

Long-Term Performance of In Situ Reactive Barriers for Nitrate Remediation

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Abstract

Nitrate is now recognized as a widespread ground water contaminant, which has led to increased efforts to control and mitigate its impacts. This study reports on the long-term performance of four pilot-scale field trials in which reactive porous barriers were used to provide passive in situ treatment of nitrate in ground water. At two of the sites (Killarney and Borden), the reactive barriers were installed as horizontal layers underneath septic system infiltration beds; at a third site (Long Point), a barrier was installed as a vertical wall intercepting a horizontally migrating septic system plume; and at the fourth site (North Campus), a barrier was installed as a containerized subsurface reactor treating farm field drainage water. The reactive media consisted of 15% to 100% by volume of waste cellulose solids (wood mulch, sawdust, leaf compost), which provided a carbon source for heterotrophic denitrification. The field trials have been in semicontinuous operation for six to seven years at hydraulic loading rates ranging from six to 2000 L/day. Trials have been successful in attenuating influent NO₃⁻ (or NO₃⁻ + NH₄⁺ at Borden) concentrations averaging from 4.8 mg/L N at North Campus to 57 mg/L N at Killarney, by amounts averaging 80% at Killarney, 74% at Borden, 91% at Long Point, and 58% at North Campus. Nitrate consumption rates were temperature dependent and ranged from 0.7 to 32 mg L N/day, but did not deteriorate over the monitoring period. Furthermore, mass-balance calculations indicate that carbon consumption by heterotrophic denitrification has so far used only about 2% to 3% of the initial carbon mass in each case. Results suggest that such barriers should be capable of providing NO₃⁻ treatment for at least a decade or longer without carbon replenishment.

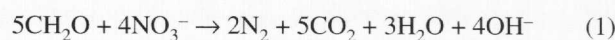
Reactive barriers have now been used to treat nitrate contamination from a variety of sources including septic systems, agricultural runoff, landfill leachate, and industrial operations. This demonstration of successful long-term operation should allow this technology to become more widely considered for nitrate remediation, particularly at sites where passive treatment requiring a minimum of maintenance is desired.

Introduction

Nitrate (NO₃⁻) has become recognized as one of the most common ground water contaminants worldwide (Spalding and Exner 1991; Bogardi et al. 1991; Rudolph et al. 1998), and although agricultural activity is generally acknowledged as the dominant source of nitrate in rural areas (Spalding and Exner 1991; Komor and Anderson 1993; Rudolph et al. 1998) waste water disposal, particularly in septic systems, has also been implicated (Kreitler et al. 1979; Aravena et al. 1993). Furthermore, it has been demonstrated that the dispersive potential of many sand aquifers is less promising than was previously thought (Sudicky 1986; Molyaner and Killey 1988) with the result that nitrate plumes above the drinking water limit have been found to extend more than 100 m from even small septic systems (Robertson et al. 1991). Considerable interest has therefore arisen in the development of on-site waste water treatment systems that minimize nitrate loading. However, conventional nitrogen removal methods used in larger municipal treatment systems (ammonia volatilization, batch sequencing, effluent recirculation, methanol dosing, reverse osmosis, ion exchange;

Koch and Seigrist 1997; Kapoor and Viraraghavan 1997), are mechanically complex, require maintenance, and are generally cost-prohibitive for use with smaller waste water treatment systems such as septic systems.

Nitrogen removal techniques for use with septic systems have tended to focus on more passive in situ methods that are mechanically simple and that do not impose significant additional maintenance requirements (Laak 1981; Brooks et al. 1984; Robertson and Cherry 1995). In the latter study, three small-scale field trials demonstrated the use of nitrate-reactive permeable subsurface barriers to passively attenuate nitrate from septic systems. These barriers were installed as layers below otherwise conventional septic system infiltration beds (Killarney and Borden sites) and as a vertical wall intercepting a horizontally flowing septic system plume (Long Point site). The barriers contained waste cellulose solids (sawdust and leaf compost), which provided a carbon source for heterotrophic denitrification (Delwiche 1981), i.e.,



The earlier study (Robertson and Cherry 1995) indicated that the barriers were successful in attenuating 60% to 100% of input nitrate levels of up to 125 mg/L N over their first year of operation. It was also suggested that they contained sufficient carbon mass to potentially provide nitrate treatment for decades without carbon

