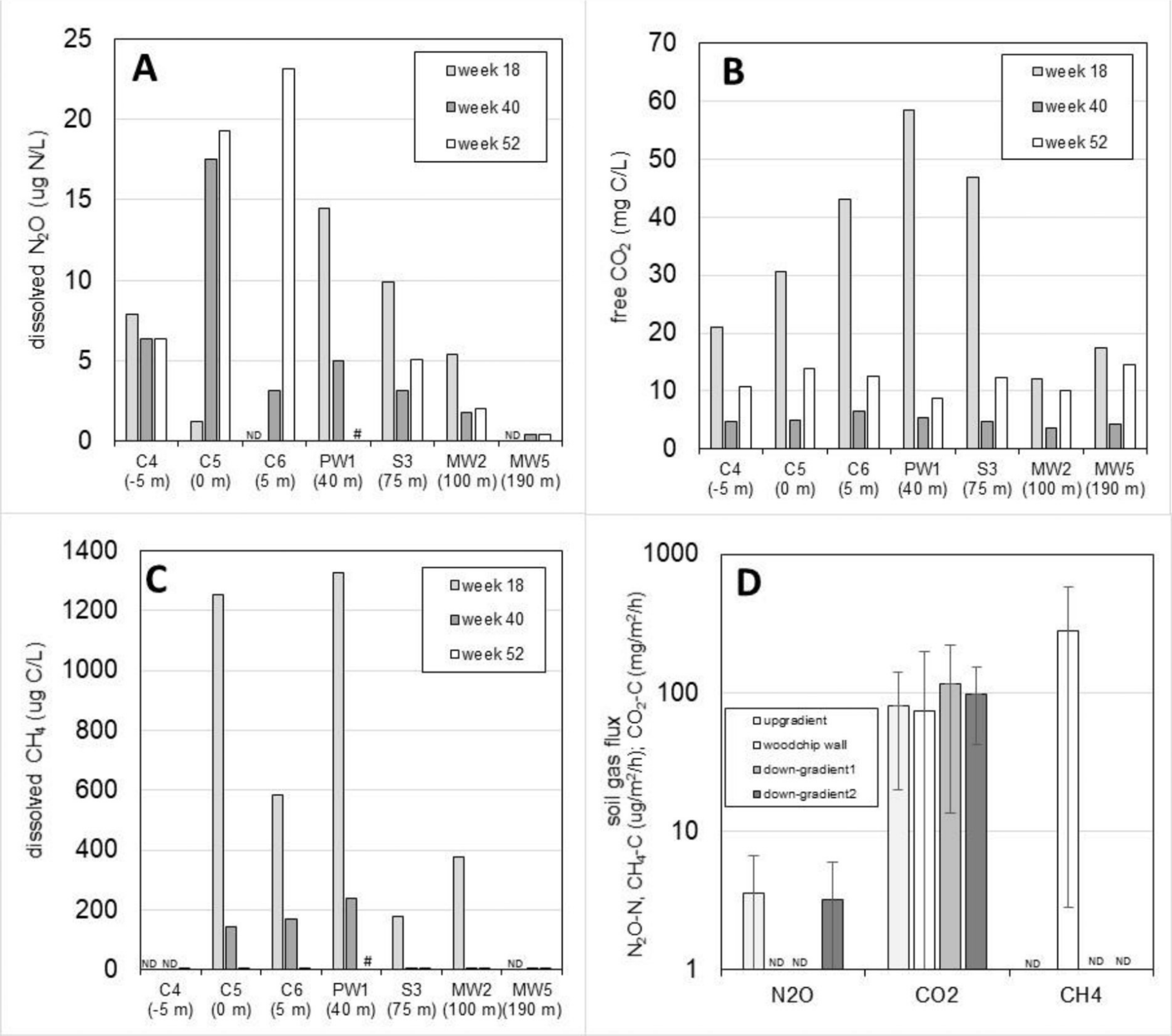

Fig. 5. Concentrations of greenhouse gases N_2O, CO_2 and CH_4. A-C: dissolved in groundwater sampled from the transect of monitoring wells on three occasions following installation of the wall, D: emitted from the land surface, as measured 52 weeks following installation. ND = non-detect, i.e. below the method detection limit; # = missing data point.

