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Engineered Bioretention for Removal of Nitrate from Stormwater Runoff

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ABSTRACT: A bioretention unit is a simple, plant- and soil-based, low-impact treatment and infiltration facility for treating stormwater runoff in developed areas. Nitrate, however, is not attenuated in conventional bioretention facilities. Thus, this study systematically evaluated a reengineered concept of bioretention for nitrate removal via microbial denitrification, which incorporates a continuously submerged anoxic zone with an overdrain. Experimental studies were performed in four phases. In the first two phases, column studies demonstrated that, overall, newspaper is the best solid-phase electron-donor substrate for denitrification out of the set studied (alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, wood chips, and elemental sulfur) based on superior nitrate removal and effluent water quality. The nitrate loading and hydraulic loading studies in the second phase provided design information. In the third phase, system viability after 30- and 84-day dormant periods was evaluated in column studies, demonstrating that newspaper-supported biological denitrification should be effective under conditions of intermittent loadings. Finally, in the fourth phase, pilot-scale bioretention studies demonstrated the effectiveness of the proposed design, showing nitrate plus nitrite mass removals of up to 80%. These results indicate that engineered bioretention for the removal of nitrogen from stormwater runoff has the potential for successful application as an urban stormwater treatment practice. *Water Environ. Res.*, **75**, 355 (2003).

KEYWORDS: bioretention, nitrate, denitrification, urban runoff, biological treatment, best management practice.

Introduction

Nitrogen-containing compounds, particularly nitrate, are important water pollutants. High nitrate and ammonia concentrations that are discharged to surface-water systems promote eutrophication, and nutrient enrichment (nitrogen and phosphorus) has been shown to stimulate toxic *Pfiesteria* strains (Glasgow et al., 2001). In addition, nitrate levels in U.S. drinking water are limited to 10 mg/L as nitrogen because of health concerns; therefore, it is important to limit the input of nitrogen to water supplies. Controlling nitrogen inputs from runoff is important in water supply areas with existing or continuing development because recent investigations of urban stormwater runoff have shown high levels of several nitrogen species, indicating the significance of this source (Barrett et al., 1998a, 1998b; DER, 1993; Line et al., 1996; Wu et al., 1996, 1998).

One potential approach to addressing urban stormwater runoff pollution is a bioretention system, a simple, plant- and soil-based, low-impact treatment and infiltration facility for use in developed areas. Previous research by Davis et al. (2001) using pilot bioretention boxes demonstrated high reductions in metals (copper, lead, and zinc; >92%) and moderate reduction for phosphorus (~80%), total Kjeldahl nitrogen (TKN) (65 to 75%), and ammonia (60 to 80%). However, little nitrate was removed and, in fact, nitrate production was frequently noted. This is because accumulated organic and ammonia nitrogen captured during stormwater events can be converted to nitrate in the time between storm events, presumably via the biologically mediated processes of ammonification and nitrification. This nitrate is then washed from the facility by succeeding precipitation events.

Consequently, modifications are required to engineer bioretention facilities for more complete removal of nitrogen pollutants, in particular nitrate. The overall goal of this study was to systematically evaluate a reengineered concept of bioretention, which incorporates a continuously submerged anoxic zone with an overdrain, for its capacity for nitrate removal via denitrification (Figure 1). Such an approach requires an appropriate electron donor and carbon source in the anoxic zone to promote biological denitrification. The selected electron donor and carbon source should be cost effective and stable in the subsurface (e.g., a solid) for extended periods of time, although the decomposition rate should not limit the denitrification process. Either an organic substrate could be used for supporting chemoorganotrophic denitrifying bacteria or an inorganic substrate could be used for promoting chemolithotrophs. With respect to solid organic carbon substrates, a variety of cellulose-based waste materials have been studied and applied in the field to enhance in situ heterotrophic denitrification for treating various types of nitrate-contaminated water, including tree bark, wood chips, and leaf compost (Blowes et al., 1994) as well as sawdust (Robertson and Cherry, 1995; Schipper and Vojvodić-Vuković, 1998, 2000). Furthermore, Soares and Abeliovich (1998) and Volokita et al. (1996a, 1996b) studied microbial denitrification of drinking water in laboratory columns packed with various types of cellulose-based materials (newspaper, cotton, and wheat straw).

Alternatively, in terms of chemolithotrophic denitrification systems, sulfur–limestone autotrophic denitrification (SLAD) has been studied and applied, especially to remove nitrate from drinking water sources (van der Hoek et al., 1992) and also from septic tank effluents (Sikora and Keeney, 1976; Zhang and Shan, 1999). Recently reported studies related to SLAD systems have demonstrated that they are effective for denitrification, although production of sulfate and hardness and the existence of sulfide in the effluent may be limiting factors in their application (Flere and Zhang, 1999; Zhang and Lampe, 1999; Zhang and Shan, 1999). In addition, elemental sulfur is a promising substrate candidate as an electron donor because of its low cost and ease of storage and handling.

This research experimentally evaluated the modified bioretention system for its capacity for nitrate removal from urban runoff via denitrification. In this experimental evaluation, the optimal conditions for promoting the denitrification reaction under urban runoff conditions were determined so that design parameters could be established for use in bioretention facilities. The investigation

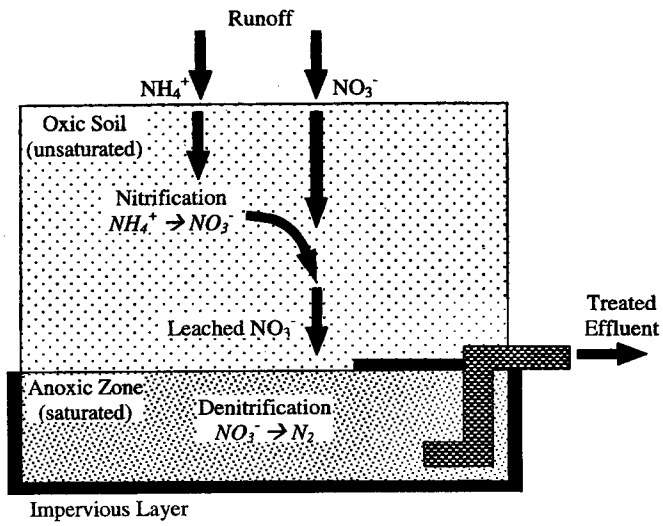

Figure 1—Diagram of modified bioretention cell with anoxic zone for denitrification.

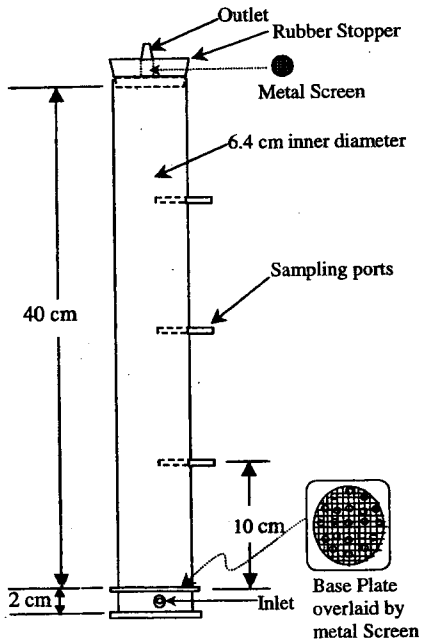

Figure 2—Basic column reactor design.

had four specific objectives, which corresponded to the following four experimental phases: (1) electron-donor evaluation and selection, (2) nitrate loading and flowrate optimization, (3) evaluation of performance after long dormant periods, and (4) pilot-scale bioretention demonstration.

Materials and Methods

Synthetic Runoff. Synthetic runoff was used in all of the experiments to provide controlled input conditions. The synthetic stormwater runoff was made using tap water with the amendments listed in Table 1. The concentrations of the amendments were selected based on previously reported stormwater characteristics (DER, 1993). The tap water was generally dechlorinated using activated-carbon column cartridges (Hose Nipple Cartridge catalog no. D8904, Barnstead Thermolyne Corporation, Dubuque, Iowa). However, dechlorination was performed by adding a stoichiometric amount of sodium bisulfate ($NaHSO_3$) when the carbon column was not available. The dechlorinated water was continuously purged with nitrogen gas to remove oxygen, resulting in influent dissolved oxygen (DO) concentrations of less than 2 mg/L. After normalization to room temperature, proper volumes of stock solutions of sodium nitrate ($NaNO_3$), calcium chloride ($CaCl_2$), and monobasic sodium phosphate (NaH_2PO_4) were added to the tap water to produce the concentrations listed in Table 1.