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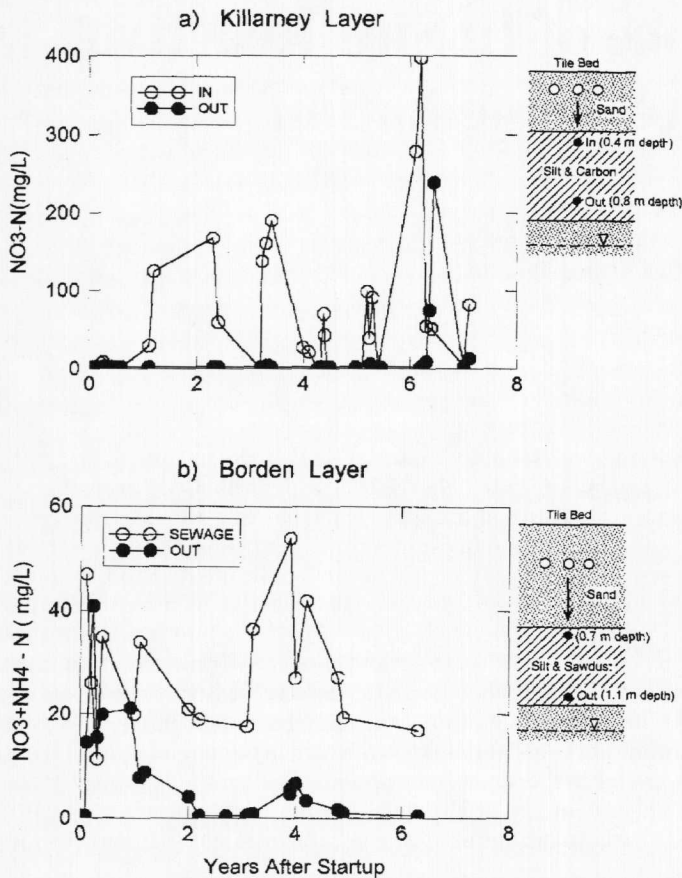


Figure 1. NO_3^- (or $\text{NO}_3^- + \text{NH}_4^+$) removal trends at two sites where reactive barriers are installed as layers below septic system infiltration beds. At the Killarney site, the effluent source after year 1 was "black water" from a low-flow toilet ($\text{NH}_4^+\text{-N} \sim 200$ to 400 mg/L); periodic low "in" values represent dilution from precipitation during nonuse periods; high "out" values in year 6 occurred during a dry period at the end of the summer when the barrier layer may have become unsaturated. At the Borden site, septic tank effluent was used directly for comparison because substantial N attenuation was evident in the shallowest monitoring point (0.7 m depth).

replenishment. However, this was contingent upon a significant portion of the carbon being sufficiently labile to contribute to denitrification and also that other consumption reactions such as excess dissolved organic carbon (DOC) leaching, dissolved oxygen (DO) reduction, and sulfate reduction did not excessively deplete the reactive material. Considering these uncertainties, it was recognized that only by the long-term monitoring of field installations could the life of such barriers be established. In many cases barrier technology would not be cost-effective if frequent carbon replenishment was required, thus longevity of the carbon source is an important consideration.

This paper summarizes the results of six to seven years of operation of the Killarney, Borden, and Long Point field trials during the period 1992 through 1999. In addition, results are presented from a fourth long-term field trial, not previously reported, where the nitrate barrier is in the form of a containerized reactor that has been treating farm field drainage water on a semicontinuous basis since 1993. The latter experiment was carried out on agricultural land that is part of the University of Waterloo and is referred to as the North Campus site. It is a larger scale demonstration of a single-pass reactor described previously by Blowes et al. (1994) for treatment of agricultural runoff.

Field Installations

All of the field experiments are small- to medium-sized (0.6 to 9 m^3) subsurface barriers that were installed in 1992 and 1993 and have been in semicontinuous operation since then. The Killarney and Borden layers were installed at depths of approximately 0.5 to 1 m below conventional septic system infiltration beds (Figure 1) and consisted of approximately 15% by volume of waste cellulose solids mixed with silty, fine sand. Silty matrix material was used so that a condition of tension saturation could be maintained even though the layers were positioned above the water table in both cases. Saturation of the nitrate-reactive media is essential so that atmospheric oxygen is excluded and anaerobic conditions necessary for denitrification can develop. Use of fine-grained matrix material allows the reactive layer to be installed at a convenient depth regardless of the water table position at the site. Coarse hardwood sawdust was the primary carbon source at both sites, although at Killarney the barrier was subdivided into three sublayers: the uppermost containing sawdust, the middle layer containing leaf compost, and the bottom layer containing unprocessed grain seed. The Killarney layer was dosed manually with waste water from a seasonal-use cottage septic tank during the nonfreezing period (May through October) in 1992 and 1993, and then beginning in 1994 sewage loading was provided by "black water" generated by a single low volume (6 L) flush toilet. The seasonal average (May through October) loading rate was estimated at 6 L/day during 1992 and 1993 based on the measured dosing rate (Robertson and Cherry 1995) but then increased to about 13 L/day during 1994 through 1999, based on records of toilet usage that were maintained throughout the 1997 season. This led to a hydraulic retention time in the 0.35 m thick sawdust layer (0.68 m^3 in volume) of about 40 days during 1992 and 1993 and about 17 days during 1994 through 1999, assuming barrier porosity of 0.32.