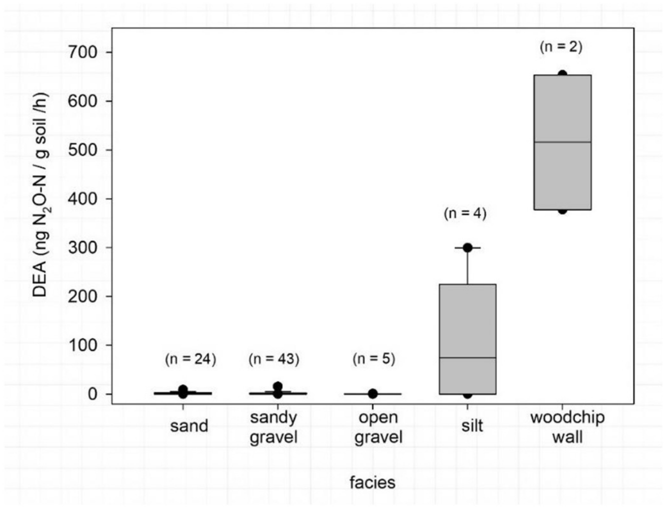

Fig. 6. Denitrifying enzyme activity (DEA) measured for sedimentary aquifer material at the study site, also woodchip wall material. Sediment samples were collected before installation of the wall and are classed by facies. Material from the woodchip wall was sampled from cell 1, 11 weeks following construction.

period of one year tend to confirm this result. Despite a lot of variability expressed in the datasets, positive fluxes of N_2O (3.5 ± 3.2 μg N/m^2/h) and CO_2 (80 ± 60 mg C/m^2/h) were detected from the natural grass-covered soil at the site, upgradient of the wall and assumed to represent a reference state. At 73 ± 126 mg C/m^2/h, CO_2 emissions from atop of the woodchip denitrification wall were not significantly different. N_2O emissions from the woodchip wall were immeasurably low and consequently significantly less than the reference natural soil cover condition. The opposite relationship was observed for methane emissions, in so much that no methane emission was detected from soils at the site, yet a positive flux was detected in two of the three soil flux chamber tests made atop of the woodchip wall, providing a mean flux rate of 279 ± 295 μg CH_4-C/m^2/h. The large variance in the flux measured from the top of the woodchip wall however meant that the apparent flux was not statistically different ($p > > 0.05$) from the background natural soil condition.

4. Discussion

4.1. Hydraulic performance of the woodchip wall

Hydraulic function is one of the two fundamental requirements of any permeable reactive barrier system (the other requirement being its reactivity). Since the binary woodchip/gravel mixtures we used as wall fill were more permeable than natural OFG we can be confident that the woodchip wall is hydraulically efficient and not restrictive to groundwater flow, as was the case of one early wall trial where sawdust was interred to a sand aquifer containing silt laminae (Schipper et al., 2004). The hydraulic effectiveness of the wall can be seen in the piezometric contours, which converge about the wall (Fig. 1). From the results of a flow budget conducted from simulating the woodchip wall in the numerical MODFLOW model that was calibrated to the constant rate pump test data, we estimate the flow induced through the 375 m^3 wall is probably about 15% more than the original flow through the same volume of undisturbed aquifer. Such flow suggests a mean hydraulic residence time of about 39 h in the woodchip wall. Future hydrogeophysical testing at the study site will focus on verifying this assumption and include an examination of any differences in the solute transport and mixing offered by the binary mixtures of cell 1, versus cell 2. Repeat testing over time will enable us to evaluate how the hydraulic performance of the woodchip wall degrades with age.

Coincidentally, whilst we have not presented any data on the topic in this paper, we note that we failed to detect any obvious vertical stratification in water chemistry within the monitoring wells positioned down-stream of the wall when low-flow sampling methods were deployed at different depths in the water column of a single well. This is despite the wall only partially penetrating the saturated thickness of the phreatic aquifer. We suspect the absence of any notable stratification may be an effect of massive mixing effects from both advection and hydrodynamic dispersion, induced by the contrasting permeability of the woodchip wall versus the natural aquifer. It is our intention to conduct further saline tracer and ERT tests in the future to examine if this is the case and to assess any differences between the hydraulic performance of the two different woodchip/gravel media from which the wall is sectioned. Monitoring the hydraulic performance of the woodchip wall over the long-term, along with its reactivity, constitute two key objectives of the pilot study.

It is useful to note that in a simplified hypothetical modelling study Robertson et al. (2005) made on the design of permeable reactive barrier systems, the philosophical argument of “go wide, not deep” was presented. Whilst we do not dispute the findings of Robertson et al. (2005), we found that in highly transmissive heterogeneous aquifers site specific construction requirements (and subsequently costing) may dominate the design considerations. In our wall the excavation stabilisation and massive dewatering requirements meant that “going deep” was the most cost-efficient option, that at the same time increased the interception potential of the small and highly transmissive OFG. As such, in the case that a woodchip wall is to be entrenched in a gravel aquifer where no prior information on where preferential flow channels might be located, we consider going deeper rather than wider to be more pragmatic. This is further reinforced by the numerical analysis undertaken during the wall design phase using the site calibrated flow model. These results indicate that the 3.0 m deep wall would intercept 50% more flow than a 5 m or 2 m deep wall with the same total volume, or 33% more flow than a 1.5 m deep design. This suggests that any knowledge regarding the spatial distribution of the heterogeneous flow field should be incorporated in the wall design, if available.

