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Nitrate removal rate, efficiency and pollution swapping potential of different organic carbon media in laboratory denitrification bioreactors

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ABSTRACT

Laboratory denitrifying bioreactors, which use an organic carbon (C) rich media to enhance microbial reduction of nitrate (NO_3^-) to nitrogen (N) gases, are used worldwide to protect surface and groundwater. To highlight potential adverse effects of denitrifying bioreactors, NO_3^- removal rates (g NO_3-N m^{-3} d^{-1} removed), NO_3^- removal efficiencies (% removed minus production of other N species) and release of greenhouse gases and solutes (ammonium (NH_4^+), phosphorus (P) and organic carbon (C)) were compared in this study using different media: lodgepole pine woodchips (LPW), cardboard, lodgepole pine needles (LPN), barley straw (BBS) and a soil control. Results showed that NO_3^- removals were consistently >99% for all media for initial leaching and steady-state periods. When pollution swapping was considered, this ranged from 67% for LPW to 95% for cardboard. Sustained P releases over the threshold for the occurrence of eutrophication were measured in all media. Greenhouse gas emissions were dominated by carbon dioxide (CO_2) and methane (CH_4) fluxes with little nitrous oxide (N_2O) release due to the anaerobic conditions prevalent within the bioreactors. Comparisons of different media, under steady-state conditions, showed that C fluxes were highest for cardboard and BBS bioreactors. Carbon fluxes from cardboard bioreactors ranged from 11.6 g C m^{-2} d^{-1} to 13.9 g C m^{-2} d^{-1}, whilst BBS emissions ranged from 3.9 g C m^{-2} d^{-1} to 4.4 g C m^{-2} d^{-1}. These C emissions were correlated with the total surface area exposed within the media. Such investigations highlight the need to consider pollution swapping during the initial leaching period and should improve design criteria for field-scale bioreactors used to mitigate shallow groundwater NO_3^-.

1. Introduction

Excess reactive nitrogen (N) may occur in soil, aquatic and atmospheric environments (Stark and Richards, 2008). Legislative instruments such as the European Union (EU) Water Framework Directive (WFD; 2000/60/EC, Council of the European Union, 2000) and basic programmes of measures such as the Nitrates Directive (91/676/EEC, Council of the European Union, 1991) aim to reduce N losses to sensitive receptors by removing pollution sources and accounting for the connectivity between waterbodies. Even after the removal of the pollution source, flushing of nitrate (NO_3^-) to deeper groundwater or towards a surface waterbody may take a long time (Fenton et al., 2011a). In Ireland, NO_3^- varies spatially and temporally in shallow groundwater (<30 m) due to variable denitrification potential of glaciated subsoils, recharge variation and soil physical characteristics (Fenton et al., 2011b). In such settings, supplementary measures may be required in low denitrification potential areas to remediate NO_3^- already migrating along subsurface pathways.

In situ denitrification bioreactors are engineered structures, which intercept contaminated water (e.g. shallow groundwater, or outlets of natural or artificial drainage systems). Denitrification, or reduction of NO_3^- to N_2 gas by microbial degradation of organic carbon (C), occurs naturally in soils and aquifers. Natural conditions, such as high dissolved oxygen (DO) concentrations, low organic C bioavailability or low transit times, can limit natural attenuation. Denitrifying bioreactors use a variety of C-rich reactive media (Table 1), creating ideal conditions for high rates of denitrification (Schipper et al., 2010).

Of the various media used, woodchip-based materials are the most popular (Schipper and Vojvodic-Vukovic, 2001; Robertson and Merkley, 2009) due to their low cost and high C/N ratio (Gibert et al., 2008). In addition, they do not require replenishment as C is not rapidly depleted from them, although the duration of their effectiveness will be affected by the longevity of the C supply to the denitrifying microorganisms (Moorman et al., 2010). For

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Table 1
A selection of laboratory bioreactor studies.

Media used	Influent concentration	Loading rate	NO_3^- removal	Reference
Polystyrene	1.13 kg NO_3-N m^{-3} d^{-1}	3.0 m h^{-1}	>99%	Phillips and Love (2002)
	2.52 kg NO_3-N m^{-3} d^{-1}	3.0 m h^{-1}	>99%	
Sawdust and native soil			67% (TN)	Bedessem et al. (2005)
Soil			31% (TN)	
PVC plastic and powdered activated carbon (PAC)	45 mg NO_3-N L^{-1}	1.9 g NO_3-N m^{-2} d^{-1}	>90%	Vrtovšek and Roš (2006)
Woodchip and sand	200 mg L^{-1}	2.9 mg NO_3-N kg^{-1} d^{-1}	97%	Healy et al. (2006)
Woodchips and wheat straw	200 mg NO_3-N L^{-1}		99%	Saliling et al. (2007)
Softwood and sand	50 mg NO_3-N dm^{-3}	0.3 cm^3 min^{-1}	>96%a	Gibert et al. (2008)[a]
		1.1 cm^3 min^{-1}	66%	
Woodchip and soil	50 mg L^{-1}	2.9 cm d^{-1}	100%	Greenan et al. (2009)
		6.6 cm d^{-1}	63%	
		8.7 cm d^{-1}	52%	
		13.6 cm d^{-1}	29%	
Maize cobs	n.a.	n.a.	15–19.8 g N m^{-3} d^{-1}	Cameron and Schipper (2010)
Green waste	n.a.	n.a.	7.8–10.5 g N m^{-3} d^{-1}	
Wheat straw	n.a.	n.a.	5.8–7.8 g N m^{-3} d^{-1}	
Softwood	n.a.	n.a.	3.0–4.9 g N m^{-3} d^{-1}	
Hardwood	n.a.	n.a.	3.3–4.4 g N m^{-3} d^{-1}	

[a] Considers pollution swapping, n.a. not available.

a comprehensive review of the performance of various materials used in denitrifying bioreactors, the reader is referred to Schipper et al. (2010). NO_3^- removal rates – expressed in terms of reactor volume – from these systems range from 0.62 (Jaynes et al., 2008) to 203 g NO_3-N m^{-3} d^{-1} (Xu et al., 2009). They are affected by operation temperature (Cameron and Schipper, 2010), influent DO concentration (Robertson, 2010), hydraulic loading rate (HLR) (Xu et al., 2009), NO_3^- loading rates, and C concentrations and bioavailability (Schipper et al., 2010).

In this paper, laboratory bioreactors were used to reproduce NO_3^- bioremediation in shallow groundwater in heterogeneous glacial tills. Nutrients lost from agricultural systems originate from organic and inorganic fertilizer sources. In such subsoils, NO_3^- occurrence in shallow groundwater varies spatially and temporally, and has been correlated with saturated hydraulic conductivity (k_s) and denitrification parameters such as nitrogen gas (N_2)/argon (Ar) ratios (Fenton et al., 2011a). The k_s of glacial tills can vary considerably e.g. sandy, silty tills in Scandinavia range from 5×10^{-9} m s^{-1} to 5×10^{-4} m s^{-1} (Lind and Lundin, 1990). The scenarios covered in this paper represented k_s of moderate permeability tills ranging from 5×10^{-8} m s^{-1} to 5×10^{-4} m s^{-1} (Fenton et al., 2011b).

1.1. Potential adverse effects of denitrification bioreactors

In general terms, 'pollution swapping' may be defined as 'the increase in one pollutant as a result of a measure introduced to reduce a different pollutant' (Stevens and Quinton, 2009). Such a definition must include: (1) greenhouse gases (GHG) and ammonia (NH_3) (which may be lost vertically above a bioreactor, as well as down-gradient as de-gassing/diffusion occurs from a surface and/or subsurface waterbody) and (2) dissolved contaminants such as NH_3, phosphorus (P), dissolved organic carbon (DOC) and metals, which can adversely affect aquatic ecosystems (Fig. 1). In the present study, consideration of pollution swapping goes beyond N transformations.

In order to assess total pollution swapping and the associated risk in terms of GHG emissions and release of dissolved contaminants, the following parameters need to be quantified: (1) losses of dissolved and gaseous N species (2) leaching of non-nitrogen species from the soil and carbon media (e.g. DOC and P); and (3) production of gases (e.g. CH_4) or solutes resulting directly (e.g. manganese (Mn) or iron (Fe)) or indirectly (e.g. metals or P) from microbially mediated reactions occurring at low redox potential in bioreactors (Gibert et al., 2008). Researchers evaluate the performance of treatment systems, but infrequently include this factor (Gibert et al., 2008). High N inputs into bioreactors may result in gaseous N losses via either NH_3 volatilisation or nitrous oxide (N_2O) emission in the absence of complete denitrification to N_2. Whilst no previous studies have examined NH_3 emissions from bioreactors directly, there is ample evidence of NH_3 measurement from other sources (e.g. directly from slurry tanks and waste stabilization ponds) in the literature. The principle determinants of NH_3 volatilisation are: (1) an ammonium (NH_4^+) source (2) temperature (3) pH > 7 and (4) a concentration gradient between the source and the atmosphere (Ni, 1999). Other dissolved N species, such as NH_4^+, can be lost. In addition, microbial decomposition and/or anaerobic digestion of the organic C media has the potential to lead to both gaseous losses as carbon dioxide (CO_2) and methane (CH_4), as well as DOC losses, or other solutes.