During 1992 through 1995 the Borden layer received waste water from a seasonal-use trailer camp and a utility building that was used year-round; however after 1995, the washhouse facility at the trailer camp was removed so that effluent was derived solely from the washroom in the utility building. Tile bed loading was not measured directly but was estimated at about 200 L/day , based on the number of persons using the facility (two per day average during the May through October usage period from 1992 through 1995) and an assumed per capita water usage rate (100 L/day). This led to a hydraulic retention time in the 0.5 m thick (9 m^3 volume) barrier of about 15 days, again assuming porosity of 0.32 (Robertson and Cherry 1995). After 1995, the loading rate was estimated from the reduced usage pattern to be about one-half the prior value, thus doubling the hydraulic retention time in the barrier to about one month.

The Long Point wall was installed at a location 10 m down-gradient from a large tile bed at a seasonal-use campground where the septic system plume was migrating horizontally in a permeable sand aquifer (Figure 2). In this case, the reactive wall (1.2 m wide by 0.6 m thick) was installed, with the aid of a trenchbox, to a depth of 0.8 m below the water table in the path of the plume and consisted of the excavated sand material mixed with approximately 20% by volume of coarse hardwood sawdust. The ground water flow rate through the barrier was observed to be proportional to the rate of effluent loading to the tile bed. During peak-use in July and August, the flow rate was estimated from the Darcy equation to be about 6 cm/day , leading to a hydraulic retention time of about 10 days in the barrier (Robertson and Cherry 1995) and a flow volume migrating through the barrier of about 18 L/day . During periods of lesser waste

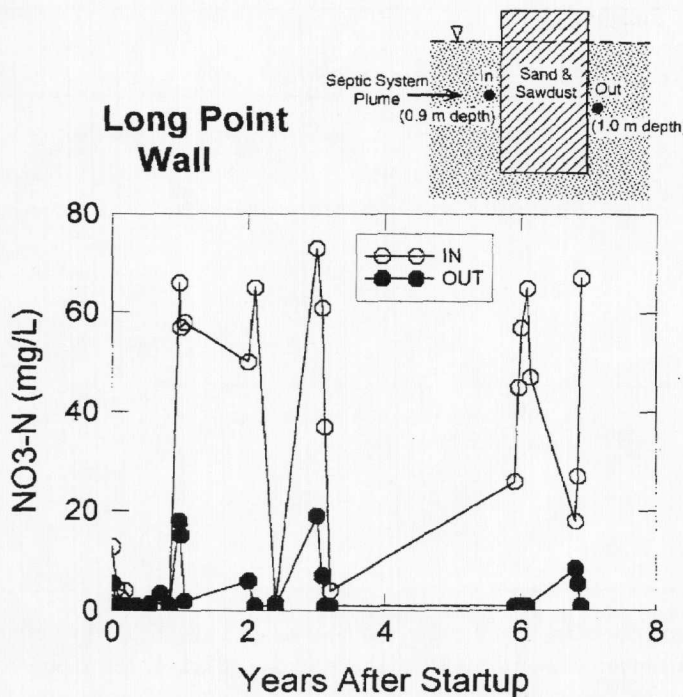


Figure 2. NO_3^- removal trend at a site where a reactive barrier is installed as a vertical wall intercepting a horizontally migrating septic system plume. Low "in" values indicate dilution from background ground water during nonuse periods.

water loading, longer retention times resulted; in addition, during 1995 through 1997, all of the park waste water was diverted to a second tile bed located away from the nitrate barrier. During this period and also during the winter season when the campground was not used, the ground water flow system changed direction causing uncontaminated background ground water to migrate through the barrier. The flow rate through the barrier, averaged over the seasonal (May through October) usage period (excluding 1995 through 1997), was estimated to be about 15 L/day based on the park water usage records, assuming that sewage loading to the tile bed (and hence the ground water velocity through the barrier) was proportional to water usage. This led to an estimate of 13 days for the average hydraulic retention time in the barrier during May through October. A more detailed description of the Long Point wall and the Killarney and Borden layers is provided in a previous publication (Robertson and Cherry 1995).