Construction of our woodchip wall required some trench stabilisation method, because we discovered in advance from a test pit that running sand would be a potential problem. We purposely sought to minimise disturbance of the aquifer structure, to avoid compromising the hydraulic function of the groundwater system, like Schipper et al. (2004) suffered. In our case, six-metre long sheet-piles were used to shore the excavation and had we invested in bracing, we might have trenched the woodchip wall to the bottom of the phreatic aquifer, which would have mitigated any risk groundwater could deviate under the wall. A reason we did not do this was that we purposely aim to study the function of a partially-penetrating woodchip denitrification wall, which numerical analysis also deemed the most efficient in intercepting through flow. This aspect of our study will be addressed in the future through practical ERT saline tracer tests. Whilst we have yet to evaluate an accurate costing model for nitrogen removal being offered by the woodchip wall, we recognise that sheet-piling was a significant cost burden - accounting for more than 50% of the construction cost. As such, we foresee examining alternative, cheaper ways of entrenching woodchip below the water table that do not totally jeopardise the hydraulic function of the treatment system, as a worthwhile exercise towards the goal of making woodchip denitrification walls more cost-effective N-mitigation option.

4.2. Reactivity of the woodchip wall

Over the first 39 weeks of its life, the woodchip denitrification wall was evidently more reactive than required for nitrate to be the TEAP. Such a result was to be expected considering fresh *Pinus radiata* woodchip contains a significant fraction (around 7% by dry weight) of labile, water-soluble extractives that are related to hemicellulose material (McDonald et al., 2008). As an enquiry of what might have constituted the reactive carbon in the DOC leached from the wall, we examined cold water extract from fresh samples of the *Pinus radiata* woodchip by nuclear magnetic resonance (NMR). NMR spectra revealed a mixture of mainly long-chain aliphatic, O-alkyl, amino-acid, aromatic and phenolic compounds. Relative mass ratios were 10:6:1, low-medium weight monomeric compounds: heavier molecular weight compounds: low-ish molecular weight phenolic/benzoic compounds. These general observations are consistent with those of Paterson (1975) who identified sugars, cyclitols, organic and amino acids to be the principle water-extractable compounds from *Pinus radiata* at a temperature of 40 °C. Of the water-soluble polysaccharide component in *Pinus radiata,* glucomannan, xylan and galactan are reportedly the main constituents (Brasch, 1983; Mcdonald et al., 2008). We assume it was these compounds that contributed to the high reactivity of the woodchip wall initially and produced the reactive plume of DOC that was traced across the study site. Amino acids in the hemicellulose fraction of the woodchip conceivably represent a source of nitrogen that could be ammonified.

The initial flush of labile DOC from the woodchip wall at Silverstream effectively occurred within the first 28 weeks (i.e. 196 days). In another denitrification wall trial where groundwater DOC concentrations were monitored, rapid leaching of DOC was reported to happen within a similar timeframe (Schmidt and Clark, 2012b). The wall in that case was set in a sand aquifer, in Florida, USA and was constructed using sawdust (50% by volume). However, after the rapid leaching, DOC concentrations in groundwater down-gradient of that wall remained measurably higher than up-gradient (3.1 ± 1.2 mg/L vs 0.94 ± 0.61 mg/L), at least over the first year for which results were published (Schmidt and Clark, 2012b). Such sustained DOC effects were not evidenced in the gravel aquifer at Silverstream. We reason that this is because at about 3.1 m/d, the specific discharge through the woodchip wall at Silverstream is at least 3-times greater than the discharge at the Florida site ($q = 0.85$ m/d; Schmidt and Clark, 2012a). Consequently, the flushing of labile carbon from the woodchip wall was much more enhanced at Silverstream, as presumably will be the ageing of the reactive media.