Initial leaching of the media in denitrification bioreactors has been shown to favour the release of large concentrations of dissolved C, N or P (Gibert et al., 2008; Cameron and Schipper, 2010; Schipper et al., 2010). This initial period contrasts with steady-state conditions when pollution swapping due to leaching from the media is assumed to be negligible in comparison to the release of gases and solutes linked to microbial-mediated reactions. The characterisation of solute release in the initial leaching period allows for the establishment of design criteria to attenuate high pollution loads to receptors in the early stages of the experiment.

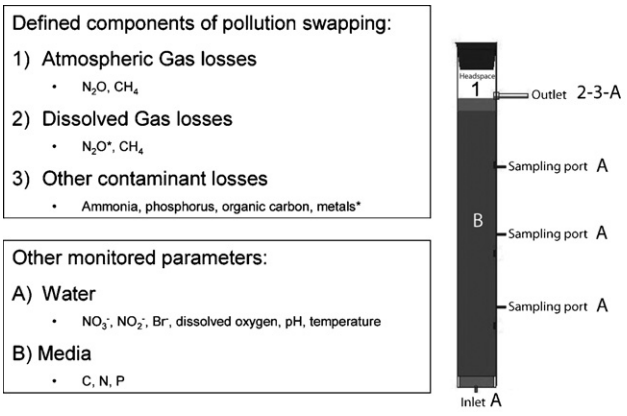

Fig. 1. Diagram of a laboratory scale bioreactor. *Not measured in current study.

The objectives of the current laboratory study were to: (1) determine the effectiveness of different media – lodgepole pine woodchips (LPW), cardboard, lodgepole pine needles (LPN), barley straw (BBS) and a soil control – in reducing NO_3^- from influent water loaded at a HLR of 3 cm d^{-1} and (2) quantify pollution swapping from the initial leaching of nutrients and subsequent losses through transformational processes and gaseous losses.

2. Methods

2.1. Construction of bioreactors

0.1 m-diameter × 1 m-deep acrylic columns, comprising a 0.015 m long 'water tank' (built using a fine metal mesh) at the base to allow uniform distribution of influent water into the column (Fig. 1), were constructed and operated in a temperature-controlled room at 10 °C. 0.8 m-deep reactive media rested on top of the metal mesh. Influent water was applied at the base of each column at a HLR of 3 cm d^{-1} using a peristaltic pump (operated continuously) and the water exited the column via a 0.01 m-diameter tube positioned just above the reactive media surface. This mode of operation was after Della Rocca et al. (2007), Saliling et al. (2007), Moon et al. (2008) and Hunter and Shaner (2010), and prevented the occurrence of preferential flow pathways that may occur if the system was loaded from the surface. Water sampling ports (rubber septum stoppers) were positioned at depths of 0.2, 0.4, 0.6 and 0.8 m along the side of the columns (Fig. 1). The C source-to-soil volume ratio was 1 and the C-rich media were placed in the bioreactors in alternating 0.03 m-deep layers with soil. All bioreactors were covered with black plastic to prevent photosynthesis. Prior to operation, each bioreactor was seeded with approximately 1 L of bulk fluid containing heterotrophic bacteria from a wastewater treatment plant and was then loaded with NO_3-N solution varying from 19.5 to 32.5 mg L^{-1}. The DO in the influent water was kept low (<2 mg L^{-1}) by bubbling Ar gas through the water daily. This was to replicate DO conditions in shallow groundwater.

2.2. Analysis of water, media and gases

Water samples from the inlet, outlet and at the 3 sampling ports (Fig. 1) along each column were tested in accordance with the standard methods (APHA, 1995) for the following parameters: pH, DO, chemical oxygen demand (COD), NH_4^+-N, NO_3^--N, nitrite-N (NO_2^--N) and ortho-phosphorus (PO_4^{3-}-P). The C, N and P of each media (including soil) are presented in Table 2. The C and N content were determined using a thermal conductivity detector, following combustion and separation in a chromatographic column, and the P content of the media was determined by inductively coupled plasma emission spectroscopy (ICP-ES) after aqua regia digestion. The soil used in the bioreactors were air dried at 40 °C for 72 h, crushed to pass a 2 mm sieve and analysed for Morgan's P (the national test used for the determination of plant available P in Ireland) using Morgan's extracting solution (Morgan, 1941).

The emission of GHG, comprising CO_2, CH_4 and N_2O, were measured from each column at specific times over their operation period using the static chamber technique (Hutchinson and Mosier, 1981). The headspace above each column was flushed with Ar gas for 5 min at a flow rate of 3 L min^{-1}. The headspace chamber was then sealed and connected in series to an INNOVA 1412 photoacoustic gas analyser (Lumasense Inc., Copenhagen, Denmark) for 12 min with measurements performed at a rate of one per min. In addition, gas samples were withdrawn at 0, 15 and 30 min, and samples were analysed using a gas chromatograph (GC) (Varian GC 450; The Netherlands) and automatic sampler (Combi-PAL

Table 2
Media used; C, N and P content of media (%); initial leaching and steady-state period boundaries (INI, initial leaching period; SS, steady-state period); total operation times (d); hydraulic retention times (HRT) (d); periods in which sufficient data existed to calculate NO_3^- removals (without pollution swapping) and NO_3^- removal efficiencies (accounting for pollution swapping); and nitrous oxide emitted per unit surface area of bioreactors (g N_2O m^{-2} d^{-1}).

Media	Col	C (%, w/w)	N (%, w/w)	P (mg kg^{-1})	Effluent INI/SS boundary (d)	Operation (d)	HRT (d)	n_e	Influent INI/SS (d-d/d-d)	NR_{EP}[b] (g NO_3-N m^{-3} d^{-1})		NO_3-N removal[c] (%)		NO_3-N removal efficiency (%)		N_2O-N emitted (g N_2O-N m^{-2} d^{-1})	
										INI	SS	INI	SS	INI	SS	INI	SS
LPW	1	49.6	0.1	41.9	300	460	17.5	0.67	44–134/293–395	1.22	1.51	99.96	99.63	73.59	87.52	[a]	1.45
	2				288		13.0	0.50	44–134/293–395	1.62	2.02	99.95	99.60	72.49	87.47	[a]	2.15
	3				288		14.8	0.56	44–105/293–395	1.43	1.79	99.98	99.73	67.08	86.61	[a]	0.11
Cardboard	1	41.6	0.2	96.1	327	438	10.2	0.39	22–109/317–370	2.09	2.52	99.98	99.65	72.98	95.23	[a]	0.02
	2				327		8.5	0.32	22–109/317–370	2.52	3.03	99.98	99.58	74.79	95.36	[a]	0.18
	3				305		11.0	0.42	22–109/304–370	1.94	2.53	99.97	99.81	71.63	93.09	[a]	0.05
LPN	1	51.2	1.1	832.0	168	278	9.9	0.38	21–153/251–269	2.67	2.56	99.88	99.76	86.78	95.38	3.63	0.24
	2				168		11.7	0.44	21–153/251–269	2.27	2.18	99.72	99.70	66.83	95.04	2.57	0.11
	3				168		10.0	0.38	30–153/251–269	2.67	2.55	99.88	99.92	74.40	94.47	3.43	0.15
BBS	1	46.0	0.7	528.0	[a]	231	14.0	0.53	9–212/[a]	1.75	[a]	99.92	[a]	74.74	[a]	0.35	0.30
	2				[a]		21.8	0.83	9–212/[a]	1.12	[a]	99.96	[a]	75.17	[a]	1.49	0.59
	3				[a]		18.2	0.69	9–231/[a]	1.34	[a]	99.94	[a]	75.17	[a]	0.31	0.52
Soil	1	0.1	<0.0	152.0	26	257	15.5	0.59	21–21/21–257	0.00	0.28	0	16.52	0	8.19	1.65	0.50
	2				29		11.8	0.45	21–21/21–257	0.00	0.62	0	28.01	0	21.40	1.47	0.28

[a] Steady-state not reached in these columns.
[b] Calculated using Eq. (2) which takes effective porosity into account.
[c] Not including pollution swapping.

autosampler; CTC Analytics, Zwingen, Switzerland). Fluxes of CO_2, CH_4 and N_2O for each chamber were measured as a function of headspace gas accumulation over time. Data analyses were performed on average daily and cumulative emissions by ANOVA, using the PROC GLM procedure of SAS (SAS Institute, Cary, NC, 2003) with post hoc least significant differences (LSD) tests used to identify differences between treatments. Difference with p value <0.05 was considered significant.