Table 1—Characteristics of the synthetic stormwater used in the denitrification experiments.

	Value	Source chemical
pH	7.0	Hydrochloric acid or sodium hydroxide
Total dissolved solids (mg/L)	120	Calcium chloride
Nitrate (mg/L as N)	2.0[a]	Sodium nitrate
Phosphorus (mg/L as P)	0.6	Dibasic sodium phosphate

[a] Unless noted otherwise.

Column Reactors. The first three experimental phases used 40-cm-long × 6.4-cm i.d. Plexiglas columns (Figure 2). Some of the columns had sampling ports that penetrated to the center installed every 10 cm along the column. The effluent port (top) of the column was sealed by a rubber stopper with an installed outlet connection. The influent port (bottom) was a Plexiglas plate with 21 0.4-cm holes to promote even distribution of flow across the cross-sectional area of the column. This plate was connected by a 2-cm piece of Plexiglas column to a solid lower base plate, creating the reactor underdrain, which had an inlet connection installed in the side. The effluent and influent ports were separated from the porous packing media by stainless steel screens.

Pool filter sand (Light House brand, U.S. Silica, Berkeley Springs, West Virginia) was used for the porous media in the column study. The effective grain size was 0.504 mm and the uniformity coefficient was 1.396 (U.S. Silica).

The supernatant from the secondary effluent of the Parkway Wastewater Treatment Plant in Bowie, Maryland, where denitrification is being performed, was used as the seed material throughout the column studies.

Phase 1: Electron-Donor Selection Study. The first task was to screen a variety of potential electron donors using synthetic stormwater runoff and sand columns simulating the anoxic zone. Based on the selection criteria and past related research, one inorganic substrate (sulfur) and six organic substrates (alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, and wood chips) were chosen as potential electron donors (Blowes et al., 1994; Robertson and Cherry, 1995; Schipper and Vojvodić-Vuković, 1998; Sikora and Keeney, 1976; Soares and Abeliovich, 1998; Vogan, 1993; Volokita et al., 1996b; Zhang and Shan, 1999).

These substrates were evaluated in three experimental sets. Set 1 consisted of alfalfa, newspaper, and leaf mulch compost; set 2 consisted of sawdust, wood chips, and wheat straw; and set 3 consisted of small sulfur–limestone, large sulfur–limestone, and large sulfur only particles. The organic substrates were prepared by cutting and sieving (alfalfa, newspaper, and wheat straw to less

than 4 mm and sawdust, leaf mulch compost, and wood chips to less than 2 mm). The sulfur (International Sulfur, Inc., Mt. Pleasant, Texas) was prepared by sieving (small sulfur particles: 0.6 to 1.18 mm and large sulfur particles: 2 to 2.36 mm). The limestone (Southdown, Inc., Easton, Pennsylvania) was sieved to obtain a size range from 0.6 to 1.18 mm. The total mass of each electron-donor substrate required for denitrification was calculated based on a 2 mg/L influent nitrate concentration, a 4 cm/h hydraulic loading rate for a 60-day experiment, and the use of appropriate reaction stoichiometry (McCarty, 1975). For these calculations, it was assumed that the organic or inorganic substrate is degraded and used only through the denitrification process. In the case of the organic electron donors, the total organic carbon (TOC) concentration used in the calculations was measured on a dry weight basis via a TOC analyzer (model 5000, Shimadzu, Columbia, Maryland). For set 3, the corresponding stoichiometric amount of limestone required for buffering in sulfur experiments was also calculated (Zhang and Shan, 1999). The calculated material requirements were multiplied by a safety factor of 20 and the mass of material was uniformly mixed with sand that had been washed following a procedure modified from that of Kunze and Dixon (1989) to minimize the effects of residual organic carbon.

Four columns were set up for each experiment including a control column that was packed with washed sand only. All four columns were operated at room temperature (22 ± 2 °C). After pumping in the seed material and recycling it through the column for 2 days, synthetic stormwater runoff was introduced to each column in an upflow mode at a flowrate of 4 cm/h (2.2 mL/min). This flowrate was based on a 1.5-cm total rainfall event over a 6-hour duration assuming a bioretention cell sized at 5% of the drainage area and a rational method runoff coefficient of 0.8 (Davis et al., 2001). The experimental columns in each set were run at this flowrate for 35 to 40 days.

Phase 2: Nitrate Loading and Flowrate Optimization Study. The second task was to optimize the process by varying the nitrate loading and hydraulic loading rate. The electron donors used in phase 2 were those that gave the best nitrate removal efficiency and effluent quality in the phase 1 studies. As discussed in a following section, these were newspaper, wood chips, and small sulfur particles. The seeding procedures and electron-donor preparations were the same as those used in the first phase. Four columns (newspaper, wood chips, sulfur and limestone, and a sand-only control column) were set up as previously described. Initially, the columns were run for 37 days at 4 cm/h with approximately 2 mg/L nitrate in the influent until those columns demonstrated steady-state nitrate removal efficiency. Afterward, variable nitrate loadings and flowrates were studied (Table 2). Operating temperatures during these studies were 21 ± 1 °C except for flowrate 2′ at which time it was 29 ± 1 °C. For each nitrate loading and flowrate tested, the columns were run until they demonstrated quasi-steady-state nitrate removal.

Phase 3: Study of Viability after Long Dormant Periods. The third task was to evaluate the performance of the optimized system under conditions of intermittent loadings such as those found in the field. Five columns were set up with newspaper as the electron donor using the same preparation and seeding procedures as those used in the first phase. Under the same environmental and input conditions, all five columns were initially run for 47 days to develop the microbial populations and attain steady-state nitrate removal. Two columns (columns 1 and 2) were used as control columns and ran continuously throughout the experiment. After 47 days, the influent feed to columns 3 through 5 was stopped. The water in the reactors was drained to field capacity by opening the inlet and outlet ports. Both ports were left open for 7 days, after which they were sealed. Columns 3 and 4 received no influent for 30 days. Column 5 sat for an 84-day dormant period. At the conclusion of the dormant periods, synthetic runoff was introduced and initial effluent nitrate and nitrite concentrations from the columns were measured on an hourly basis to investigate the recovery of the dormant columns.

Table 2—Various nitrate loading and flowrates used in phase 2, the optimization study (operated at 21 ± 1 °C, except flowrate 2′).

Items	Nitrate concentration (mg/L as N)	Hydraulic loading rate (cm/h)	Nitrate loading (mg/d as N)	Column running period (d)
Initial condition	2.07 ± 0.077[a]	4	6.51 ± 0.24	1–38
Nitrate loading 1	3.77 ± 0.29	4	11.8 ± 0.92	38–80
Nitrate loading 2	7.93 ± 0.44	4	24.9 ± 1.37	80–104
Initial condition	2.435[b]	4	7.65[b]	104–108
Flowrate 1	2.38 ± 0.19	6	11.2 ± 0.89	108–129
Flowrate 2	2.24 ± 0.29	8	14.05 ± 1.8	129–152
Flowrate 2′[c]	2.32 ± 0.24	8	14.6 ± 1.5	152–176
Flowrate 3	2.35 ± 0.16	12	22.2 ± 1.5	176–196
Flowrate 4	2.48 ± 0.067	20	39.0 ± 1.1	196–216
Initial condition	2.31 ± 0.023	4	7.26 ± 0.072	216–225

[a] Mean ± standard deviation during quasi-steady-state, unless noted otherwise.
[b] Mean only.
[c] Operated at 29 ± 1 °C.

Phase 4: Pilot-Scale Bioretention Study. The pilot-scale reactor used in the fourth experimental phase consisted of a 76-cm-long × 40-cm-wide plastic box with sufficient depth for up to 36 cm of material and a 10-cm freeboard (Figure 3). Newspaper was cut to less than 5 cm and added to a sand layer based on the volumetric ratio of the pilot-scale bioretention volume to the volume of the columns used in the previous studies. Thus, 75 kg of dried sand (same sand as used in the column studies) was mixed well with 1284 g of newspaper and the media were packed to a height of 18 cm (Figure 3). Next, a plastic liner was emplaced to cover 80% of the sand media surface to prevent the synthetic stormwater runoff from infiltrating this area. The plastic and exposed sand area were subsequently overlaid by an 18-cm-high soil layer (Figure 3). The soil used was characterized as loamy sand by the University of Maryland Soil Testing Laboratory, College Park.