The groundwater flow rate – and by association the potential degeneration of the wall - at Silverstream is even more contrasting when compared to conditions at two pioneering woodchip denitrification wall study sites – one at Long Point, Ontario, Canada (e.g. Robertson and Cherry, 1995) and one at Hautapu, Waikato, New Zealand North Island (Schipper and Vojvodić-Vuković, 2000) – where decadal studies have been made and from which prognoses on the long-term performance of denitrification walls have historically been made. The respective specific discharge in those case studies are in the order of 0.035 m/d and 0.216 m/d (Robertson and Cherry, 1995; Schipper et al., 2005). Considering such flow rates, we deduce that more groundwater probably filtered through the woodchip wall at Silverstream in its first year than has passed through the wall at Long Point over its entire lifetime, and the equivalent of 14-years flow at the Hautapu site. Robertson et al. (2008) examined the denitrifying potential of sawdust exhumed from the woodchip denitrification wall at Long Point, 15 years after it was buried. It was determined that the aged wood still had capacity to fuel denitrification reactions, albeit at rates 50% of what it was capable of, originally. At the Hautapu site, long term evaluation of the bioavailable carbon content of *Pinus radiata* sawdust that constitutes reactive fill of the denitrification wall (30% by volume) has revealed that after an initial decline in reactivity that occurred over the first 200 days, the reactivity of the wood stabilised and has not changed significantly over 14 years (Schipper and Vojvodić-Vuković, 2001; Long et al., 2011). Based on the observations from these historic studies, we speculate that the denitrification wall at Silverstream Reserve has probably entered a stable phase of its operational life.

Whilst the reactivity of the woodchip wall and its nitrate removal efficiency may have receded with age, this has not yet translated into any significant loss in nitrate reactivity that we have been able to determine from monitoring water quality along the transect of monitoring wells. The disparity between nitrate removal efficiency and nitrate reactivity values exists because the former is a relative rate and at Silverstream is affected by the trending increase in influent nitrate concentrations to the wall. Fig. 7 plots the nitrate reaction rate computed from the difference in nitrate concentrations observed in up-gradient well C4 and down-gradient well C6 (Figs. 1,2,3 and 4), assuming a constant (enhanced) specific discharge through the woodchip wall of 3.1 m/d. The rate of between 4.2 and 5.4 g N removed/m^3 wall/d, is significantly higher than what we had presumed at the design stage of the project (Table 1) and outside the range 0.2–2.4 g N removed/m^3 wall/d Addy et al. (2016) reported in their meta-analysis of woodchip denitrification wall reaction rates that was based on review of three case studies. We are mindful however that the results Addy et al. (2016) analysed were from sites where reaction rate estimates were reportedly under-estimative owing to nitrate limitations (Schipper and Vojvodić-Vuković, 2000; Schmidt and Clark, 2012b) and/or from sites where the woodchip walls experienced significant periods of time unsaturated and aerobic due to fluctuating water levels, which was shown to accelerate decomposition of the wood (Moorman et al., 2010; Schipper and Vojvodić-Vuković, 2000). The nitrate reaction rate so far determined at Silverstream is however consistent with the maximum rate of 5.5 g N removed/m^3/wall Schmidt and Clark (2012b) reported for their wall in Florida when it was 10 months old while the hydraulic residence time of about 43 h was only marginally different from the condition at Silverstream. Schmidt and Clark (2012b) assumed this rate to be most representative of actual rates without nitrate limitation. The rate at Silverstream also compares well with the rate of 5.3 g N removed/m^3 wall/d Fahrner (2002) reported for her (30%) sawdust wall in West Australia, where the treatment system conceivably benefitted from warmer temperatures than those on the South Island, New Zealand. We hypothesise that one reason why the woodchip wall at Silverstream is proving so efficient at nitrate removal is because of the background oxygen status of the groundwater system. DO levels at the site are naturally low, and at or close to the threshold of 2 mg/L, below which denitrification can be expected to occur in field settings (e.g. Burbery, 2018). This benefits operation of the wall, since it means little energy is lost from the woodchip fuelling aerobic biodegradation, as a precursory oxygen-removal step, preceding nitrate removal. In total, we predict the 375 m^3 woodchip denitrification wall to have removed at least 542 kg of nitrogen in its first year of operation. This value does not include any treatment that conceivably also occurred down-gradient of well C6 and around the fringes of the redox plume, where further opportunities for nitrate reduction were presumably possible, because of groundwater mixing effects.