2.3. Nitrate removal

In this study, NO_3^- removal rates considering bed (NR_{BV}) or media volume (Eq. (1), Schipper and Vojvodic-Vukovic, 2000) and effective porosity (NR_{EP}) or fluid volume (Eq. (2), Schipper et al., 2010) were calculated using:

$$\mathrm{NR_{BV}} = \frac{q \times A \times \Delta[\mathrm{NO_3^-\text{-}N}]}{\text{media volume}} \ (\mathrm{g\ N\ m^{-3}\ d^{-1}}, \text{units of media volume}) \quad (1)$$

$$\mathrm{NR_{EP}} = \frac{\mathrm{NR_{BV}}}{n_e} \ (\mathrm{g\ N\ m^{-3}\ d^{-1}}, \text{units of fluid volume}) \quad (2)$$

where q is Darcy velocity ($\mathrm{m\,d^{-1}}$), A is cross-sectional area of the bioreactors ($\mathrm{m^2}$) and n_e is effective porosity. Effective porosity was calculated using hydraulic retention time (HRT), the length of the bioreactor and Darcian velocity. A conservative tracer (NaBr, $10\,\mathrm{g\,L^{-1}}$) was used to estimate the average HRT using methods detailed in Levenspiel (1999). The tracer was applied as a pulse in one constant hydraulic loading interval to each bioreactor using a peristaltic pump. A fraction collector (REDIFRAC, Amersham Pharmacia Biotech, Bucks, UK), positioned at the outlet of each bioreactor, collected effluent samples in timed increments. The sample volumes were subsequently measured and tested for bromide (Br^-) concentration using a Konelab 20 Analyser (Konelab Ltd., Finland). Bioreactor HRTs and n_e are presented in Table 2.

NO_3^- removal efficiencies of the reactive media were defined as the % of NO_3^- converted to di-nitrogen (N_2) gas in the column by accounting for the HRT of each bioreactor. Any measured concentrations of intermediary products of denitrification, such as N_2O or NO_2^-, as well as other N species produced by other NO_3^- reduction processes (e.g. dissimilatory NO_3^- reduction to ammonia (DNRA) leading to NH_4^+) or leaching of the media, were subtracted from the measured NO_3^--N concentrations at the effluent port. Instead of estimating average removal using the total running period of the bioreactors, the bioreactor data were separated into leaching and steady-state periods. Such periods were defined as occurring when COD in the effluent reached equilibrium. NO_3^- concentrations were also taken into account for the soil control (e.g. soil N and release of NO_3^- from the soil due to mineralisation). For equivalent initial leaching and steady-state periods, the NO_3^- removal (%) was also calculated not including pollution swapping.

3. Results

3.1. Column media and influent/effluent parameters

Initial leaching and steady-state period boundaries are presented in Table 2. Discrimination between the initial leaching and steady-state periods was possible for all media except BBS, as these bioreactors did not reach steady-state as defined by effluent COD concentration. Soil had a much earlier boundary between initial leaching and steady-state periods (26, 29 d), followed by LPN (168 d), whilst LPW (300, 288 d) and cardboard (327, 305 d) were similar. Temporal variation of NO_3^--N concentration in influent and effluent solutions is presented in Fig. 2. For all media, effluent NO_3^--N concentrations were much lower than influent concentrations. Maximum NO_3^--N concentration in effluent water occurred in the early stage of the experiment for LPN ($4.5\,\mathrm{mg\,L^{-1}}$) and BBS ($0.9\,\mathrm{mg\,L^{-1}}$). In contrast, high concentrations occurred later in the experiment for LPW ($1.8\,\mathrm{mg\,L^{-1}}$) and for cardboard ($0.2\,\mathrm{mg\,L^{-1}}$). Soil effluent NO_3^--N concentrations were generally much higher than in the other media (maximum of $82.2\,\mathrm{mg\,L^{-1}}$ at the beginning of the experiment), and after 107 d operation, influent and effluent NO_3^--N concentrations were similar. Barley (14.0–21.8 d) and LPW (13.0–17.5 d) had the highest HRT (meaning that the n_e was therefore highest), whilst cardboard (8.5–11.0 d) and LPN (9.9–11.7 d) had the shortest (n_e therefore lowest) (Table 2). Soil HRT was between these two ranges (11.8–15.5 d). Carbon content of media was similar and ranged from 41.6% for cardboard and 51.2% for LPN. N content was variable and ranged from 0.1% for LPW to 1.1% for LPN. For soil, both C and N contents were 0.1% and under detection limits, respectively.

NO_3^- removals and efficiencies (taking average NO_3^--N and NH_4^+-N effluent concentrations into account) for the assigned periods are denoted in Table 2. In the soil only bioreactors, NR_{BV} ranged from 0.00 to $0.28\,\mathrm{g\,NO_3^-\text{-}N\,m^{-3}\,d^{-1}}$ in the initial and steady-state periods, respectively (Fig. 3a). In all other media, this varied from 0.81 (LPW, initial leaching period) to $1.06\,\mathrm{g\,NO_3^-\text{-}N\,m^{-3}\,d^{-1}}$ (cardboard, steady-state period). NO_3^- removals per unit of media volume were smaller in the initial period for all media except for LPN (Fig. 3a). No correlation with HRT was observed.

The NO_3^- removal rate (NR_{EP}) (Table 2), measured in all bioreactors (except the study control), ranged between approximately 1.12 and $2.67\,\mathrm{g\,NO_3^-\text{-}N\,m^{-3}\,d^{-1}}$ in the BBS and LPN bioreactors during the initial leaching period and 1.51 and $3.03\,\mathrm{g\,NO_3^-\text{-}N\,m^{-3}\,d^{-1}}$ in the LPW and cardboard bioreactors during the steady-state period. From Eq. (2) (as n_e is calculated from HRT), decreasing NR_{EP} is expected for increasing HRT between bioreactors for the same media (Fig. 3b).

NO_3^- removal (%) in all media showed comparable values of >99.72% (Fig. 3c). When pollution swapping was considered, NO_3^- removal efficiency (Fig. 3d) in the initial period ranged from 66.83% (LPN, column 2) to 86.78% (LPN, column 1). In the steady-state period, removal efficiencies varied from 86.61% (LPW, column 3) to 95.38% (LPN, column 1). Pollution swapping decreased between initial leaching and steady-state periods for LPW, cardboard and LPN. For both initial leaching and steady-state periods, cardboard and LPN NO_3^- removal efficiencies tended to increase when HRT significantly decreased. For LPW, NO_3^- removal efficiency in the initial leaching and steady-state periods tended to increase with increasing HRT. For all other media, the highest NO_3^- removal efficiencies were often observed at the lowest HRT. The soil media exhibited smaller NO_3^- removal efficiencies in both periods, with increasing removal for shorter HRTs.

The range of pH in the effluent water was similar for soil, barley and LPW treatments (from 7.3 to 8.5). Cardboard and LPN media had generally lower pH in the initial period (as low as 5.1 for LPN and 6.6 for cardboard) and higher pH in the steady-state period (up to 7.2 for LPN and 8.6 for cardboard). General COD and NH_4^+-N patterns within the initial leaching and steady-state periods were comparable for LPW and cardboard media, whilst other patterns were more variable (Fig. 4a and b). In the initial leaching phase, COD concentrations were higher in the LPN and BBS media (Fig. 4c and d), and smaller in the soil media (Fig. 4e). LPN had the highest initial leaching and steady-state COD concentration (over $10{,}000\,\mathrm{mg\,L^{-1}}$ and $1000\,\mathrm{mg\,L^{-1}}$, respectively). This media also had the strongest red pigmentation in the effluent, which was indicative of COD release (results not illustrated). The range of NH_4^+-N concentrations was similar for all media, except for a minority of samples