The North Campus reactor consists of a plywood-framed subsurface container, 1.9 m³ in volume, filled entirely with coarse wood mulch derived from local tree debris (Figure 3). The reactor treats water discharging from a 10 cm diameter drainage tile, which collects ground water from an adjacent farm field. The field is rotationally cropped with corn, alfalfa, and wheat and receives annual applications of nitrogen-containing chemical fertilizer. The reactor was operated seasonally, primarily in the spring and fall when adequate flows were available from the drainage tile, and also periodically during the winter months, including continuous operation through the winters of 1996 and 1997. The hydraulic loading rate was generally in the range of 800 to 2000 L/day, leading to a hydraulic retention time in the reactor of three to seven hours.

Sampling

More intensive monitoring occurred in the first year, after which the installations were generally sampled at monthly to quar-

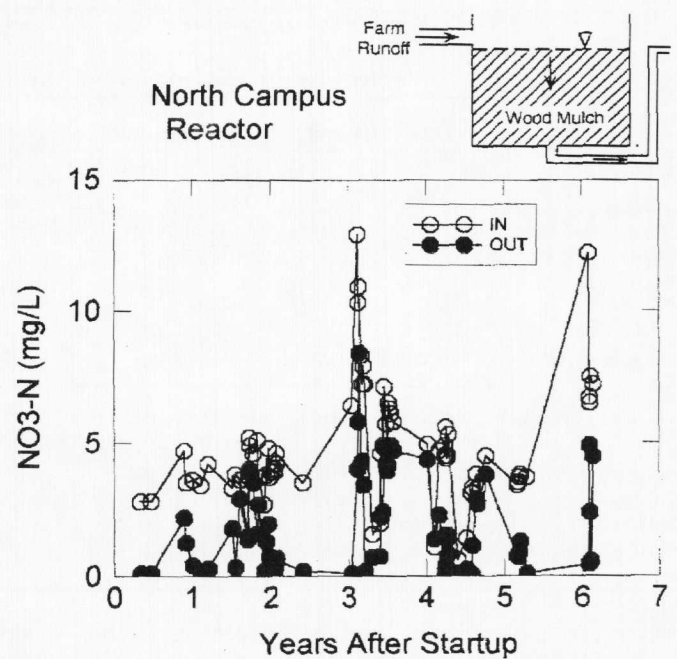


Figure 3. NO_3^- removal trend at a site where a reactive barrier is installed as a containerized reactor treating water from a farm field drainage tile.

terly intervals during their periods of operation, which varied seasonally. Samples were collected primarily for inorganic nitrogen (NO_3^- and NH_4^+), Cl^- , and DOC. Cl^- served as a conservative tracer, enabling quantification of dilution effects, and DOC served as an indicator of excess carbon leaching. Samples were filtered (0.45 μm) immediately after collection and were acidified (pH < 2) with H_2SO_4 or HCl. Samples were collected from 5 cm diameter porous-cup suction lysimeters that were installed in the barrier layers at Killarney and Borden and from 1.3 cm diameter short-tipped piezometers that were installed into the water table zone immediately upgradient and downgradient from the barrier wall at Long Point. Sampling focused on several primary sampling points at each site, which were selected by their position to be representative of pore water entering (in) and leaving (out) the barriers (Figures 1 and 2).

At the Borden site, the shallowest monitoring point in the barrier (lysimeter at 0.7 m depth; Figure 1) only occasionally exhibited elevated NO_3^- levels typical of oxidized sewage and consistently had total inorganic nitrogen ($\text{NH}_4^+ + \text{NO}_3^-$) values that were substantially less than the septic tank effluent. This was interpreted as indicating that nitrogen attenuation was already active at the depth position of the shallowest monitoring point. Thus, in order to provide a better indication of N attenuation, pore water exiting the barrier (1.1 m depth) was compared directly to the septic tank effluent rather than to the nitrified effluent, as was the case at Killarney and Long Point.

At the North Campus site, samples were retrieved directly from inlet and outlet pipes (Figure 3).