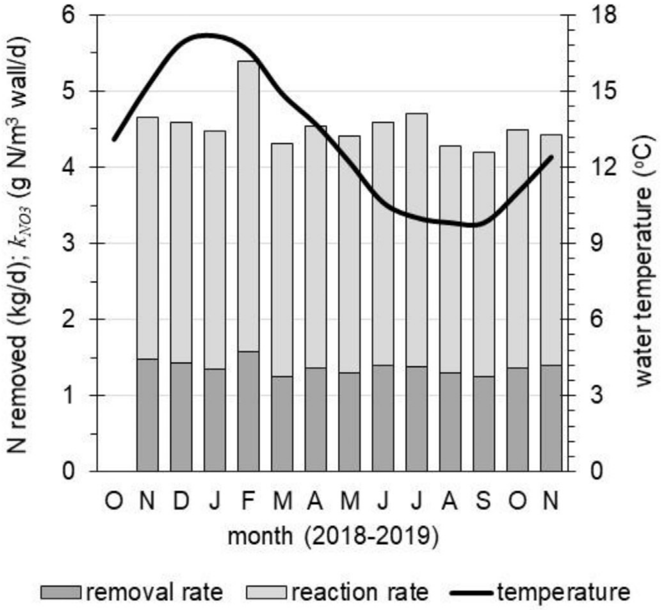

Fig. 7. Monthly variation in nitrate reaction rate, daily mass of nitrogen removed, and groundwater temperature, for the first year of operation of the woodchip denitrification wall at Silverstream Reserve. The wall was installed November 2018.

Interestingly, the apparent nitrate reaction rate has been relatively constant, despite the known changes in reactivity of the woodchip media and seasonal variation in temperature, to which microbial metabolic activity is sensitive. We assume that no significant change in the nitrate reaction rate has been detected yet, due to the system having been nitrate-limited over the 12 months we've been monitoring it.

Cameron and Schipper (2010) examined the effect of temperature on woodchip bioreactor performance and determined a mean Q_{10} value (the factor by which reaction rate increases with a 10 °C temperature rise) to be 1.6, which is close to the range $2.2 < Q_{10} < 2.9$, Hoover et al. (2016) subsequent calculated in a similar study. Schmidt and Clark (2013) on the other hand found denitrification in woodchip bioreactors to be more sensitive to temperature than this and reported calculated a Q_{10} value of 4.7 from numerous controlled experiments. The woodchip wall at Silverstream was installed at the end of the austral spring when the groundwater temperature was 14 °C, which is close the annual average of 13 °C (Fig. 7). Groundwater temperature ranged between 9 and 17 °C due to seasonal fluctuations, from which we infer microbiological reactivity in the summer (i.e. close to the start and end of the study period we have presented herein) was likely almost double, if not more than that experienced in the winter. Whilst the woodchip wall appears to have now been flushed of its labile carbon fraction and we predict has entered a stable stage of its life, we are conscious it has reached such a milestone at a warm time of the year. We expect that over the second year of the woodchip walls life, temperature effects will become more noticeable in the treatment performance.

As can be seen in Fig. 4, significant increases of dissolved iron and manganese were observed in groundwater at the height of the woodchip reactivity. The source of these elements were Fe(III) and Mn(IV) mineral-coatings on the greywacke aquifer sediment (e.g. Hinton and Close, 1998). ICP-MS analysis of woodchip used in the wall construction detected no iron or manganese content. The small amount of Fe(II) and Mn(II) detected in the pore water of the wall itself was from the gravel clasts used in the wall fill to provide some structural integrity. From the pattern exhibited in the spatio-temporal dataset for these parameters (Fig. 4) we deduce that mobilisation of these elements was restricted to a zone extending less than 75 m down-stream from the wall. Presumably the elements precipitated back out of solution at the fringes of the redox plume. It is conceivable these reduced species may have served as electron donors and promoted nitrate reduction reactions through a complex mix of redox reactions, discussed below. This could partly explain the unexpectedly high nitrate reaction rates so far evaluated at the site.

4.3. The fate of nitrate

Our study did not incorporate measurement of either excess di-nitrogen or organic-N that would otherwise have completed a total nitrogen mass balance. Nevertheless, it seems implausible that much of the nitrogen filtered through the wall at Silverstream was converted to biomass, otherwise the system would inevitably have suffered from massive bio-clogging effects that would have affected its hydraulic function. The piezometric gradient through the wall has so far remained constant, indicating no such loss in function. By and large, N-assimilation is an insignificant N-sink in groundwater systems (Rivett et al., 2008; Schipper and Vojvodić-Vuković, 1998, 2001) detected no significant changes to biomass in the woodchip denitrification wall at Hautapu to suggest denitrifying walls are an exception. Supporting the model of low N-assimilation potential are the results Hiller et al. (2015) obtained from a metagenomic analysis made of groundwater sampled from a 7-year old woodchip denitrification wall. They revealed that despite the wall hosting a diverse microbial community, much of it was either dead or inactive.