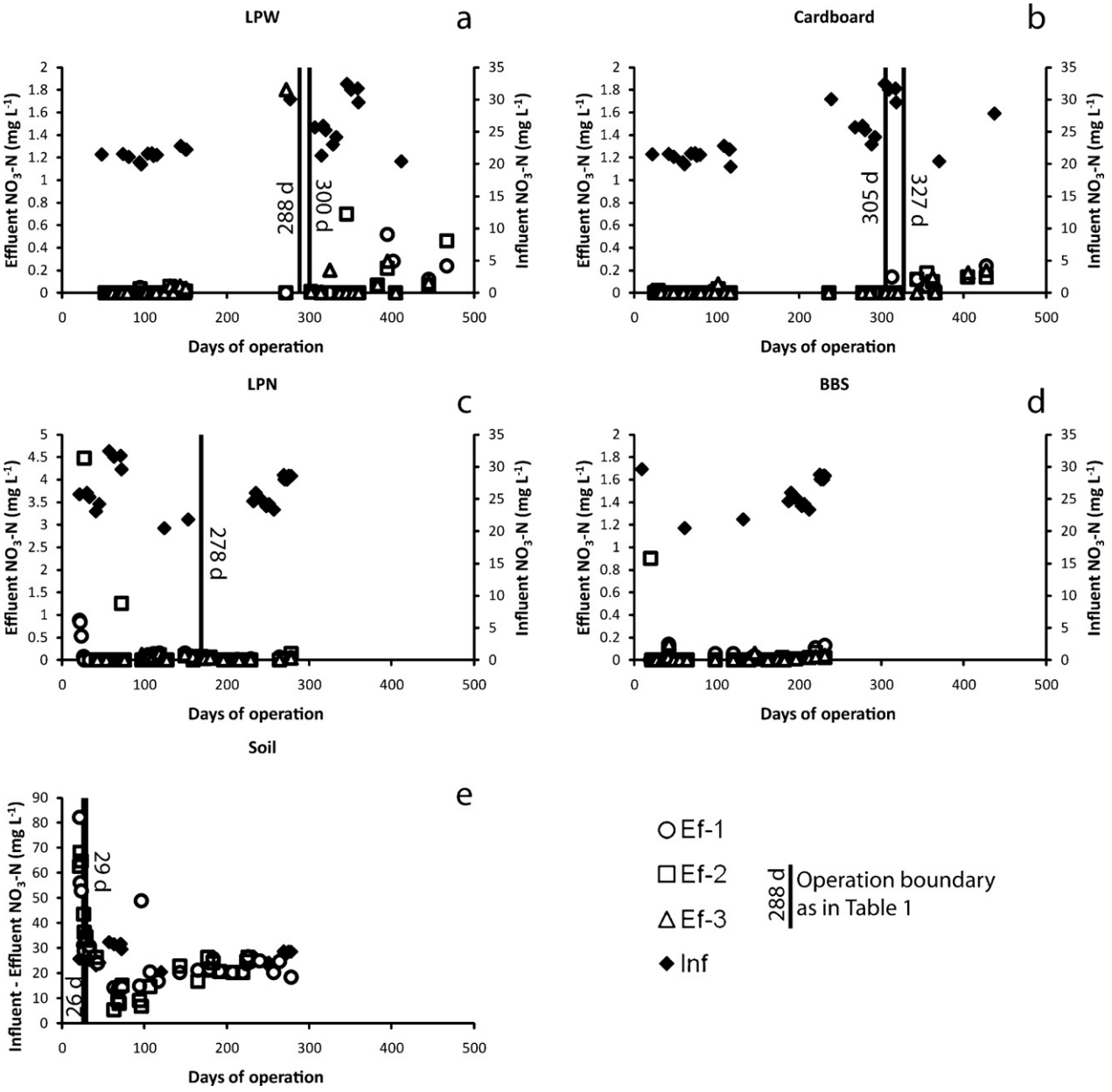

Fig. 2. Influent and effluent NO_3^- concentrations and operation boundaries for each media. Ef 1, 2, 3 are from 3 different bioreactor replicates.

which displayed high concentrations in the LPN (Fig. 4c) and BBS (Fig. 4d) media. Such columns had the highest HRTs. In both periods, except for the soil media, NH_4^+-N and COD concentrations did not show correlated trends.

Ortho-phosphate concentrations in the initial leaching period were generally greater than in the steady-state period (max concentration up to 1.1 mg L^{-1} for LPW). These differences were more significant for both LPW and the cardboard media (Fig. 5a and b) than for the LPN media (Fig. 5c). The BBS media (Fig. 5d) displayed similar PO_4-P concentrations to the LPN media. In the steady-state period, LPN displayed the lowest PO_4-P concentrations. In the soil media (Fig. 5e), PO_4-P concentrations were similar to LPN. Generally, variations of concentrations between media were higher than between columns of the same media. Phosphorus concentrations in the different media ranged from 41.9 mg kg^{-1} for LPW to 832.0 mg kg^{-1} for LPN (Table 2). The soil used in the columns had a low soil test phosphorus (STP) concentration of 4.95 ± 1.75 mg P L^{-1}, expressed as Morgan's plant available P.

3.2. Longitudinal patterns of NO_3-N and NH_4-N in steady state period

NO_3^- reduction to near or below detection limits was observed for LPW, cardboard and LPN bioreactors at a maximum distance of 0.4 m from the inlet (Fig. 6a–i). For all media, no significant differences in NO_3^- removal patterns were observed. The bioreactors showing the smaller HRT (Fig. 6b and e) generally showed higher NO_3^--N concentrations at a distance of 0.2 m from the inlet than in all other bioreactors. NH_4^+-N generally increased in concentration along the column. The LPW bioreactor displayed smaller concentrations of NH_4^+-N at the shortest HRT (Fig. 6a–c), as well as significant increases and decreases in concentration between adjacent ports. In contrast, NH_4^+-N patterns in the cardboard

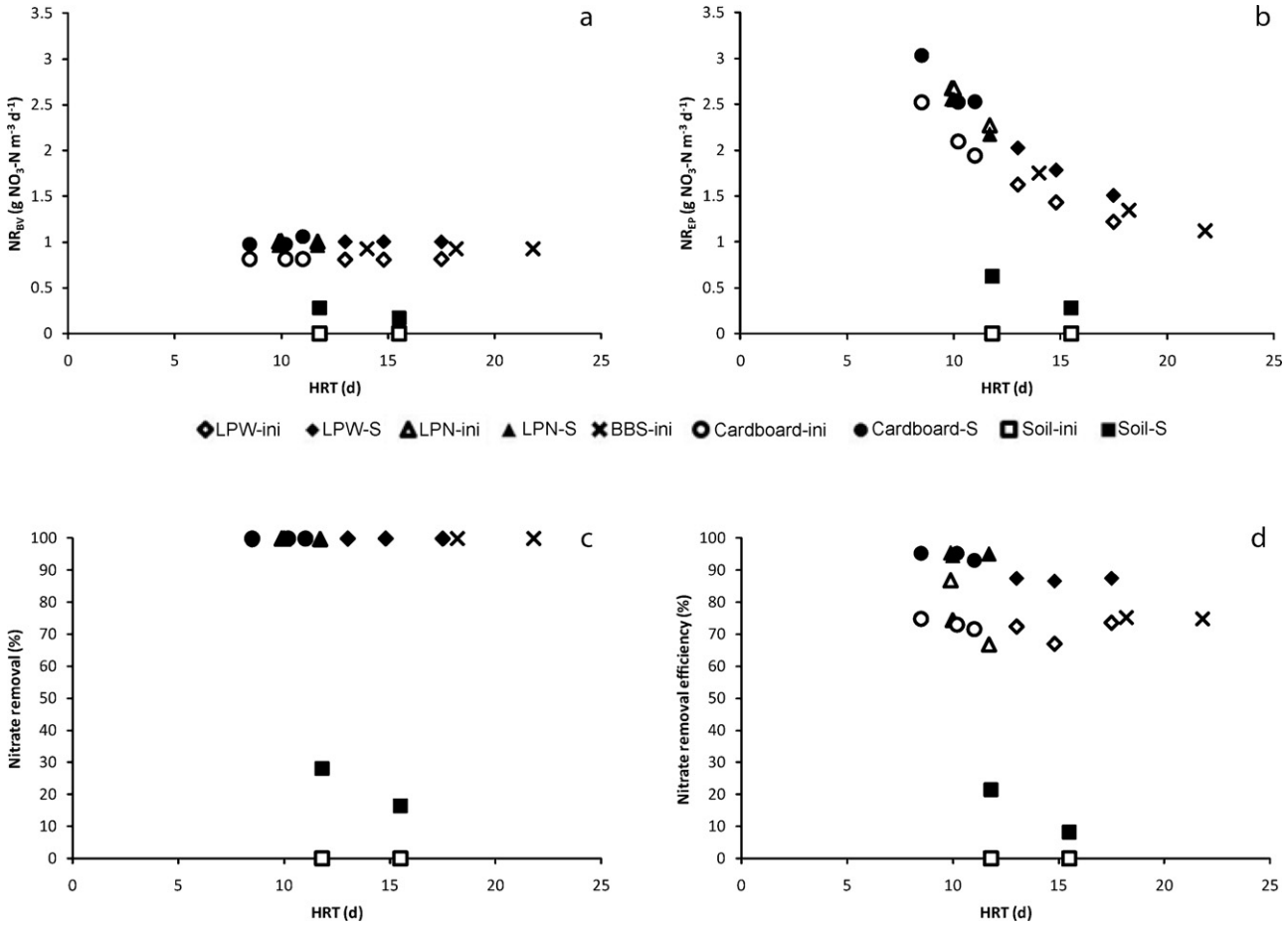

Fig. 3. For initial (ini) and steady-state (SS): (a) NO_3^- removal (bed volume, NR_{BV}), (b) NO_3^- removal (effective porosity, NR_{EP}), (c) NO_3^- removal without pollution swapping and (d) NO_3^- removal efficiency which considers pollution swapping.

bioreactors were more similar between bioreactors, except for the third sampling interval (Interval C, Fig. 6d–f) where NH_4^+-N remained constant or decreased along the bioreactors.