After packing the media in the pilot-scale reactor as previously described, synthetic stormwater runoff was introduced to the reactor until water just came out from the effluent tubes. The reactor was then allowed to sit for 1 day to inoculate the layer. Denitrifying bacteria in the overlying soil were expected to inoculate the sand layer as in a field installation; thus, activated-sludge seeding material was not used in this phase. Subsequently, synthetic runoff was applied to the pilot-scale bioretention facility at a hydraulic loading of 4 cm/h (206 mL/min) for 6 hours. Two additional 6-hour experiments were also completed using this box by following the same procedure.

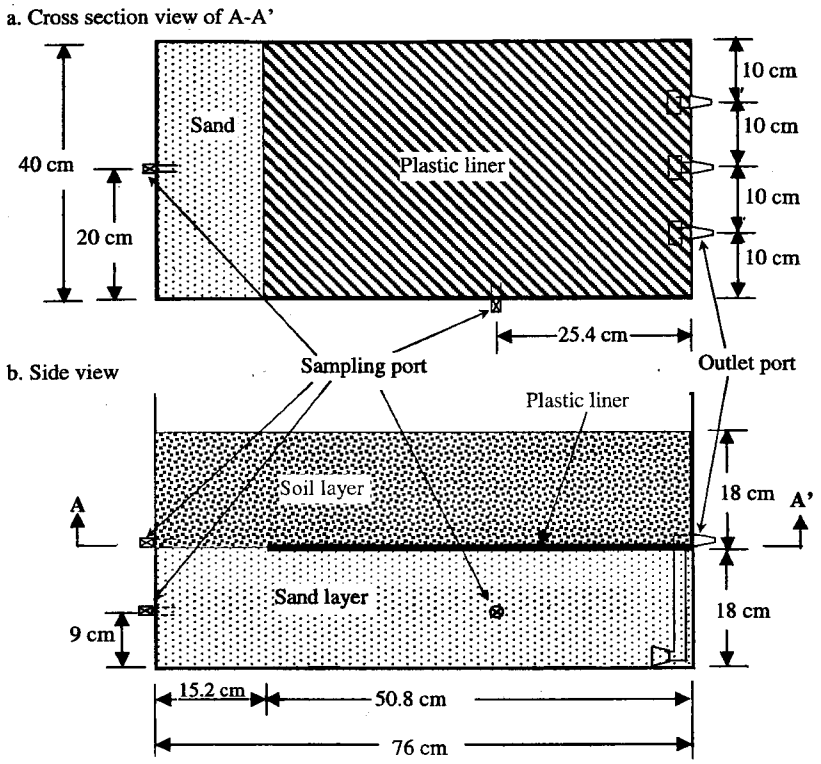

Figure 3—Basic pilot-scale bioretention design: (a) cross-section view of A–A′ and (b) side view.

Analytical Methodology. Nitrate and sulfate concentrations in all of the samples were quantified via ion chromatography (model DX-100, Dionex, Sunnyvale, California) using a Dionex AS4 column. A 1.3-mM:1.5-mM sodium carbonate:sodium bicarbonate solution was used for the eluent. Total Kjeldahl nitrogen was measured via *Standard Methods* (method 4500-N_{org}, Macro-Kjeldahl Method; APHA et al., 1995). *Standard Methods* (method 4500-NO_2^- B, Colorimetric Method; APHA et al., 1995), was used for nitrite analysis, with the absorbance at 543 nm measured via spectrophotometry (Spectronic 21, Bausch and Lomb, Rochester, New York). Turbidity was measured using *Standard Methods* (model 2130 B, Nephelometric Method; APHA et al. 1995) and a turbidity meter (model 200N, Hach Co., Loveland, Colorado). Total organic carbon was quantified using *Standard Methods* (method 5310 B, Combustion-Infrared Method; APHA et al., 1995), via a TOC analyzer (model TOC-5000, Shimadzu), which has both liquid (model ASI-5000, Shimadzu) and solid (model SSM-5000, Shimadzu) sampling modules. Alkalinity was measured following *Standard Methods* (method 2320 B, Titration Method; APHA et al., 1995). Dissolved oxygen was measured using *Standard Methods* (method 4500-06, Membrane Electrode Method; APHA et al., 1995), with an oxygen meter (model 860, Orion Research, Inc., Beverly, Massachusetts) and DO electrode (part no. 086010). The probe and meter were calibrated before every DO measurement.

Results and Discussion

Phase 1: Electron-Donor Selection and Evaluation Study. The phase 1 column study using various electron donors was performed to select a promising candidate or candidates for supporting denitrification in bioretention. Ideally, the decomposition rate of the added electron donor is just fast enough to allow complete reduction of any introduced nitrate to nitrogen gas via the denitrifying process. An excessive decomposition rate may result in the addition of surplus organic materials to the stormwater, causing undesirable effluent water quality such as high TOC, turbidity, color, odor, and TKN.

The average percentage of nitrate removal was calculated after the columns reached a quasi-steady-state condition with respect to nitrate removal (total steady state $\geq$15 days) (Figure 4). In experimental set 1, essentially 100% nitrate removal was observed in the alfalfa and newspaper columns, while that in the leaf mulch and control columns was approximately 60 and 7%, respectively (Figure 4a). However, the alfalfa column had elevated effluent TKN and turbidity compared with the other columns (Table 3), making this material less attractive for practical use.

In set 2, the saw dust, wheat straw, and wood chips columns all performed well, with greater than 95% nitrate removal compared with 6% for the control column (Figure 4b). However, the wheat straw column had somewhat higher effluent TKN and turbidity than the other two columns. Effluent TKN was similar in the sawdust and wood chips columns, although turbidity was somewhat higher in the wood chips' effluent (Table 3). Nevertheless, the wood chip system had consistently better nitrate removal and showed greater removal of nitrate along the column length (data not shown).

One possible explanation for the high effluent TKN from the alfalfa and wheat straw columns is that both have a lower carbon/nitrogen ratio than sawdust, wood chips, and newsprint (Rynk, 1992). Therefore, it is possible that some ammonification occurred in the alfalfa and wheat straw systems, resulting in increased TKN. In addition, some microorganisms can also reduce nitrate to