Assuming organic-N to be an insignificant fraction of the overall N-mass balance, then by account of the masses of the other N-species we did monitor for, we can confidently deduce that the bulk of the nitrogen in the treatment system was reduced to di-nitrogen gas. The heightened DEA activities measured for the wall media support the notion of heterotrophic denitrification being the main nitrate-reduction pathway, such is the theoretical basis of woodchip denitrification walls. Interestingly, the DEA activities (378–653 ng/N_2O-N/g wall/h – equivalent to circa. 12–21 g N/m^3 wall/d if it is assumed the wall has a bulk density of 1360 kg/m^3 (Burbery et al., 2014)) measured 11 weeks after the wall was installed were very similar to activities Schipper and Vojvodić-Vuković (1998) measured for media from the sawdust wall at Hautapu tested at a similar elapsed time since installation. In that case, DEA dropped 90% over the following five years (Schipper and Vojvodić-Vuković, 2001), diminishing to values comparable to those Schmidt and Clark (2012a) reported for media from the sawdust wall in Florida, 540 days after its installation. From those historic observations, we assume DEA in the woodchip wall at Silverstream has probably decreased substantially from when we tested it.

Whilst we are confident the woodchip wall promoted heterotrophic denitrification, we hypothesise that other active nitrogen-reduction processes were also activated by the altered redox state, forced by addition of woodchip to the gravel aquifer sediments. Molecular assays and isotopic tracing techniques were not available to us to assess any of these alternative processes directly in this study, which would have been exceedingly challenging anyway, given the dynamic condition of the shallow groundwater system. In Table 3 we list nitrogen-reduction reactions known to occur in anoxic or sub-oxic sedimentary environments that we propose probably contributed to effective N-removal at the Silverstream site.

Small amounts of NH_4^+ were detected both within the wall (well C5) and in groundwater immediately down-gradient of the wall (well C6), indicating ammonification reactions (eqs. 5 and 6, Table 3). Ammonium production in the wall followed an apparent lag, peaking 14 weeks after the woodchip was emplaced in the ground. At peak production, ammonium-N equated to less than 2.4% of the N-mass equivalent of NO_3-N inputs to the system, declining to under 1% by week 24. This result is consistent with what was observed at the Hautapu experimental denitrification wall site (Schipper and Vojvodić-Vuković, 1998), also findings from laboratory batch tests made on softwood material (Gibert et al., 2008) where ammonification was reported to account for less than 2% of observed nitrate losses. Like Schipper and Vojvodić-Vuković (1998), we presume that mineralisation of organic-N (e.g. amino-acids in the hemicellulose extracts of the fresh woodchip) and/or dissimilatory nitrate reduction to ammonium (DNRA) were the processes by which ammonium was produced.

From the patterns in the time-series datasets - notably the poor correlation between DOC and NH_4^+, and what appears to be some sustained production of NH_4^+ in groundwater immediately down-gradient of the wall (between well C5 and C6) - we are inclined to suspect DNRA to be the more likely candidate ammonification reaction, or at least the more dominant of the processes. It has long been considered that DNRA gains prominence under highly reducing environments where electron donors are non-limiting (Tiedje, 1988), which we know were simulated by the woodchip wall. C/N ratios in groundwater the vicinity of wells C5 and C6 where ammonium was detected were in the range 1.5–11,000, compared to $C/N < 0.5$ across much of the rest of the site. Kraft et al. (2014) recently demonstrated that in addition to carbon/nitrogen ratios, nitrate/nitrite ratios and microbial generation time are also important controls over the competing nitrate respiration processes of denitrification or DNRA. Accordingly, we suspect the delay in onset of ammonium production witnessed at Silverstream might have been symbolic of a microbial lag effect and acclimatisation of fermentative obligate anaerobic DNRA organisms, the activity of which continued to vary over time in response to the decline in available carbon substrate. Anecdotally, where ammonium was detected at Silverstream, so were sulphate-reducing conditions. Brunet and Garcia-Gil (1996) and Kraft et al. (2018) have shown DNRA to share a complex relationship with the sulphur-cycle and it is conceivable that the sulphate-reducing conditions could have enhanced ammonification (Kraft et al., 2018).

It is worthy to note that DNRA is not a nitrogen sink, hence not a favorable outcome in a nitrate remediation system. However, we saw no evidence of any accumulation of ammonium in the groundwater down-stream of the wall at Silverstream, suggesting it was likely consumed. Groundwater at the site has maintained circum-neutral pH values, which suggests low potential for nitrogen losses via NH_3-volatilisation. Hydrochemical conditions were however conducive for anaerobic ammonium oxidation (anammox) – the microbial respiration process whereby nitrite serves as the electron acceptor and ammonium as the electron donor (eq. 7, Table 3). There is growing evidence that anammox is a larger contributor to N-cycling in groundwater than has previously been thought (Smith et al., 2015; Wang et al., 2017; Moore

Table 3
Stoichiometric equations for nitrate reduction/N-cycling processes conceivably active in the anaerobic environment stimulated by the woodchip denitrification wall at Silverstream Reserve.