3.3. Greenhouse gas column emissions

Greenhouse gas emissions were dominated by CO_2 and CH_4 fluxes with little N_2O release. Nitrous oxide emissions were extremely low, with the highest values observed during the initial loading phase for LPN bioreactors (Table 2). Once steady-state was achieved, the values for all amendments were lower than 0.6 mg N_2O-N m^{-2} d^{-1}, with the exception of LPW 1 and 2, where N_2O emissions were 1.45 mg N_2O-N m^{-2} d^{-1} and 2.15 mg N_2O-N m^{-2} d^{-1}, respectively (Table 1). Emissions varied both in terms of total C lost and the proportions of CO_2 and CH_4 comprising the total emissions (Fig. 7). During the initial phase, there was a large increase in CO_2 efflux from the LPN and BBS bioreactors relative to the soil control, with these emissions comprising the entire C lost from the system (Fig. 7). Initial phase CO_2 fluxes were 12.5 g CO_2-C m^{-2} d^{-1} for LPN and 5.7 g CO_2-C m^{-2} d^{-1} for BBS, compared to the baseline flux of 0.43 g CO_2-C m^{-2} d^{-1}. Once steady-state conditions were achieved, CO_2 fluxes decreased substantially to 1.2 g CO_2-C m^{-2} d^{-1} for LPN (Fig. 7). Barley did not reach steady-state during the experiment. However, the total C flux from LPN was not significantly higher than the soil control at steady-state.

In contrast, carbon fluxes from the cardboard bioreactors were 11.6 g C m^{-2} d^{-1} and 13.9 g C m^{-2} d^{-1} for sampling times 1 and 2, respectively. Whilst there were no significant differences of total C loss between the two sampling dates for cardboard, there was a trend towards increasing CH_4 over time. The proportion of CH_4 comprising the total C flux ranged from 31 to 47% for the cardboard bioreactors. The C flux from the LPW bioreactors, whilst significantly higher than both LPN and the soil control, was much lower (1.8 g C m^{-2} d^{-1}) than the above C-amendments, with CO_2 comprising over 80% of total C flux.

These C emissions were correlated with the total surface area exposed within the media (Fig. 8, $R^2 = 0.637$). Both the BBS and cardboard had similar average surface areas of media at 4.7 m^2 per bioreactor. As a result, there was a greater area of C substrate available for microbial degradation.

When all GHG emissions were expressed in terms of global warming potentials and cumulated to annual fluxes (i.e. CO_2-equivalents per unit area), there was a similar trend in that the highest emissions were recorded for the cardboard-amended bioreactors, followed by BBS and then LPW (Fig. 9). Total GHG emissions were dominated by CH_4, which comprised 91%, 86% and 54% of BBS, cardboard and LPW emissions, respectively. By contrast, N_2O emissions were highest for the soil control (0.8 t CO_2-equiv. ha^{-1} yr^{-1}) and zero for the LPW.

4. Discussion

The HLR on the columns represented a Darcy flux (q) of 3.47×10^{-7} m s^{-1}. For a typical groundwater hydraulic gradient of 1%, such a Darcy flux implies a k_s value of 3.47×10^{-5} m s^{-1}. Effective porosity in glacial tills can vary from 2.5 to 40%. These

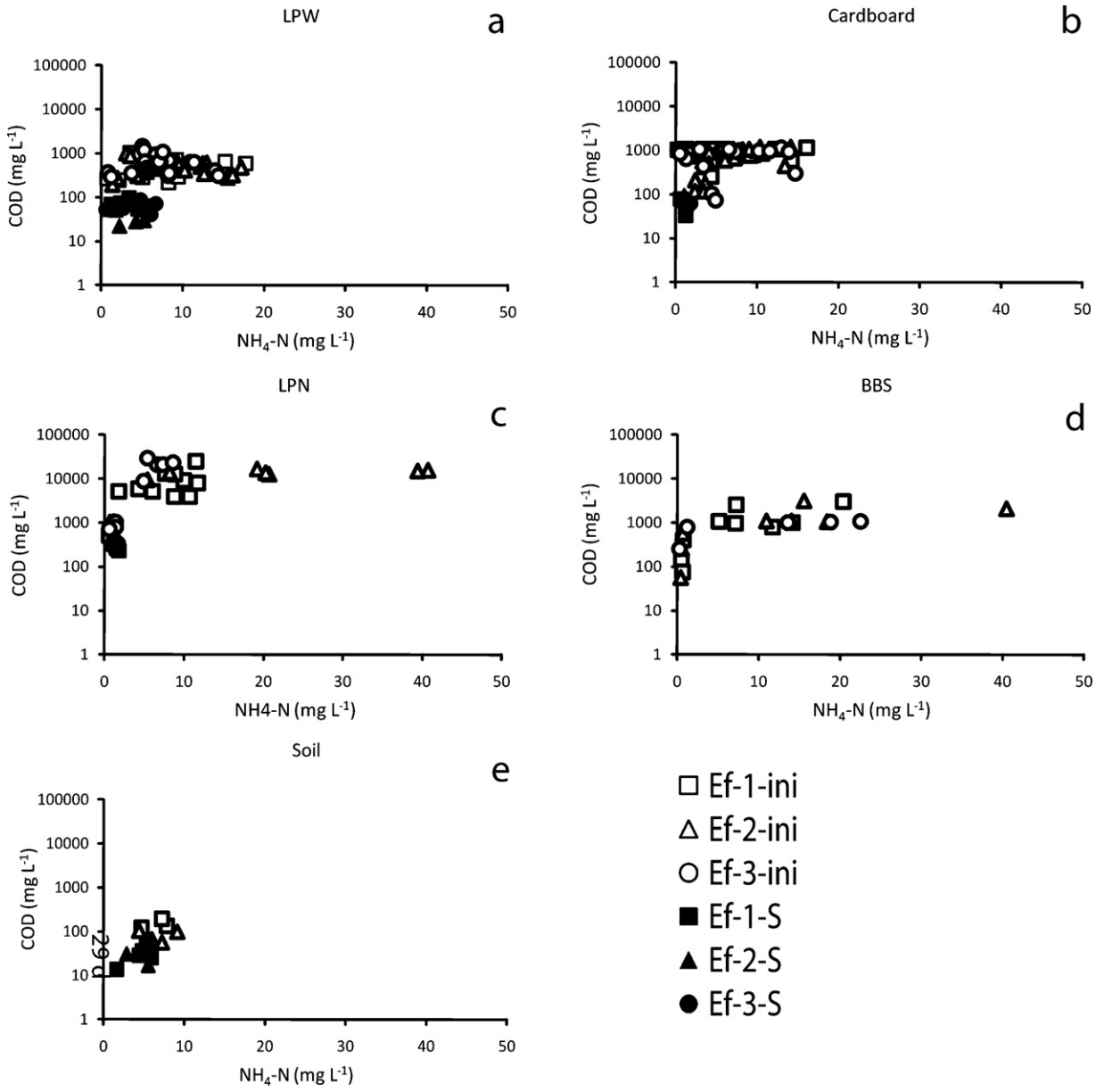

Fig. 4. Scatter plots of effluent (Ef) COD and NH_4-N for initial leaching (ini) and steady state (SS) periods.

values are generally smaller than those observed in the present study (Table 2). Nevertheless, present values imply groundwater velocities typical of a high permeability zone in glaciated tills where low denitrification potential is expected. Higher denitrification potential zones, or hotspots, occur in areas of lower k_s and natural attenuation is likely to protect waterbodies in such zones. In situ bioreactors in glaciated tills should nevertheless be installed in more permeable zones where NO_3^- fluxes are higher and denitrification potentials are lower.

Dissolved oxygen concentrations in the columns were below the threshold value for denitrification in groundwater of <2 mg L^{-1} as presented by Rivett et al. (2008). However, some studies show that concentrations of up to 4 mg L^{-1} can facilitate denitrification (Rivett et al., 2008). Circumneutral pH was observed in this study and present favourable conditions for denitrification. The temperature inside the bioreactors was kept constant at 10 °C, which is close to the mean annual groundwater temperature of 11.6 °C measured at the field site from which the soil was extracted. Influent NO_3^- concentrations used in the study are at least twice that of the EU maximum admissible concentration for groundwater bodies (11.3 NO_3^--N mg L^{-1}).