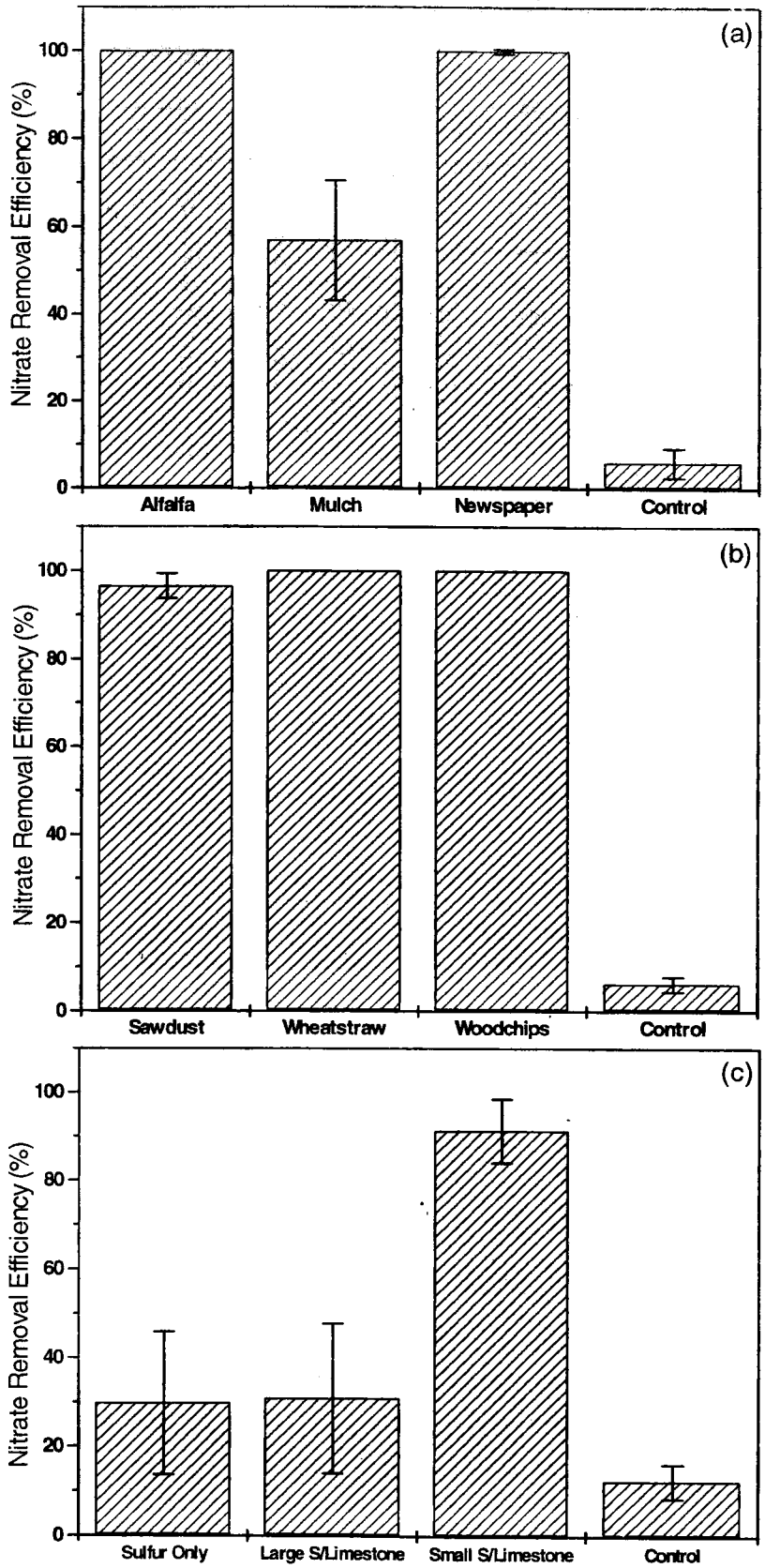

Figure 4—Average quasi-steady-state nitrate removal (%) for the columns in phase 1 (error bars represent ±1 standard deviation): (a) experimental set 1, (b) experimental set 2, and (c) experimental set 3.

Table 3—Effluent water characteristics from electron-donor selection study, phase one.

Study	Column	TKN (mg/L as N)[a]	Turbidity (NTU)[b]	Sulfate (mg/L)[b]	Alkalinity (mg/L as $CaCO_3$)[b]
Organic electron donor					
Set 1	Alfalfa	2–3	27 ± 21	–	–
	Leaf mulch compost	0.3–0.4	0.7 ± 0.19	–	–
	Newspaper	0.1–0.5	1.8 ± 0.27	–	–
	Control	0.1	0.21 ± 0.06	–	–
	Influent	0.1	0.24 ± 0.03	–	–
Set 2	Sawdust	0.2–0.7	0.75 ± 0.56	–	–
	Wheat straw	0.5–1.4	7.3 ± 5.8	–	–
	Wood chips	0.3–0.5	2.4 ± 1.7	–	–
	Control	0.1–0.2	0.14 ± 0.03	–	–
	Influent	0.1	0.15 ± 0.03	–	–
Inorganic electron donor					
Set 3	Large sulfur only	–	0.25 ± 0.02	11 ± 2.0	24.4 ± 1.8
	Sulfur and limestone: large particles	–	0.26 ± 0.26	9.9 ± 1.9	27.6 ± 2.1
	Sulfur and limestone: small particles	–	0.34 ± 0.34	21 ± 1.93	31.3 ± 2.5
	Control	–	0.20 ± 0.2	7.6 ± 0.1	27.9 ± 1.3
	Influent	–	0.20 ± 0.2	7.5 ± 0.12	27.1 ± 0.9

[a] Range.
[b] Mean ± standard deviation.

ammonia via the process of dissimilatory nitrate reduction (DNR), and it is possible that this is the source of the TKN in the effluent. Dissimilatory nitrate reduction has been observed to be favored in anaerobic environments when carbon availability is high relative to nitrate availability (Tiedje et al., 1982). This was the case in these columns, in which nitrate was essentially completely removed from the pore water by the 20-cm height. Qualitative evidence of sulfate reduction in these columns was also observed and some sulfate-reducers can perform DNR to ammonia (Hansen, 1994). Dissimilatory nitrate reduction is an undesirable process in bioretention because nitrogen is conserved in the form of ammonia.

In experimental set 3, only the small sulfur particle–limestone combination performed satisfactorily during the course of the experiment, with 91% nitrate removal during the quasi-steady-state period (Figure 4c). Interestingly, although the mass of sulfur added was the same, the large sulfur particle only and large sulfur–limestone columns produced only approximately 30% quasi-steady-state nitrate removal, while the control had approximately 10% removal. This is probably a result of the increased number of sulfur particles and the increased available surface area with the smaller sulfur particles, allowing more surface area for contact with the nitrate-laden water, and for attached growth of the denitrifying microorganisms (Koenig and Liu, 2001). However, the small sulfur–limestone column effluent had relatively high nitrite levels during the quasi-steady-state period (approximately 0.5 to 0.6 mg/L nitrogen). Nitrite accumulation is a characteristic of the chemolithotrophic denitrifying bacterium, *Thiobacillus denitrificans* (Baalsrud and Baalsrud, 1954), but has been shown to be decreased with longer residence times (Sikora and Keeney, 1976). Effluent sulfate concentrations in all three columns were approximately equal to the stoichiometric amount expected based on nitrate removal. Based on the alkalinity data, the buffering capacity was sufficient whether limestone was added to the columns or not. This was expected given the alkalinity levels in the simulated stormwater runoff (roughly 30 mg/L as calcium carbonate), which should be sufficient to buffer the acid production at the treated nitrate concentration. Relatively low TKN and turbidity values were found from sulfur–limestone systems compared with those from the organic columns, which can hold significant advantages for a bioretention system using denitrification.

Interestingly, a suitable inoculum was provided in all cases by the settled supernatant of a secondary effluent sample. The secondary effluent provided a suitable cellulose-degrading inoculum as well as a sufficient inoculum of chemolithotrophic denitrifying bacteria. The latter is consistent with other research suggesting that these organisms are present in a variety of environments, including domestic wastewater (Zhang and Lampe, 1999; Zhang and Shan, 1999).

Based on these results, newspaper, wood chips, and small sulfur–limestone were selected as the best electron-donor candidates out of the three sets tested. Therefore, these substrates were tested further in phase 2.

Phase 2: Nitrate Loading and Flowrate Optimization Study. *Nitrate Loading Study.* Three different nitrate loadings were studied by changing the influent nitrate concentration while maintaining a flowrate of 4 cm/h (Table 2). The results of these experiments are summarized in Figure 5 for comparison. Complete removal of nitrate (NO_3^-) plus nitrite (NO_2^-) was observed during the quasi-steady-state period at the first nitrate loading for all three columns used in this study, while an average nitrate plus nitrite removal of only 3.2% was observed for the control column (Figures 5a and 5b). However, both nitrate only and nitrate plus nitrite percent removals for all three columns decreased approximately linearly as the nitrate loading increased (Figures 5a and 5b). Of the three electron donors, the newspaper column showed the best percentage of nitrogen removal efficiency throughout the nitrate loading studies, the difference being most pronounced at the higher nitrate loadings.