heterotrophic denitrification	$4NO_3^- + 5CH_2O \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O$	(4)[1]
fermentation (of organic-N from woodchip)	$(CH_2O)_x(NH_3)_y \rightarrow {}^x\!/_2 CH_3COO^- + y\,NH_4^+$	(5)[2]
dissimilatory nitrate reduction to ammonium	$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$	(6)[3]
anammox	$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$	(7)[4]
autotrophic denitrification	$NO_3^- + 5Fe^{2+} + 7H_2O \rightarrow {}^1\!/_2 N_2 + 5FeOOH + 9H^+$	(8)[1,5]
abiotic reaction/chemodenitrification	$2NO_2^- + 4Fe^{2+} + 5H_2O \rightarrow N_2O + 4FeOOH + 6H^+$	(9)[5]

[1] Appelo and Postma (2005); [2] Kristensen and Hansen (1995); [3] Mohan and Cole (2007), [4] Robertson et al. (2012); [5] Bryce et al. (2018);

et al., 2011), and whilst there are limitations in making a direct comparison with the conditions at Silverstream, Rambags et al. (2019) nonetheless proved anammox to be active in experimental woodchip denitrifying bioreactors prepared from *Pinus radiata*, treating partially-treated wastewater. We have made no effort in our study to examine anammox reactions, yet we strongly suspect they were active at Silverstream. From the context of asserting the viability of the woodchip wall as a groundwater nitrate treatment system, anammox is favorable, for it represents a pathway by which ammonium can be scavenged and is a true nitrogen-sink, with di-nitrogen gas being the end-product.

We know the woodchip wall at Silverstream to have generated a plume of dissolved iron that can be traced a distance of at least 40 m down-gradient from the wall and within this plume nitrate is available (Fig. 3). Furthermore, it is widely accepted that microbially-mediated NO_3^- reducing Fe(II) oxidation (NRFO) plays a role in iron-cycling within anoxic, freshwater and sedimentary environments (e.g. Straub et al., 1996; Bryce et al., 2018). We therefore see no obvious reason to dismiss the notion that NRFO might also be an active nitrate removal process at the site. In Table 3, we present microbially-mediated NRFO as autotrophic denitrification, as Straub et al. (1996) originally identified the process. It is worthy to note however that most bacteria coupling NRFO are mixotrophs, and require an organic co-substrate to continually oxide Fe(II) and reduce nitrate (Picardal, 2012; Liu et al., 2019), as per heterotrophic denitrifiers. Intrinsically coupled to microbial iron-oxidation reactions are abiotic nitrogen-reduction processes that serve to enhance NRFO (Picardal, 2012; Liu et al., 2019). Whereas chemical oxidation of Fe(II) by nitrate is known to be slow without the presence of a solid phase metal catalyst, such as copper, silver or cadmium (e.g. Buresh and Moraghan, 1976; Ottley et al., 1997) the same is not true of nitrite or nitric oxide. These intermediate products of biological nitrate reduction are capable of chemically reacting with Fe(II) more rapidly without reliance of a catalyst, and particularly in the presence of iron-oxyhydroxides to which the Fe(II) can sorb (Picardal, 2012). Anecdotally, surface encrustations of iron-oxyhydroxides happen to be an inherent feature of the outwash sediments that form the Canterbury Plains and shallow aquifer at Silverstream Reserve, further demonstrating the potential for NRFO to be contributing to nitrogen cycling at the site, along with the effective removal processes we have mentioned above.

4.4. Greenhouse gas emission

Whilst subject to significant variance and marking only a single event in time, the positive flux of methane confirmed from atop of the woodchip denitrification wall measured after 12 months nonetheless suggests the system does promote emission of this GHG, above the background natural state at least, which we measured to be effectively zero. We saw no evidence however of methane being emitted from the plume of treated groundwater down-gradient of the wall. The flux we measured from the top of the woodchip bioreactor (279 ± 295 μg CH_4-C/m^2/h) is substantially lower than fluxes Gibert et al. (2019) recorded from a field-scale woodchip denitrification wall trialled in Northern Ireland (17,287 ± 3000 μg CH_4-C/m^2/h), also methane emissions reported from constructed wetlands in New Zealand (Tanner et al., 1997) (1500–15,062 μg CH_4-C/m^2/h), which are promoted as an alternative edge-of-field N-mitigation practice. Given the high groundwater flow rate through the woodchip wall at Silverstream, we are not surprised gas emissions are lower than what has been measured at other sites, yet equally we are cognisant that methane emissions were likely to have been greater prior to when we tested them on the woodchip wall's anniversary. This is because in the early stages of the woodchip walls life the redox state was more-reducing, hence more conducive for methanogenesis, which is reflected in the dissolved methane concentrations we did measure.