Results

Long-Term Nitrate Treatment

Figures 1 through 3 show the history of nitrate treatment at the four sites. Table 1 compares average NO_3^- , NH_4^+ , DOC, and Cl^- val-

Table 1
Water Chemistry Before (In) and After (Out) Treatment in the Denitrification Barriers

	Killarney Layer		Borden Layer		Long Point Wall		North Campus Reactor	
	In	Out	In ^a	Out	In	Out	In	Out
Cl ⁻ (mg/L)	78	76	49	43	30	23	19	20
DOC	41	39 ^c	27	33	5.7	9.9	2.9	4.3 ^b
NO ₃ ⁻ -N	57.0	11.6	1.2	0.2	33.9	2.9	4.8	2.0
NH ₄ ⁺ -N	26.2	29.6	27.3	7.1	<0.1	0.3	0.06	0.29
NO ₃ ⁻ removal ^d		80%		74%		91%		58%

Values are averages of all data obtained during six to seven years of operation (1992 to 1993 to 1998 to 1999) except as noted. Monitoring points are indicated on Figures 1 through 3. Number of data values (n), 16 to 73 for NO₃⁻; 16-49 for NH₄⁺; 16 to 40 for Cl⁻; 11 to 31 for DOC.

^aUntreated septic tank effluent.

^bExcludes initial value at day 7 (102 mg/L).

^cExcludes year 1 values (246-4040 mg/L).

^d(NO₃⁻ [in-out]/ NO₃⁻ in) × 100, except (NO₃⁻ + NH₄⁺) at Borden.

ues entering and leaving the barriers. Nitrate concentrations entering the barriers are shown to vary widely from up to 400 mg/L N at Killarney to about 4 mg/L N at North Campus, reflecting the contrasting nature of the source waters at these sites (septic tank effluent and farm field drainage water). The unusually high nitrate concentrations at Killarney are a result of the waste water being dominated by black water from a low-flow toilet, which caused NH₄⁺ concentrations in the septic tank effluent to average 267 mg/L N during 1994 through 1998.

Significant temporal variations in input nitrate levels were also observed, particularly at Killarney and Long Point. At Killarney, lower nitrate levels were noted in the spring and early summer when dilution from spring snowmelt was present and when higher water table levels occasionally impeded effluent oxidation. At Long Point, low input nitrate levels were associated with the nonuse period when background ground water migrated through the barrier.

Each of the barriers has exhibited significant nitrogen attenuation, averaging 58% to 91% for NO₃⁻ (or NO₃⁻ + NH₄⁺ at Borden; Table 1). The erratic nature of input NO₃⁻ levels made statistical assessment of treatment trends difficult; it is apparent from examination of Figures 1 through 3 that substantial nitrogen attenuation continued throughout the study period at each site. The abrupt spike in output NO₃⁻ levels at Killarney in year 6 (up to 237 mg/L N) is thought to reflect the extremely high input NO₃⁻ levels that occurred at that time (up to 400 mg/L N). Also, the spike occurred at the end of an unusually dry summer season, raising the possibility that evapotranspiration had allowed the barrier layer to become unsaturated at that time, a condition that would halt denitrification. Nonetheless, output NO₃⁻ levels returned to their previous low values (<16 mg/L N) the following year (Figure 1). Robertson and Cherry (1995) provide a more detailed assessment of barrier chemistry at Killarney, Borden, and Long Point.

Overall, the data suggest that there has been little or no deterioration in treatment performance at any of the sites over six to seven years of operation.

Reaction Rates

The containerized North Campus reactor has an accessible discharge pipe that allows flow rates to be measured directly, thus enabling nitrate consumption rates to be determined precisely. Figure 4 shows reaction rates, which were calculated as the dif-

ference of input and output nitrate levels, divided by the hydraulic retention time in the reactor. The reaction rate is assumed to be zero order, consistent with the observation that complete consumption of nitrate to below detection (<0.05 mg/L N) often occurred. Rates were temperature dependent, as expected (correlation coefficient = 0.55; Figure 4), ranging from about 5 mg N/L/day at temperatures of 2°C to 5°C increasing to about 15 to 30 mg N/L/day at 10°C to 20°C. Furthermore, reaction rates measured in years 4 through 7 remained equally as high as those measured during earlier operation (Figures 4 and 5). Thus there was little indication of deteriorating performance during longer-term operation. The highest reaction rate was, in fact, measured during the summer of year 4 (32 mg N/L day; Figure 4).