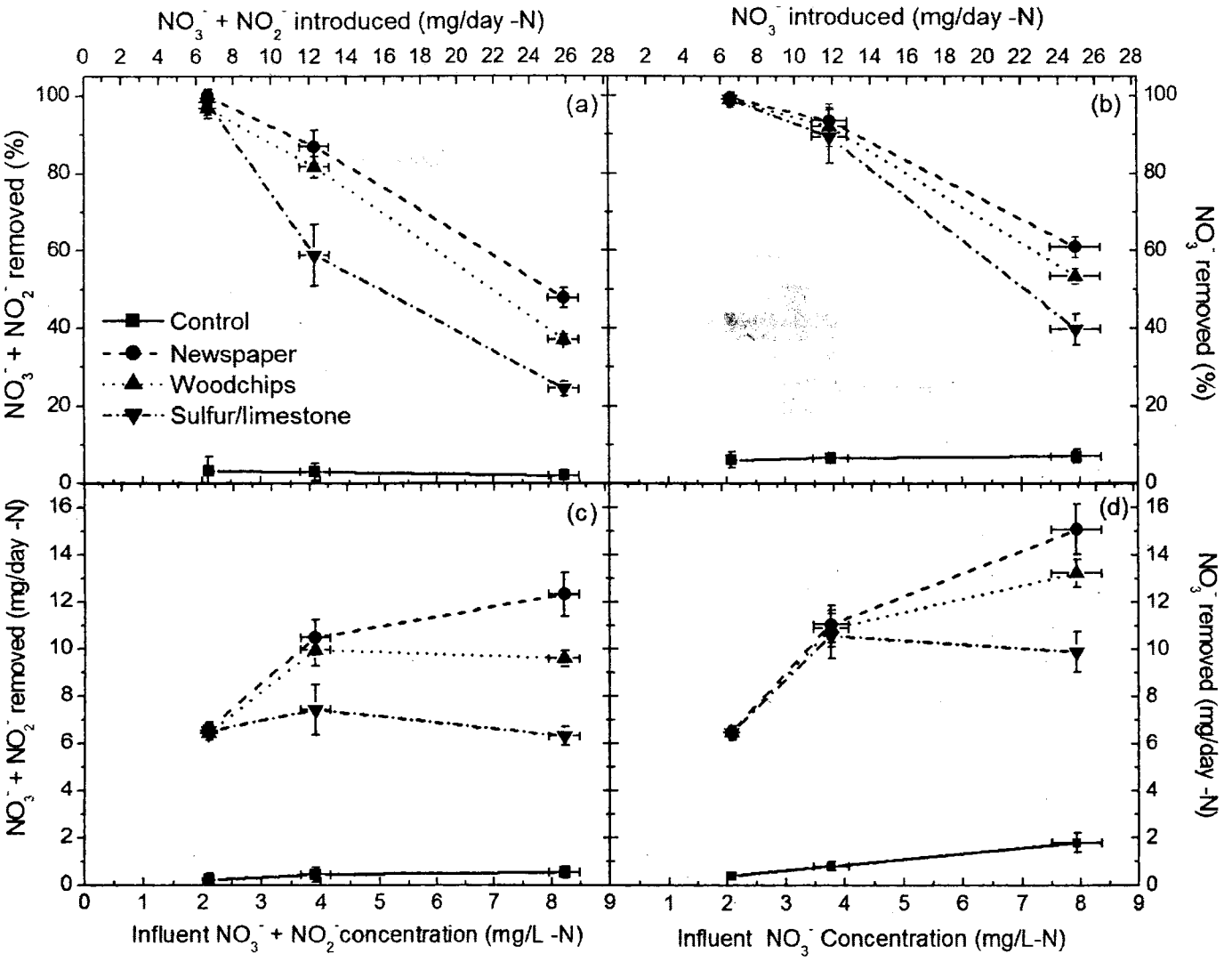

Figure 5—Effect of nitrate concentration on quasi-steady-state nitrogen removal: (a) nitrate plus nitrite percent removal, (b) nitrate percent removal, (c) mass of nitrate plus nitrite removed per day, and (d) mass of nitrate removed per day (error bars represent ±1 standard deviation).

Relatively similar values of the mass of nitrite removed per day (nitrate mass removal rate) for all three columns were observed at the first and the second nitrate loadings (Figure 5d). However, significant differences in the nitrate mass removal rate among the three columns were observed at the highest nitrate loading, in which case the average nitrate mass removal rate was 15.1 mg N/d for newspaper, 13.2 mg N/d for wood chips, and 9.9 mg N/d for sulfur–limestone. For the sulfur–limestone column, the nitrate mass removal rate at the highest third nitrate loading was slightly lower than that at the second nitrate loading.

The nitrate plus nitrite mass removed per day (Figure 5c) increased consistently for the newspaper column as the nitrate influent loading increased, although the rate of increase fell. However, for the wood chips and sulfur–limestone columns, the nitrate plus nitrite mass removed per day did not increase at the higher nitrogen loading (Figure 5c). In fact, for the wood chips column, the nitrate plus nitrite mass removal rate slightly decreased at the highest loading, although the nitrate mass removal rate increased (Figure 5d). These observations suggest that nitrate respiration was out-competing nitrite respiration for limiting electron-donor substrates, resulting in nitrite accumulation. Specifically, this can be attributed to a limiting rate of supply of the electron (energy) donor at the higher nitrate loading and competition between the electron transport reductase enzymes for electrons (i.e., competition between nitrate and nitrite reductases) when the electron donor is scarce (Oh and Silverstein, 1999).

Effluent sulfate concentrations from each column were also measured (Table 4) to monitor for sulfate reduction or production. The disappearance of sulfate across the reactor (influent to effluent) decreased as the influent nitrate concentration increased for the newspaper and wood chips columns, indicating decreasing amounts of sulfate reduction. At the highest nitrate concentration, essentially no sulfate reduction was observed. These trends are reasonable given that sulfate reduction follows denitrification when nitrate becomes depleted. Sulfate reduction in a denitrifying system is undesirable because of the resulting production of hydrogen sulfide, which is malodorous and can be toxic. In addition, as previously noted, some sulfate-reducing bacteria can reduce nitrate

Table 4—Sulfate disappearance across the reactor (influent to effluent), phase 2.

Influent nitrate concentration (mg N/L)	Net sulfate concentration reduction (mg/L)			
	Newspaper	Wood chips	Sulfur–limestone	Control
2.07 ± 0.077[a]	4.0 ± 2.0	2.3 ± 1.4	−13.6 ± 1.7[b]	−0.16 ± 0.26[b]
3.77 ± 0.294	0.72 ± 0.42	0.48 ± 0.41	−17.6 ± 2.2[b]	0.02 ± 0.32
7.93 ± 0.437	0.07 ± 0.53	−0.01 ± 0.42[b]	−14.6 ± 1.5[b]	0.05 ± 0.19

[a] Mean ± standard deviation during quasi-steady-state.
[b] Negative value implies sulfate production.

to ammonia via DNR (Hansen, 1994), thereby conserving nitrogen in the system in the form of ammonium. Furthermore, sulfide, under highly reduced conditions, may inhibit denitrification and thereby promote DNR by microorganisms (deCatanzaro et al., 1987). Although some sulfate reduction did occur in the newspaper and wood chips columns at the lowest influent nitrate concentration, the level of sulfate reduction was relatively low and significant odor was not detected.

Sulfate generation from the sulfur–limestone column is related to the net reduction in nitrate concentration. In these experiments, an average (± standard deviation) ratio of 6.6 ± 0.58 mg sulfate generated/mg nitrate removed was observed during the first nitrate loading study, which is somewhat lower than the theoretical value of 7.5 mg sulfate generated/mg nitrite removed (Koenig and Liu, 1996).

Effluent TOC was also measured during the nitrate loading study. The TOC values from all three columns throughout the experiment were low, with most values less than 5 mg/L. These values decreased with time, eventually approaching that of the influent. Effluent TOC values from the sulfur–limestone column were as low as influent water throughout the study.

Flowrate Study. Five different flowrates were studied with a nominal influent nitrate concentration of 2 mg N/L, giving five different nitrogen loading rates (Table 2). The results of these experiments are summarized in Figure 6. Complete removal of nitrate and nitrite was observed at the first (lowest) nitrate loading (flow 4 cm/h) for all three columns, while an average nitrate plus nitrite removal of only 3.2% was observed for the control column (Figure 6a). The nitrate plus nitrite percent removals for all three columns, however, decreased as the nitrate loading increased. The percent nitrogen removals with the wood chips and sulfur–limestone columns decreased more significantly than those with newspaper as the influent flowrate increased from 4 to 6 cm/h (Figures 6a and 6b). In fact, the newspaper column showed the best nitrogen removal efficiency throughout the flowrate studies.

Based on the mass of nitrogen removed per day for both nitrate only and nitrate plus nitrite, an optimum flowrate for each electron donor is observed at which the maximum nitrogen mass removal can be achieved (Figures 6c and 6d). The nitrogen removed per day for the newspaper column was always higher than that for the wood chips and sulfur–limestone columns, especially at the higher flowrates. The significant decrease in the mass removal rate at flowrates greater than 12 cm/h for the wood chips and sulfur–limestone columns could be due to the washout of bacteria, enzymes, or substrates (Volokita et al., 1996b). This suggests that newspaper is a more effective electron donor that is less affected by flowrate, possibly because newspaper provides better microbial colonization to which bacteria can adhere. Alternatively, it could be that the decomposition rate and the supply of carbon and electrons from the newspaper are more rapid than that for the wood chips and sulfur substrates. Thus, although all of the systems are limited by the electron-donor supply rate at the higher flowrates, the newspaper column is less limited than the other two columns.

Sulfate reduction was negligible for the newspaper and wood chip columns except at the lowest flowrate (4 cm/h) and at flowrate 2′ (8 cm/h at 29 °C), which showed better nitrate removal efficiencies than the other studies (data not shown). This likely is due to the occurrence of sulfate reduction sequentially following the consumption of the nitrate.

Again, all three columns showed low effluent TOC values (less than 5 mg/L) throughout the flowrate study, demonstrating that both the newspaper and wood chips, as solid-phase carbon sources, contribute little extra carbon to the treated water and that most of the carbon released from the substrates is consumed in the columns. The autotrophic sulfur–limestone denitrification system demonstrated the lowest effluent TOC values, although the other two columns also showed effluent concentrations close to the influent TOC values.