4.1. Bioreactor media and influent/effluent parameters

As mentioned by Schipper et al. (2010), mitigation measures are needed (e.g. pre-washing of organic carbon media) to limit initial leaching of COD, NH_4^+-N and P to groundwater. In the current study, such leaching occurred for a significant time due to very high residence times in the bioreactors, which reflect glaciated subsoil permeability.

For all carbon media, Fig. 2 illustrates almost complete NO_3^- removal. For the present study, low residence times, high C availabilities and low DO concentrations were responsible for such removals. Hydraulic residence times appear to be a key control on NO_3^- removal e.g. using softwood in 0.9 m-deep columns, Gibert et al. (2008) found >96% NO_3^- removal (removal from

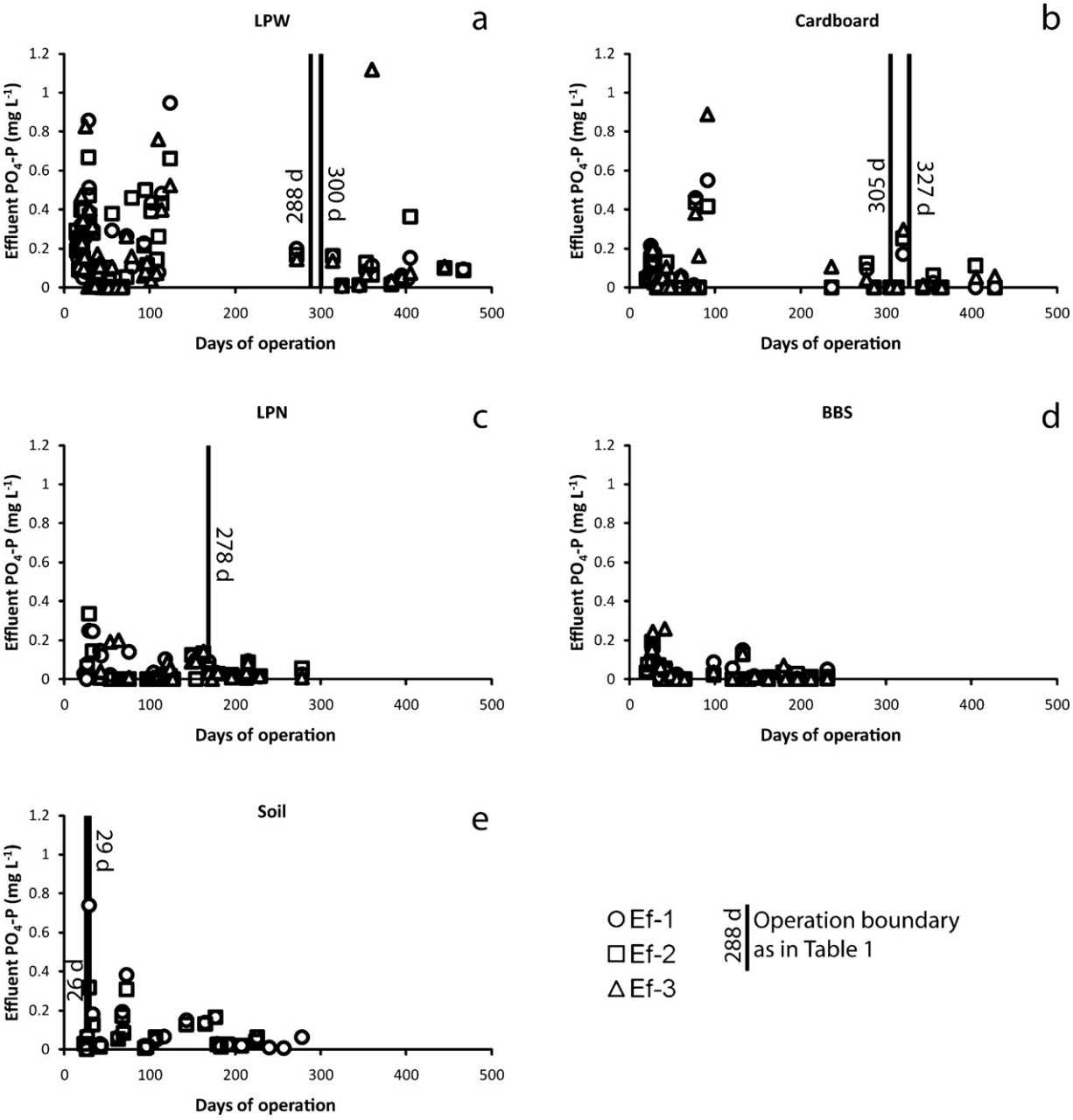

Fig. 5. Scatter plots of PO_4-P concentrations in effluent (Ef) from all bioreactors (1–3) and treatments and operation boundaries.

48 mg NO_3^--N L^{-1} to <2 mg NO_3^--N L^{-1}) for a HRT of 6.6 d. In the same experiment, a shorter HRT of 1.7 d achieved 66% NO_3^- removal. In a laboratory-scale bioreactor filled with woodchip (6.1 m length) and with influent NO_3^- concentrations of 25.7 mg NO_3^--N L^{-1}, Chun et al. (2009) observed complete NO_3^- reduction with a much shorter HRT of 19.2 h. Contrastingly, NO_3^- removal dropped to a minimum of 10% for a HRT of approximately 2 h.

At a maximum NR_{EP} of 3.03 g NO_3^--N m^{-3} d^{-1} calculated for the cardboard bioreactors, the NO_3^- removal rates measured in this study were comparable to other studies (Xu et al., 2009 and others). Greenan et al. (2009) found that when the HLR on a laboratory denitrifying bioreactor filled with a mixture of woodchip and soil was increased from 2.9 to 13.6 cm d^{-1}, the NO_3^--N removal rates increased from 11 to 15 mg NO_3^--N kg^{-1} wood d^{-1}. Gibert et al. (2008) found similar results. In the current study, complete denitrification was observed at a distance of 0.4 m from the base of the reactors (Fig. 6). In this study, for all treatments almost full NO_3^- removal was achieved (Fig. 3c). Therefore, differences in NR_{EP} between bioreactors or media, as outlined in Eq. (2), relate mostly to differences in n_e (and therefore HRT) rather than actual differences in NO_3^- removal (Fig. 3b). In the present study, NR_{EP} incorporates the total length of the column in calculations rather than merely sections where denitrification is maximal. Therefore, the calculated NR_{EP} are likely to underestimate the actual NO_3^- removal in first sections of the column (where highest denitrification occurs).

In contrast, NR_{BV} were very similar between bioreactors and across treatments. Slightly lower values in the initial leaching period were probably due to the high initial release of NO_3^--N from the soil (Fig. 2e). An increase in HLR would likely result in