Precise calculation of reaction rates was more difficult at the other sites because hydraulic loading rates were not measured directly. However, considering the amount of nitrate removal indicated from Table 1 and the estimates of average hydraulic retention time in the barriers (17 days at Killarney after 1993, one month at Borden after 1995, and 13 days at Long Point) nitrate consumption rates of 2.6 mg N/L/day at Killarney, 0.7 mg N/L/day at Borden, and 2.4 mg N/L/day at Long Point are indicated. These slower rates probably reflect the lower content of carbonaceous material in these barriers (approximately 15% to 20% by volume) compared to the North Campus reactor (100%). They should be considered as minimum values, however, because output NO₃⁻ concentrations were often below detection (<0.05 mg/L N), indicating that complete consumption occurred at some point midway through barriers and thus at a faster rate than implied in the previous calculations.

Isotopic Fractionation

A comparison of influent and effluent Cl⁻ levels (Table 1) suggests that about 25% of the nitrate attenuation at Long Point may be attributable to dilution, but at the other sites dilution appears minor. Table 1 also shows that observed NH₄⁺ increases in the barriers (<4 mg/L N) are much less than the amount of NO₃⁻ attenuated (up to 45 mg/L N), indicating that nitrate attenuation is not primarily the result of dissimilatory nitrate reduction to ammonium (Tiedje 1988). The important consumption mechanisms are thus likely to be denitrification (Equation 1) and possibly nitrate assimilation into biomass. A limited amount of NO₃⁻ isotopic data is available consisting of single comparisons of influent and effluent

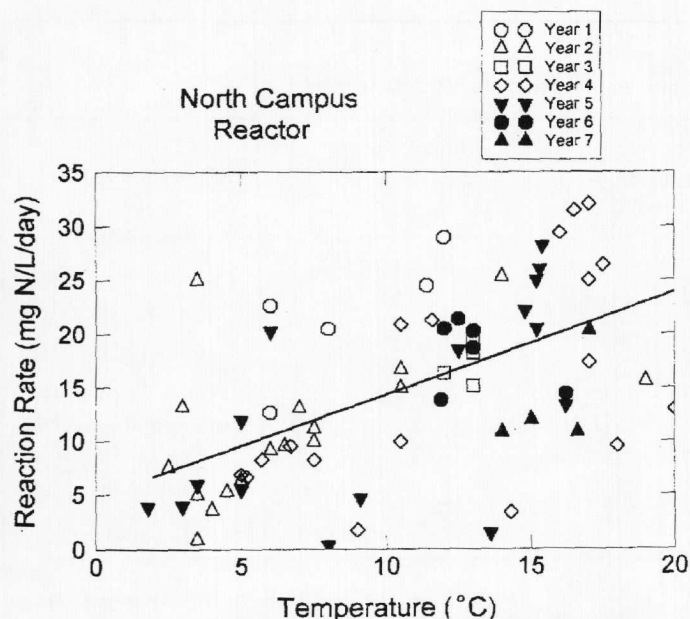


Figure 4. Temperature dependency of NO_3^- removal rates in the North Campus reactor. (First-order regression fit: $y = 4.9 + 0.93x$, correlation coefficient = 0.55).

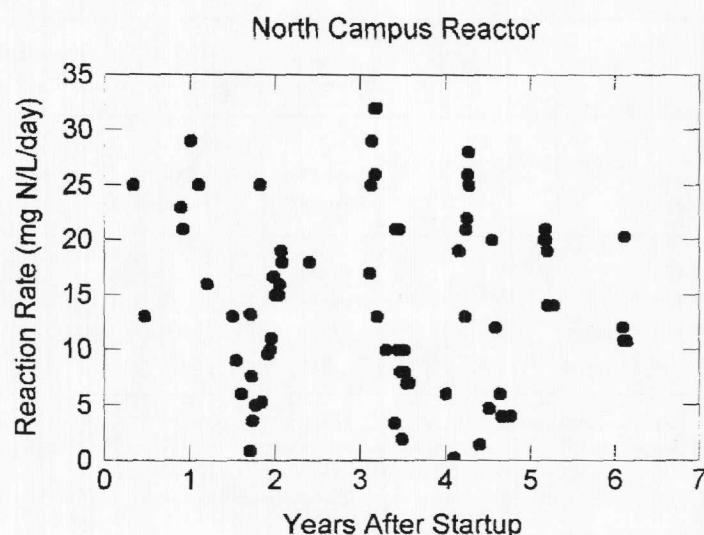


Figure 5. Long-term trend of NO_3^- removal rates in the North Campus reactor. Low values correspond with winter season operation.

	NO_3^- -N (mg/L)		NO_3^- - ^{15}N (per mil)		f^a	ϵ^b (per mil)
	In	Out	In	Out		
North Campus 10/97	4.4	1.5	16.4	24.2	0.34	-7.8
Long Point 10/95	67.5	10.8	6.9	16.2	0.16	-5.7

^aFraction of initial nitrate remaining.
^bIsotopic enrichment factor.