Overall, the nitrate loading and flowrate optimization studies indicate that newspaper is the most promising electron donor for nitrate removal from stormwater runoff via denitrification. The combined results of the nitrate loading and flowrate studies for the newspaper column are plotted in Figure 7, which shows the mass of nitrate only, nitrate plus nitrite, and total nitrogen removed per day as a function of the volumetric nitrate loading. The lines in Figure 7 were drawn for convenience to aid in discerning the trends in the data. Based on these data, the optimum volumetric nitrate nitrogen loading for a newspaper–sand media mixture is approximately 17 mg nitrate (L·d). This value was used in sizing the anoxic zone of the pilot-scale reactor.

Phase 3: Viability after Long Dormant Periods. The third task of this work was to evaluate the performance of the optimized system under conditions of intermittent loadings, which are expected in the field. This is a unique challenge of bioretention that distinguishes it from many other engineered systems for biological denitrification. Therefore, in this phase of the investigation, the initial recoveries of newspaper columns after two dormant periods (30 and 84 days) were studied by measuring initial effluent nitrate concentrations. The results obtained during the initial recovery periods are presented in Figure 8.

The first effluent flow started after 2.25 hours for the 30-day dormant period experiment and after 2.33 hours for the 84-day experiment. Essentially no nitrate or nitrite was detected in the first effluent sample collected in both experiments because of washout of the water retained in the column. However, the effluent nitrate concentration increased as time elapsed (Figure 8). For the 30-day

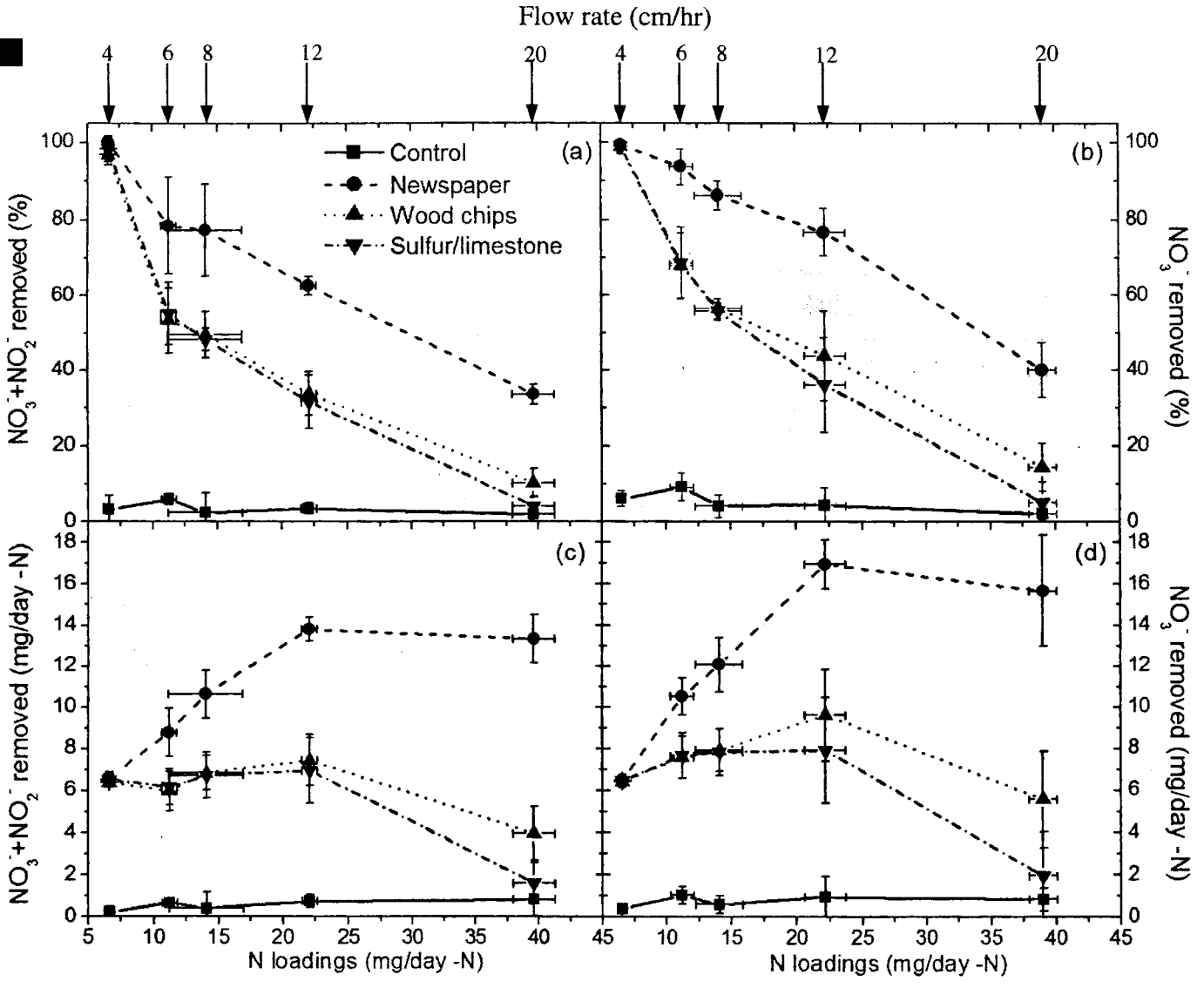

Figure 6—Effect of flowrate on quasi-steady-state nitrogen removal: (a) nitrate plus nitrite percent removal, (b) nitrate percent removal, (c) mass of nitrate plus nitrite removed per day, and (d) mass of nitrate removed per day (error bars represent ±1 standard deviation).

dormant period experiment in columns 3 and 4, the effluent nitrate peak was observed at approximately 4 hours after the first effluent flow began (Figure 8a). At this time, the columns demonstrated roughly 50% nitrate removal efficiency. Beyond the peak, the effluent nitrate concentration decreased as time elapsed and, within 14.5 hours after the first effluent flow began, columns 3 and 4 showed greater than 90% nitrate removal efficiency. The pattern for nitrate plus nitrite was similar to that for nitrate only (Figure 8b).

Similarly, the effluent nitrate peak in column 5 for the 84-day dormant period experiment was observed at approximately 3 hours after the first effluent flow and, thereafter, the effluent nitrate concentration decreased (Figure 8c). However, in this case only approximately 40% nitrate removal was observed at the time of the nitrate peak. Furthermore, it took a total of 30 hours for column 5 to reach 90% nitrate removal compared with 14.5 hours after the 30-day dormant period. Interestingly, after peaking at 3 hours, the effluent nitrate concentration decreased relatively slowly for the next 16 hours (total time: 19 hours). As a result, the effluent nitrate concentration at 19 hours of 1.21 mg/L was little changed from the peak concentration of 1.46 mg/L at 3 hours. The nitrate concentration, however, did decrease relatively rapidly from 19 hours to 30 hours. Again, the pattern for nitrate plus nitrite was similar to that for nitrate (Figure 8d). Based on these results, it seems that the longer the dormant period, the greater the length of time required for the system to recover. This suggests that a change occurred in the columns during the dormant period, presumably having something to do with the newspaper electron-donor source or the microbial population.

At the end of the experimental period, the newspaper in the columns was still visible and most of the newspaper in the media remained similar in appearance to the original material. These observations are consistent with other studies that indicate that newspaper is somewhat resistant to bacterial degradation under

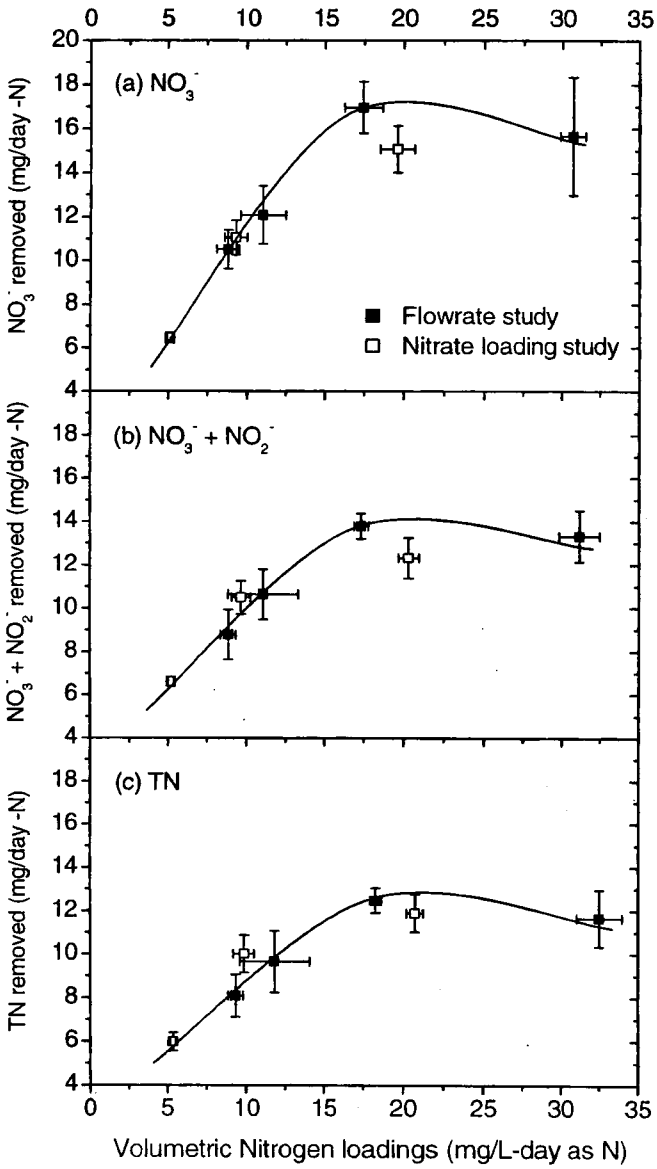

Figure 7—Mass of nitrogen removed vs volumetric nitrate loading in the newspaper column: (a) nitrate, (b) nitrate plus nitrite, and (c) total nitrogen.