Having a global warming potential 265-times that of CO_2 and 9-times that of CH_4 (Myhre et al., 2013), nitrous oxide is the most potent of the three greenhouse gases we examined and thus of most concern. The N_2O flux (3.4 ± 2.7 μg N_2O-N/m^2/h) measured from the undisturbed grassland in Silverstream Reserve, up-gradient and 25 m down-gradient of the woodchip wall is consistent with the values typically associated with unfertilised grassland (Bouwman, 1996). Published results of nitrous oxide emissions from field-scale woodchip denitrification walls has so far been limited to the study made by Gibert et al. (2019). In that case, positive N_2O fluxes (254 + 241 μg N_2O-N/m^2/h) were detected from the experimental woodchip denitrification wall, although the measurements were taken when the wall was deliberately subjected to a high nitrate load, such that its capacity to completely reduce all influent nitrate was compromised. In the case of the denitrification wall at Silverstream, N_2O emissions from both the top of the woodchip wall, and from soils immediately down-gradient of the structure, were immeasurably low (< 2.2 μg N_2O-N/m^2/h), from which we are inclined to suggest that if anything, the woodchip wall is acting to mitigate N_2O emissions.

CO_2 emission rates from the woodchip denitrification wall were indifferent from rates evaluated for the surrounding grassland. Factoring the global warming potentials of the three GHGs and the fluxes we measured for each then we determine that because of the scale of the methane emissions, the denitrification wall at Silverstream is conceivably making a small net positive contribution to global warming if compared against the original site condition. However, as alternative edge-of-field N-mitigation practices go, indications are GHG emissions from the woodchip wall are probably less than would be expected from a constructed wetland, for example.

5. Summary and conclusions

A woodchip denitrification wall has successfully been installed within a fast-flowing, nitrate-contaminated gravel aquifer on the South Island, New Zealand. The work represents the first time such passive remediation technology has been applied in a gravel aquifer setting and constitutes part of a study examining whether woodchip denitrification walls represent a viable edge-of-field nitrate-mitigation option for the New Zealand hydrological landscape. The groundwater flow rate through the wall is estimated to be 3.1 m/d, which is significantly higher than flow rates reported for any other published woodchip denitrification wall case study. Whilst initially, we predicted the 5 m-wide woodchip wall was built to a sub-optimal size, so far we stand corrected, for it has demonstrated a nitrate removal efficiency of between 93 and 100% over its first year of operation. Under the high flow regime, water soluble extracts in the fresh *Pinus radiata* woodchip that constitutes the reactive component of the wall were effectively all leached away within 200 days of the wall being built, yet this did not appear to impact on the wall's efficiency at removing nitrate. Nitrate reaction rates have so far remained almost constant, due to the system being limited with respect to nitrate. At between 4.2 and 5.3 g N removed/m^3 wall/day, the nitrate reaction rates we have determined at the site rank towards the top end of what has been reported for woodchip denitrification walls.

We estimate the 375 m^3 wall has removed at least 542 kg of nitrogen in its first year of operation. Whilst we conclude heterotrophic denitrification is a significant process contributing to nitrate removal at the site, we infer from water chemistry indicators that DNRA and anammox reactions are likely occurring too. Furthermore, we speculate that NRFO might also be active, given the woodchip wall has stimulated an abundance of Fe(II) in the gravel aquifer that can potentially react with nitrate and nitrite. Further study is required to elucidate the true N-removal processes.

Measurement of GHG emissions from the land surface at the site has shown the woodchip wall is exporting some methane yet appears to be mitigating N_2O losses. Whilst we determine the woodchip wall promotes a net efflux of potential global warming gas relative to the original, undisturbed site condition, when compared to GHG emissions from constructed wetlands, which are another edge-of-field N-mitigation option, the nitrate treatment system at Silverstream does not represent a significant polluter.

It is too early to specify if woodchip denitrification walls are a viable N-mitigation option for fast flowing alluvial aquifers. From a technological perspective we have found no evidence to suggest they are not viable, although much remains to be learned from on-going study of the longer-term performance. In particular, whether or not the system replicates the significant drop in denitrifying capacity that has consistently been reported in historic case studies, after 12 months operational life. We remain cognisant that the viability of woodchip denitrification walls as an N-mitigation option in New Zealand will probably be determined by economic and socio-political values, more so than any technical limitations we have yet to identify. From a costing perspective, we suggest that testing different ways by which woodchip can be interred below the water table in a gravel aquifer without compromising the hydraulic function of the aquifer and avoiding reliance on costly sheet-piling would be a useful exploratory exercise.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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