NO_3^- - ^{15}N values at the Long Point and North Campus sites (Table 2). In both cases, ^{15}N was enriched in the residual nitrate, which is indicative of denitrification (Mariotti et al. 1988). The isotopic enrichment factors (ϵ) implied from the data in Table 2 (-7.8 per mil, North Campus; -5.7 per mil, Long Point) are, however, at the low end of the range reported in the literature for denitrification in ground water environments (-13.9 to -30 per mil) (Vogel et al. 1981; Mariotti et al. 1988; Bottcher et al. 1990; Aravena and Robertson 1998). The latter study, in particular, provides a detailed assessment of denitrification that is occurring naturally in the Long Point septic system plume in an area away from the reactive barrier. Complete depletion of nitrate occurs at the bottom of the plume as a result of denitrification that is induced by the presence of trace quantities of carbon and sulfur solids in the aquifer sediments. The isotopic enrichment factor indicated for "natural" denitrification at Long Point is -22.9 per mil (Aravena and Robertson 1998), which is substantially greater than the value indicated for the barrier (-5.7 per mil). However, denitrification in the barrier probably occurs at a faster rate (approximately 13-day residency), which normally leads to a lesser degree of isotopic fractionation (Harrison and Thode 1958). Thus, the isotopic evidence is consistent with attenuation resulting from denitrification; however, the data leaves open the possibility that NO_3^- loss may also be occurring as a result of assimilation into biomass.

Barrier Longevity

Assuming that denitrification is the dominant NO_3^- attenuation mechanism, mass-balance calculations can provide predictions of barrier longevity beyond the present six to seven years of operating history. Denitrification by Equation 1 consumes 1.25 moles of carbon for every mole of NO_3^- converted to N_2 gas; thus carbon is being depleted from the barriers. Table 3 provides estimates of the total flow volumes that have passed through the barriers and the average nitrate amounts that have been attenuated. Flow volumes vary from 14 m^3 at Killarney to 1400 m^3 at North Campus, and nitrate loss varies from 0.6 kg N at Killarney to 4.2 kg N at Borden. Carbon consumption from denitrification would thus range from 0.6 kg at Killarney to 4.5 kg N at Borden, which represents only about 2% to 3% of the carbon mass present (Table 3). Although carbon loss also occurs from other reactions such as DO reduction, excess DOC leaching, and possibly sulfate reduction, calculations presented previously (Robertson and Cherry 1995) indicated that these reactions would each consume less carbon than does denitrification at these sites. Thus, it is likely that only a relatively small percentage of the initial carbon mass (<10% to 20%) has been consumed so far. This was supported by visual inspection of the barrier materials by coring in year 6 at Killarney and in years 4 and 6 at North Campus, which showed that the carbon solids (sawdust at Killarney and wood chip mulch at North Campus) had darkened in coloration but otherwise remained similar in texture to the original material. Furthermore, the cores revealed no obvious indication of biomass buildup or permeability deterioration in the barriers.

Discussion

Field and laboratory trials have now demonstrated that a wide variety of carbonaceous solids can be used to induce heterotrophic denitrification in ground water environments and in waste water treatment processes. These include such diverse materials as straw, newspaper, raw cotton, jute pellets, vegetable oil, compost, wood mulch, and sawdust (Boussaid et al. 1988; Wakatsuki et al. 1993; Blowes et al. 1994; Volokita et al. 1996a, 1996b; Hunter et al. 1997; Schipper and Vojvodic-Vukovic 1998; Robertson and Anderson 1999). Vogan (1993) demonstrated, in a series of laboratory column tests using a variety of carbonaceous solids (wheat straw, alfalfa, wood pulp, and sawdust), that nitrate consumption

Table 3
Carbon Consumption Estimates Based on Flow Volumes and Nitrate Attenuation

Site	Start Date	Total Flow (m ³) ^a	Pore Volumes	Nitrate-N Loss		Initial Carbon	Carbon Consumed	
				(mg/L) ^b	(kg)	Mass (kg)	(kg) ^c	(%)
Killarney	5/92	14	54	45	0.6	22	0.7	3
Borden	7/92	200	70	21 ^d	4.2	150	4.5	3
Long Point	9/92	18	104	31	0.5	26	0.6	3
North Campus	5/93	1400	6360	2.8	3.9	190	4.2	2