anaerobic conditions (Cummings and Stewart, 1994; Volokita and co-workers, 1996b). This resistance seems to be at least partly the result of two factors. One factor is the ink on the newspaper, which, although not directly toxic to the bacteria, masks the paper surface, thereby covering cellulose fibers and preventing microbial adhesion and cellulolysis. A second factor is the chemical composition of newspaper, in particular the relatively high lignin content.

It is possible that the microbial culture in the columns had changed during the dormant period without nitrate addition and required the initial lag time to adapt to the new environmental conditions. For example, the denitrifiers may have shifted to an alternative kind of metabolism during the dormant period and required some time to recover their denitrifying activity after the period of electron acceptor starvation. This explanation is supported by the results of Jorgensen and Tiedje (1993), who studied the survival of denitrifiers in nitrate-free anaerobic environments. They concluded that some conventional respiratory denitrifiers have the capacity to survive in nature for long periods without oxygen or nitrate by performing a low level of fermentation.

The results of this study of viability after dormant periods demonstrate that bioretention systems engineered for biological denitrification should work under conditions of intermittent loadings, with fast initial recovery times after extreme dormant periods. However, it seems that the initial system recovery time may increase with increasing lengths of time without nitrate addition. Nonetheless, after recovery of the dormant columns, steady nitrate removal (greater than 90%) was observed for all of the columns.

Phase 4: Pilot-Scale Bioretention Study. The first phase 4 experiment was performed using the pilot-scale bioretention reactor 1 day after setup and did not show any nitrate removal, probably as a result of a relatively small inoculum and insufficient time for the appropriate microorganisms to accumulate to significant densities. In the second experiment, however, performed 1 week after the first, significant nitrate removal was observed. In that experiment, effluent flow began immediately after the influent was introduced to the system at 206 mL/min. The effluent flowrate increased as time elapsed and relatively quickly approached the influent flowrate (180 mL/min at 30 minutes and 201 mL/min at 2 hours). During the 6-hour duration of influent feeding, no significant buildup of water head on the soil surface was observed. Effluent flow ended at 6.75 hours (i.e., 45 minutes after the influent flow was stopped).

The average influent nitrate concentration during the second experiment was 2.33 mg/L as nitrogen (Figure 9a). No nitrate (<0.02 mg/L as nitrogen) or nitrite (<0.01 mg/L as nitrogen) was observed in the treated effluent until 2.5 hours after the start of the experiment. This probably is due to the fact that the effluent flow up to that point consisted of the water that had been introduced to the pilot-scale reactor during the first experiment, which had sat stagnant in the reactor for a week. Beyond 2.5 hours, the effluent nitrate and nitrite increased to 0.54 and 0.38 mg/L as nitrogen, respectively. An estimated total nitrate mass of 173 mg was introduced to the pilot-scale reactor. The total mass of nitrate plus nitrite (as nitrogen) leaving the pilot-scale reactor in the effluent was calculated to be 31 mg of nitrogen and was based on numerically integrating the effluent nitrate and nitrite concentrations and flowrate over the effluent time. These results demonstrate an overall nitrate plus nitrite mass removal of approximately 80%. The observation of no nitrate (<0.02 mg/L as nitrogen) or nitrite (<0.01 mg/L as nitrogen) in the initial effluent demonstrated that the nitrate remaining in the anoxic zone of the reactor can be completely removed with as little as 1 week between stormwater events.

The third experiment was performed 37 days after the second experiment following the same procedure. Like the second experiment, the effluent flow began immediately after influent was introduced to the system. During the 6-hour duration of influent feeding, a moderate buildup of water head (less than 10 cm) was observed on the soil surface. The sand and soil media in the reactor apparently became more tightly packed as time elapsed and the experiment proceeded, resulting in increased headloss.

Initially, the effluent flowrate increased as time elapsed, but, unlike the second experiment, it never reached that of the influent flowrate. The maximum effluent flowrate measured in this case was 186 mL/min. The effluent flow ended at 7.83 hours (i.e., 1 hour and 50 minutes after the influent flow was stopped).

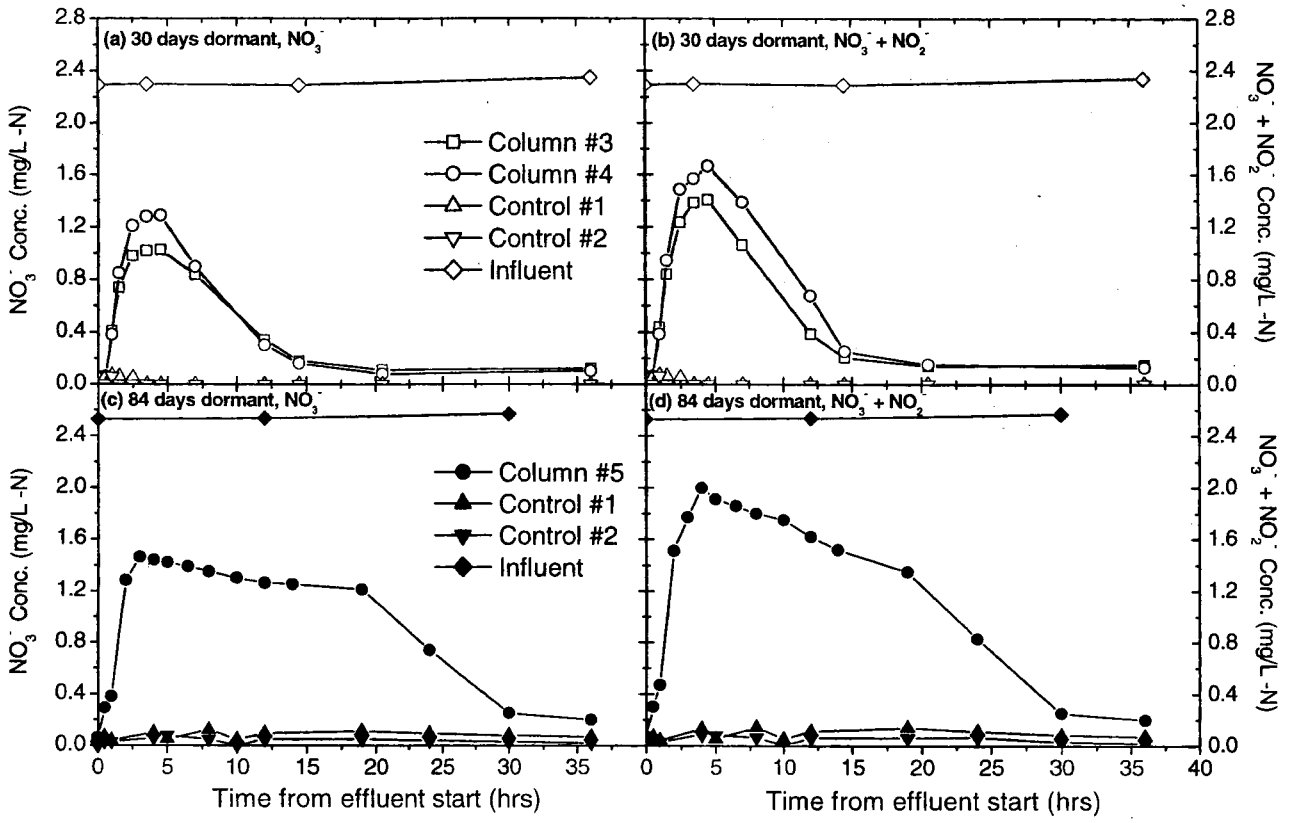

Figure 8—Column recovery after dormant periods: (a) effluent nitrate and (b) effluent nitrate plus nitrite after 30-day dormant period; and (c) effluent nitrate and (d) effluent nitrate plus nitrite after 84-day dormant period.