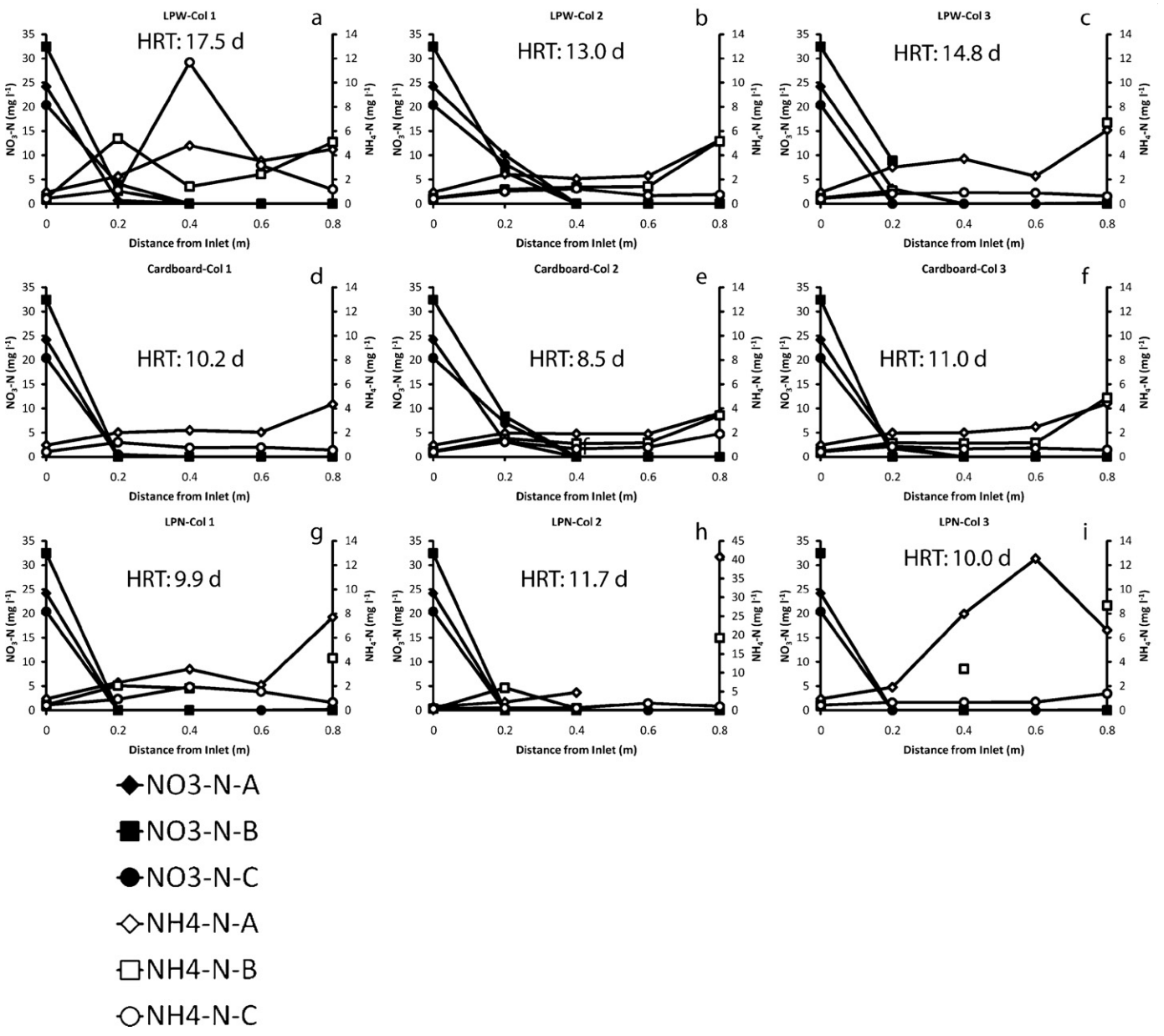

Fig. 6. Steady state port profiles of NO_3-N and NH_4-N concentrations in the 3 columns (Col 1 to Col 3) for LPW (a–c) (for different periods A–C), cardboard (d–f) (for different periods A–C) and LPN (g–i) (for different periods A–C). HRT refers to hydraulic retention times for each column.

a decrease in NO_3^- reduction (i.e. an increase in the length of column needed to achieve nearly complete denitrification). As a consequence, NR_{BV} would increase with increasing HLR until a threshold could be reached wherein a decrease in NO_3^- reduction would not compensate for an increase in HLR. Schipper et al. (2010) recommended the use of NR_{BV} instead of NR_{EP} to allow a direct comparison of removal rates across bioreactor studies. Such an approach, as confirmed by the present study, enables one to investigate the efficacy of different media to remove NO_3^- at laboratory-scale. Some authors have reported that denitrification can follow zero order (Robertson and Cherry, 1995; Greenan et al., 2006; Gibert et al., 2008) or first order Monod kinetics (Chun et al., 2009). In this study, it is likely that denitrification followed different kinetics before and after the 0.2 or 0.4 m sampling ports. Even if the HRTs reported in this study are longer than those from the literature (mentioned earlier), they appear to have a significant impact on denitrification transformational processes along the columns: typically, higher HRT leads to complete denitrification at shorter distances from the influent port of the columns (Fig. 6).

Even if these low residence times allow for nearly complete NO_3^- removal, they are also responsible for the production of unwanted solutes and gases. This is illustrated in Fig. 3c and d when comparing NO_3^- removal and NO_3^- removal efficiency (accounting for NH_4^+-N production). In the current study, high C release and low NO_3^--N concentrations were observed in the two first ports of the bioreactors (Fig. 6). These conditions and the subsequent increase of NH_4^+ along the bioreactors suggest that DNRA may have occurred. In this process, under anaerobic conditions, NO_3^- is reduced to NH_4^+ according to:

$$2CH_2O + NO_3^- + 2H^+ \rightarrow NH_4^+ + 2CO_2 + H_2O \quad (3)$$

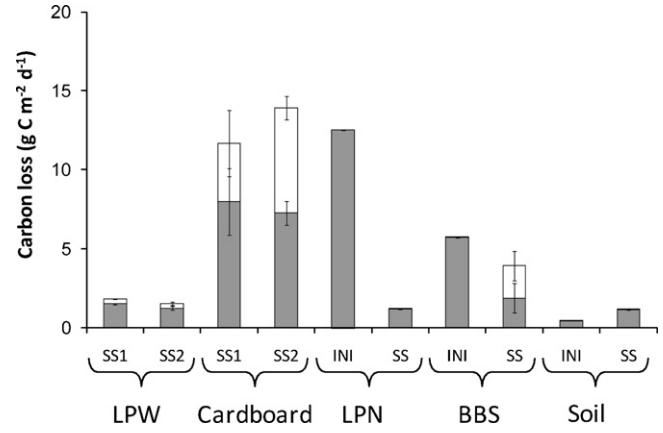

Fig. 7. Daily carbon efflux associated with CO_2-C (■) and CH_4-C (□) for lodgepole pine woodchip (LPW) and cardboard at steady state and lodgepole pine needles (LPN), barley straw (BBS) and soil only during both initial loading (INI) and steady state (SS) conditions.

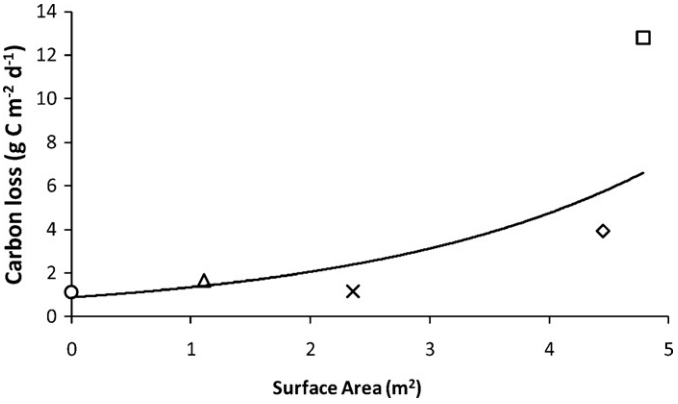

Fig. 8. Correlation between total daily C losses at steady state and the total effective surface area within each column of LPW (Δ), cardboard (□), LPN (×), BBS (◊) and soil only (○), $y = 0.89e^{0.42x}$, $R^2 = 0.721$. Total volume of each media type was 3 L.

Dissimilatory NO_3^- reduction to NH_4^+ is a counter-productive process that has been identified as a potential fate of NO_3^- by Gibert et al. (2008) and Greenan et al. (2009), and results in sustainable NH_4^+ increases in the effluent rather than removal of N as N_2 gas. In a 135-d batch study examining the denitrification potential of various organic substrates, Gibert et al. (2008) found that DNRA contributed up to 9% of the NO_3^- removal in some substrates, but

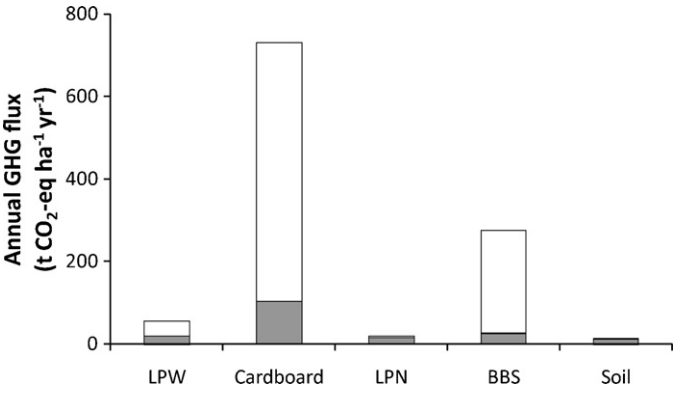

Fig. 9. Annual greenhouse gas emissions associated with CO_2 (■), nitrous oxide (■) and methane (□) for the various treatments at steady state.

varied with media used. Greenan et al. (2009) also found similar results, and speculated that NH_4^+-N release was independent of the NO_3^- loading rate and may have been related to the media within the bioreactors. Wildman (2002) showed in woodchip and woodchip/gravel bioreactors that NO_3^- removal improved from low (3–11%) to high (95%) in the first few months and subsequent operation periods. Accounting for NH_4^+-N production is particularly valid for the initial leaching period, where NO_3^- removal efficiencies (Fig. 3d) are significantly lower than NO_3^- removal (Fig. 3c). This approach also enables us to differentiate the performances of different media or differences in HRT between columns with regard to pollution swapping. Typically, a higher HRT will favour higher NH_4^+-N production, as observed for several media in this study. This implies that a HRT that maximises NO_3^- reduction and minimises NH_4-N release is critical design criterion for bioreactors.