^aDaily flow rates through the barriers (15 L/day, Long Point; 6 L/day 1992 to 1993, 13 L/day 1994 through 1999, Killarney; 200 L/day 1992 through 1995, 100 L/day 1996 through 1998, Borden; 800 to 2000 L/day, North Campus) x number of days in operation during 1992 through 1999.
^bDifference of influent and effluent nitrate from Table 1.
^cTotal carbon consumed assuming nitrate loss by denitrification during six to seven years of operation = (total flow × nitrate loss × 1.07).
^d(NO₃+NH₄)-N.

rates varied substantially, by a factor of about 50, depending on the lability of the carbonaceous materials. In another laboratory study using sawdust of varying grain size, Carmichael (1994) observed that the nitrate consumption rate was not correlated with the specific surface area of the sawdust. A possible explanation is that denitrification is associated with reaction rims that penetrate, by diffusion, into the carbonaceous solids rather than being restricted to the grain surfaces. In support of this, examination of the North Campus media in year 4 revealed that the larger centimeter-sized wood particles exhibited dark-colored rims that extended several millimeters into the particles, but the centers of the particles remained light-colored and appeared unaltered from their original condition. The darker rim presumably indicated the zone where denitrification was occurring. The smaller particles were dark-colored throughout.

Thus, selection of a carbon source for use in nitrate-reactive barriers is expected to be governed by site-specific factors, such as the hydraulic retention time in the barrier, permeability requirements, acceptable frequency of maintenance, and local availability of materials.

It is of interest to compare the reaction rates determined from these longer-term demonstrations to those obtained from other laboratory and field trials that also used wood-based carbon sources. The laboratory column study of Vogan (1993) used a reactive mixture containing 2.5wt% organic carbon derived from sawdust (approximately 10% to 20% by volume), which was eluted with simulated ground water containing approximately 70 mg/L NO₃⁻-N. They obtained nitrate consumption rates of 2.8 to 6.5 mg L/day from two separate but similar columns after 74 days of operation at approximately 22°C, with a hydraulic retention time of about one day. Of the four carbonaceous solids tested in this study, sawdust was found to be the least reactive (cellulose reaction rate, 86 to 116 mg L/day; alfalfa, 27 to 100 mg L/day; wheat straw, 46 to 62 mg L/day), but it was considered to be the most long-lived and thus most suitable for applications where long-term, maintenance-free operation was desired. The column study of Carmichael (1994) used a reactive mixture of wood chip mulch (100% by volume), which was similar to the media used in the North Campus experiment. After eluting with ground water collected from a septic system plume (NO₃⁻-N, 50 to 87 mg/L), an average reaction rate of 14 mg L N/day was calculated over pore volumes 26 to 137 at 22°C with a hydraulic retention time of 1.6 days. Schipper and Vojvodic-Vukovic (1998)

calculated a maximum nitrate removal rate of 3.6 mg L N/day (projected to a field temperature of 19°C) in laboratory microcosms using sediment from a reactive wall treating agriculturally impacted ground water in New Zealand. The reactive media contained 30% by volume sawdust. Samples for microcosm rate studies were retrieved from the wall over a one-year period after installation.

Thus, our longer-term rates (0.7 to 2.6 mg L/day for the barriers containing 15% to 20% sawdust (Killarney, Borden, and Long Point) and 4 to 32 mg L/day for the barrier (North Campus) containing 100% wood chip mulch remain consistent with other studies using similar media.

Summary

These field trials have demonstrated that reactive barriers using waste cellulose solids can be used to achieve long-term, passive, in situ attenuation of nitrate originating from a variety of sources. Nitrate removal rates ranged from 0.7 to 32 mg L N/day, were temperature dependent, and did not significantly diminish over the monitoring period. Mass-balance calculations and visual inspection indicated that a substantial portion of the initial carbon remained in the barriers after six to seven years of operation, suggesting that such barriers can be readily designed to provide a decade or more of nitrate treatment without carbon replenishment.

Recently, reactive barriers have been installed to treat nitrate contamination from a fertilizer facility (McLean 1997) and have been incorporated into a commercially available waste water treatment system (Septech 1999). Nitrate barriers have the potential to provide virtually complete single-pass nitrate removal using materials that are low cost and, in most cases, locally available. They require little maintenance and should be ideally suited for use with smaller waste water treatment systems such as septic systems. Moreover, when used with septic systems, any potentially deleterious affects, such as the release of DOC from the reactive media or the reductive dissolution of redox sensitive metals such as Fe, would be mitigated by oxidation that normally occurs subsequent to tile bed discharge.

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