The average influent nitrate concentration in the third experiment was 2.43 mg/L as nitrogen (Figure 9b). Again, no nitrate (<0.02 mg/L as nitrogen) or nitrite (<0.01 mg/L as nitrogen) was observed in the treated effluent until 3 hours after the start of the experiment. The calculated total nitrate (as nitrogen) mass introduced to the influent and the total mass of nitrate plus nitrite (as nitrogen) in the effluent were calculated to be 180 and 58 mg nitrogen, respectively, demonstrating approximately 70% nitrate plus nitrite removal.

These pilot-scale studies demonstrate the feasibility of including an anoxic overdrain layer in bioretention facilities to promote denitrification. Furthermore, consistent with the column studies, the pilot-scale results indicate that: (1) newspaper is an electron donor and carbon source that will promote significant denitrification and (2) the system performance is not lost after extended dormant periods (up to 37 days). Finally, a suitable inoculum for newspaper-supported denitrification was achieved via the soil and sand in the reactor without addition of a specific inoculum culture.

An important issue in taking these results to full-scale implementation is the long-term performance and maintenance of the reengineered bioretention system, in particular the longevity of the newspaper substrate. To estimate the system longevity, an annual nitrate loading of 41 g N/m^2 was calculated by assuming 102 cm of total rainfall annually (40 in./yr) with an influent nitrate concentration of 2 mg N/L entering the bioretention area, which represents 5% of the drainage basin area. Based on this loading and the estimated reaction stoichiometry, the 2.1 kg of carbon newspaper/m^2 of bioretention that was used in the pilot-scale design (18-cm height of anoxic zone and 30 g of newspaper/1.28 L) could potentially be sufficient to support denitrification for more than 20 years. This estimated system life, coupled with the results of two recent studies (Robertson et al., 2000; Schipper and Vojvodić-Vuković, 2001) demonstrating the successful performance of in situ barriers for denitrification during long-term operation (5 and 6 years), suggests that the reengineered bioretention design can effectively support in situ denitrification in the field for extended periods of time. Nevertheless, at some point, it is anticipated that a drop in the denitrification capacity of the system will occur. At that time, it may be necessary to excavate the media and provide additional carbon source material.

Summary and Conclusions

This work evaluated a reengineered concept of bioretention, incorporating a continuously submerged anoxic zone with an overdrain for its capacity for nitrate removal via denitrification. In this evaluation, column and pilot-scale studies were completed to examine the removal of nitrate from synthetic stormwater runoff. Based on the four phases of this investigation, bioretention designed for removal of nitrogen from stormwater runoff has significant potential as an urban stormwater treatment technique.

The results of the first phase of experiments (electron-donor selection study) indicated that, on the basis of nitrate removal efficiency as well as overall effluent water quality (TKN and turbidity), newspaper, wood chips, and small sulfur particles (0.6 to 1.18 mm) were the best electron-donor candidates for supporting denitrification among those tested. Throughout the second phase of experiments (nitrate loading and flowrate study), shredded

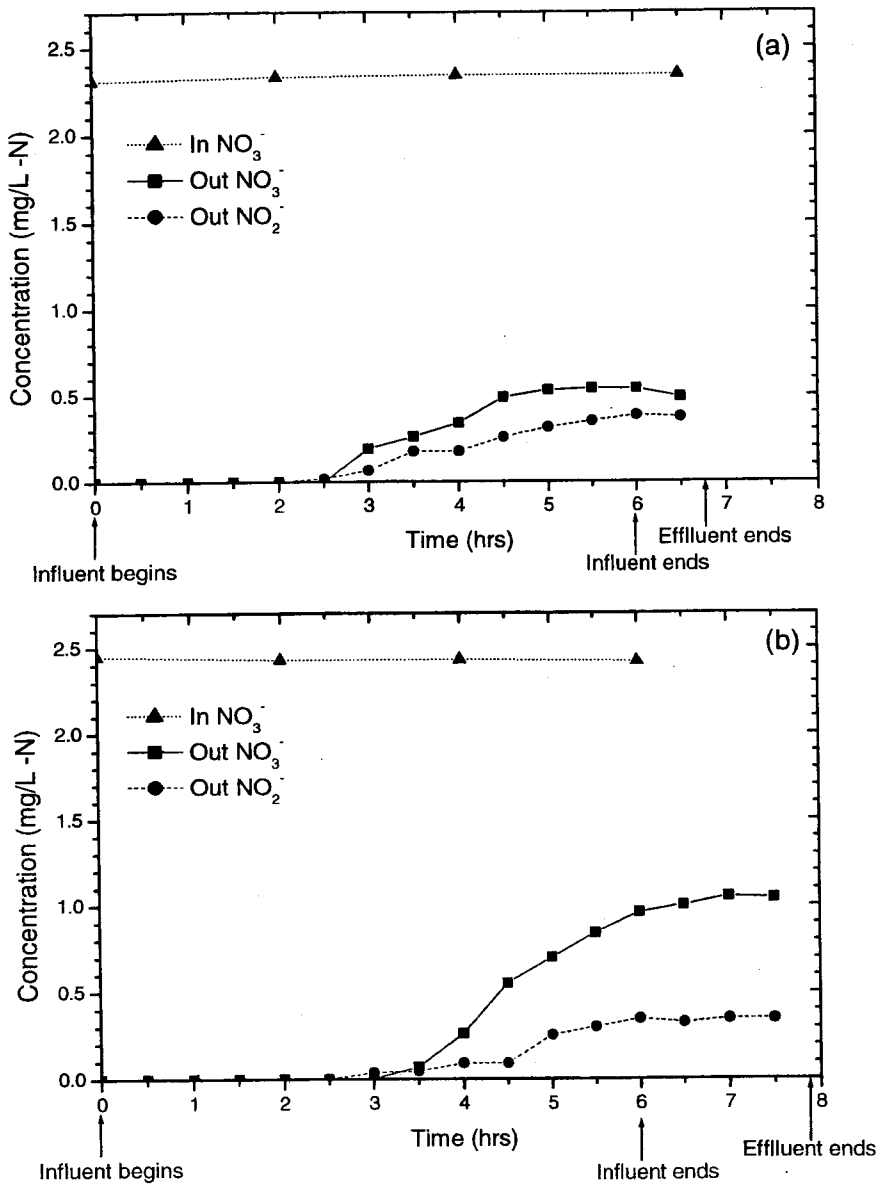

Figure 9—Nitrate plus nitrite concentrations for the pilot-scale experiments, phase 4: (a) the second pilot-scale experiment and (b) the third pilot-scale experiment.

newspaper demonstrated better nitrogen removal efficiency than the other two materials at all three nitrate concentrations (nominally, 2, 4, and 8 mg/L) and at all five flowrates (nominally, 4, 6, 8, 12, and 20 cm/h) evaluated. Thus, newspaper was selected as the best electron-donor substrate overall of the materials studied. Based on the nitrate loading and flowrate studies, an optimum volumetric nitrate loading of 17 mg (L·d) was determined.

Studies of viability after long dormant periods (30 and 84 days) demonstrated that a bioretention cell engineered using newspaper as an electron donor for biological denitrification should be effective under conditions of intermittent loadings. Specifically, rapid initial recoveries were observed after these extreme dormant periods, with a return to greater than 90% nitrate removal efficiency within 14.5 hours after a 30-day dormant period and within 30 hours after an 84-day dormant period.

Finally, pilot-scale studies confirmed the effectiveness of the proposed design to reengineer bioretention facilities, demonstrating nitrate and nitrite mass removals of 70 to 80%. Coupled with estimated system longevity calculations and the results of other recent studies demonstrating the successful performance of in situ barriers for denitrification during long-term operation, the studies reported here suggest that the reengineered bioretention facilities can also be effective in the field by performing in situ denitrification for extended periods of time.

Overall, this study demonstrates the effectiveness of bioretention incorporating a continuously submerged anoxic zone with an overdrain for nitrate removal via denitrification. The nitrate removal capacity demonstrated in this study, coupled with the metal removal shown in the previous study by Davis et al. (2001), illustrates the significant potential for pollutant removal in engineered bioretention systems. Further investigation is needed to refine the design for optimal nitrate removal (e.g., the effect of the amount of electron-donor addition on denitrification) and to examine long-term performance.

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