Under field conditions, variations of water temperature, influent NO_3^--N or DO concentrations may further complicate such criteria. On the site where the soil of this study was extracted, shallow groundwater NO_3^--N and NH_4^+-N concentrations were less than 16.9 and less than 2.8 mg L^{-1}, respectively. On this site, a point-source from an up-gradient dairy soil water irrigation system was identified (Fenton et al., 2009). If a bioreactor was installed in this glacial setting, it would result in a great increase in denitrification potential and in the generation of additional NH_4^+. Depending on the proximity of surface water bodies and on the adsorption capacity of the intermittent aquifer, this could result in increasing risk to aquatic ecosystems.

The release of organic C, as expressed in this study by COD concentrations, strongly decreased in the steady-state period to reach values comparable to those of the soil media, except for the LPN media. This is possibly due to the less resistant structure of this media. Similar COD release for all other media and soil, but with different denitrification rates in the steady-state period, implies that a greater proportion of bioavailable carbon was released from the carbon media. Long-term studies have showed that woodchip can sustain NO_3^- removals over long periods (Robertson et al., 2000; Moorman et al., 2010; Long et al., 2011). Very little data exist for the bioavailability of carbon across media types.

Besides N and organic C pollution swapping, other losses involve P in the effluent. Degradation and anaerobic conditions triggered the release of P from the reactors (Fig. 5). As P movement through soil is a function of soil type and structure, sediment and water temperature, number of flow paths, soil P and organic matter content (Sallade and Sims, 1997; Algoazany et al., 2007), special attention needs to be paid to the positioning of denitrifying bioreactors. Lodgepole pine needles and BBS phosphorus release were similar to the soil control, indicating no further inputs from the media. For LPW and cardboard, P losses were higher, indicating losses from both the soil and the media. The soil used in the columns had a low STP concentration of 4.95 ± 1.75 mg P L^{-1}, expressed as Morgan's plant available P, which minimised losses of nutrients to the environment. Such soils may achieve sufficient dry matter yields, but the herbage P concentration would not meet the dietary requirements of grazing animals. To minimise P losses in the initial leaching period, a soil with not only the required hydraulic conductivity but also a very low STP of 0–3 mg L^{-1}, should be chosen. Such soils are found in areas that have been out of production for some time and therefore ideal for excavation and transport to the bioreactor site. Schulte et al. (2010) showed that it may take many years for elevated STP concentrations to be reduced to optimum agronomic levels to reduce risk to water quality. Therefore, sustained P release in shallow groundwater could be expected where high P index soils are used.

4.2. Greenhouse gas column emissions

Anthropogenic GHG emissions are dominated by CO_2 release, which comprises 72% of global emissions and arise primarily from fossil fuel burning and land-use change (Hofmann et al., 2006). The predominant non-CO_2 GHGs are CH_4 and N_2O, which comprise 18% and 9% of global emissions, respectively. Both arise primarily from the agriculture, land-use and waste sectors, and also contribute to stratospheric ozone depletion (IPCC, 2007). In addition, atmospheric deposition of volatilised NH_3 can indirectly contribute to both increased eutrophication and N_2O emissions (Asman et al., 1998). Increases in these gaseous losses may offset some or all of the remediation benefit of particular abatement techniques. For example, in a study on constructed wetlands whilst there was decreased eutrophication, gaseous losses of N_2O and CH_4 increased by 72 t CO_2-equiv. ha^{-1} (Alford et al., 1997).

Ideally, a denitrifying bioreactor should force an endpoint to the N cascade (Galloway et al., 2002) by denitrifying all NO_3^- back to N_2 without N_2O production. Generally, N_2O emissions are lowest in a fully saturated bioreactor. In this experiment, N_2O emissions were indeed very low, ranging from 0.11 to 2.15 mg N_2O-N m^{-2} d^{-1} once steady-state conditions had been achieved. Similar results were found by Woli et al. (2010), who measured N_2O emissions of 0.24–3.12 mg N m^{-2} d^{-1} from a bioreactor bed. In a laboratory column experiment, Greenan et al. (2009) found that N_2O emissions accounted for 0.003–0.028% of the NO_3^- denitrified. In a nine-year study, Moorman et al. (2010) investigated the denitrification potential of woodchip bioreactors and found that there was no significant difference in N_2O emissions between a control (soil only) and the bioreactors. Moorman et al. (2010) found that N_2O losses exported in drainage water exiting the bioreactor accounted for 0.0062 kg N_2O-N kg^{-1} NO_3-N, or 0.62% of NO_3^- removed. Emissions from a large denitrification bed were on average 78.58 μg m^{-2} min^{-1} N_2O-N (reflecting 1% of the removed NO_3^--N), 0.238 μg m^{-2} min^{-1} CH_4 and 12.6 mg m^{-2} min^{-1} CO_2. Dissolved N_2O-N increased along the length of the bed. The bed released on average 362 g dissolved N_2O-N per day and, coupled with N_2O emission at the surface, about 4.3% of the removed NO_3-N as N_2O. Dissolved CH_4 concentrations showed no trends along the length of the bed, ranging from 5.28 μg L^{-1} to 34.24 μg L^{-1} (Warneke et al., 2011).

Whilst N_2O emissions are low, NH_3 may represent a major loss pathway for reactive N in bioreactors. Within the columns, pH conditions were generally alkaline, apart from the LPN media in the initial leaching period. Typically, such conditions will favour NH_3 volatilisation with a correlated decrease in NH_4^+ in solution. Within waste stabilization ponds, high rates of ammonia removal (99%), principally attributed to volatilisation, have been shown to result from high pH and high (>22 °C) water temperatures (Leite et al., 2011).

Methane and CO_2 efflux, resulting from acetate fermentation, also occurs from denitrifying bioreactors, but will reduce as C leaches from the system and the reactive media decays (Jaynes et al., 2008). This rate of reduction will depend on the media, temperature and HRT. Elgood et al. (2010) measured N_2O and CH_4 emissions of 2.4 mg N m^{-2} d^{-1} and 297 mg C m^{-2} d^{-1}, respectively, from a stream bed denitrifying bioreactor containing woodchips. A closer look at these average figures presents a very high CO_2 equivalent of CH_4 (30.6 t CO_2 ha^{-1} yr^{-1}). Comparable CH_4 emissions for the LPW bioreactors were observed in this experiment. However, these emissions were dwarfed by those from the BBS and cardboard bioreactors. Indeed, the rate of CH_4 release from these treatments was more comparable to those from landfills, where CH_4 emissions can range from 9 to 1800 g C m^{-2} d^{-1} (Borjesson and Svensson, 1997; Chanton and Liptay, 2000). The high initial levels of CO_2 and subsequent shift to CH_4 production under steady-state conditions were most likely due to a shift from aerobic respiration as the bioreactors saturated to acetate fermentation which produces both CH_4 and CO_2. Subsequent reduction of the produced CO_2 can generate more CH_4 (Bogner et al., 1997). Therefore, C loss, particularly CH_4 emissions – and not N_2O – from these denitrifying bioreactors appear to be most pressing issue in terms of pollution swapping. This may be partially ameliorated by the soil capping with soils of low STP of denitrifying bioreactors, as similar capping of landfill systems can oxidise up to one-third of the generated methane (Stern et al., 2007). Another way to limit methane production is to optimise the residence time within the bioreactor to ensure that NO_3^- is only just removed as it exits the bioreactor. This ensures that most of the bioreactor is not methanogenic.

5. Conclusions

1. In the initial leaching period, highest NO_3^- removal efficiencies were recorded for cardboard (~94%), followed by LPN (~75%), BBS (~74%) and LPW (~70%). Effluent COD release was one order of magnitude higher during this period for LPN. PO_4-P was highest for LPW, followed by cardboard, LPN and BBS.
2. In the steady-state period, the NO_3^- removal efficiency order did not change, but the efficiency increased. Effluent COD release in this period remained highest for LPN. PO_4-P for all media decreased, but remained above environmental thresholds.
3. Highest GHG emissions (CO_2-equivalents per unit area) were recorded for cardboard, followed by BBS, LPW and LPN. Greenhouse gas emissions were dominated by CH_4 and N_2O emissions were highest for the soil control.
4. Recognising the transitional risk of solute and gaseous losses between initial leaching and steady-state periods is important for the future design of denitrifying bioreactors. For all media, NO_3^- removal efficiencies (with pollution swapping) improved from the initial leaching to the steady-state periods.
5. NO_3^- removal efficiency (with pollution swapping) and rate (without pollution swapping) should be used to select a carbon media, which maximises denitrification and minimises adverse environmental consequences.

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