

## **ENGINEERED BIORETENTION FOR REMOVAL OF NITRATE FROM STORMWATER RUNOFF**

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### **ABSTRACT**

Control of nitrate from urban stormwater runoff can have a significant impact on nitrate levels in local waters. One option for providing treatment to urban stormwater runoff is bioretention, a simple plant- and soil-based low impact treatment/infiltration facility. The goal of this study is to re-engineer the concept of bioretention to remove nitrate from urban runoff. Specifically, a modification to incorporate a continuously submerged anoxic zone with an overdrain is being evaluated for its capacity for nitrate removal via denitrification. Work to date has focused on selecting an electron donor and carbon source that will promote significant denitrification and be stable for extended periods of time in the subsurface. The electron donor and carbon source to be used in bioretention must be readily metabolizable, as well as low cost and readily available. Two sets of organic substrates for chemoorganotrophic denitrifying bacteria were evaluated: Set #1, alfalfa, newspaper, and leaf mulch compost; and Set #2, sawdust, wood chips, and wheat straw. An inorganic substrate for chemolithotrophic denitrifying bacteria, sulfur, was evaluated in experimental Set #3, in three configurations: large sulfur particles (2 to 2.36 mm) alone, large sulfur particles with limestone, and small sulfur particles (0.6 to 1.18 mm) with limestone. All materials were uniformly mixed with washed silica sand and transferred into 40 cm long by 6.4 cm inner diameter Plexiglas columns. A total of 4 columns were used for each experimental set, including a control column packed with washed silica sand only. The columns were seeded with the supernatant of settled secondary effluent and fed anoxic synthetic stormwater runoff. Based on the Set#1 and Set#2 experiments for the organic substrates, excellent nitrate removal was observed in columns containing alfalfa, newspaper, wheat straw, wood chips, and sawdust. However, based on total nitrogen removal and other water quality characteristics, newspaper and wood chips are the best candidates out of these sets. In Set#3, significantly better nitrate removal occurred in the column with the small sulfur particles/limestone compared to the large sulfur particles, probably as a result of the increased surface area of the sulfur available per unit volume of reactor. Further studies will be performed using the electron donors that gave the best nitrate removal efficiency and effluent quality in the experiments reported here: newspaper, wood chips, and small sulfur particles/limestone.

### **KEYWORDS**

Nitrate, Urban Runoff, Biological Treatment, Denitrification

### **INTRODUCTION**

Nitrogen, in particular nitrate, is a substance of critical concern with respect to water quality. Control of nitrate from urban stormwater runoff can have a significant impact on nitrate levels in local waters. Therefore, a low impact treatment facility to remove nitrate from stormwater runoff before it enters receiving waters would be extremely beneficial. One such approach is bioretention, a simple plant- and soil-based low impact treatment/infiltration facility for use in developed areas to provide treatment to stormwater runoff.

Within the concept of bioretention for stormwater runoff treatment, two issues emerge with respect to nitrogen management. The first is the uptake of nitrogen compounds during the time scale of storm events. Based on previous research (Davis et al., 1998), ammonia is moderately removed from infiltrating stormwater due to sorptive interactions with the soil media. However, nitrate has near negligible affinity for soil components due to its anionic form, and consequently nearly no nitrate is removed. The second nitrogen issue in bioretention is on the long-term time scale. As organic and ammonia nitrogen are accumulated in the bioretention system, processes for their benign removal from the bioretention facility must be developed and optimized. The most desirable process is to promote the conversion of accumulated nitrogen species to nitrogen gas, with the off-gas release of nitrogen to the atmosphere. Work by Davis et al. (1998) indicates that this accumulated organic and ammonia nitrogen can be converted to nitrate during the days between storm events, presumably via the biologically-mediated processes of ammonification and nitrification, and that this nitrate is washed from the facility by succeeding rain events.

The goal of this study is to systematically examine the removal of nitrate from urban runoff by re-engineering the concept of bioretention. Specifically, a modification to incorporate a continuously submerged anoxic zone with an overdrain is being evaluated for its capacity for nitrate removal via denitrification (See [Figure 1 "Diagram of Modified Bioretention for Denitrification"](#)). In this evaluation, conditions that optimize the denitrification reaction will be determined so that design parameters can be established for use in bioretention systems. The work to date, which is described in this paper, has focused on selecting an electron donor and carbon source that will promote significant denitrification and be stable for a long period of time in the subsurface. The electron donor and carbon source to be used in bioretention must be readily metabolizable, as well as low cost and readily available. Systems under evaluation include organic substrates for chemoorganotrophic denitrifying bacteria, and inorganic substrates for chemolithotrophic denitrification.

## **METHODOLOGY**

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 (e.g., Vogan, 1993; Blowes et al., 1994; Robertson and Cherry, 1995; Volokita et al., 1996; Schipper and Vojvodic-Vukovic, 1998; Shikora and Keeney, 1976; Zhang and Shan, 1999). The organic substrates were evaluated in two experimental sets: Set #1, alfalfa, newspaper, and leaf mulch compost; and Set #2, sawdust, wood chips, and wheat straw. The alfalfa, newspaper, and wheat straw were prepared by cutting

the materials, and passing them through a 4-mm sieve; the sawdust and the leaf mulch compost were prepared by passing them through a 2-mm sieve. The wood chips were prepared by cutting them using a blender, and then passing the material through a 2-mm sieve. The inorganic substrate, sulfur, was evaluated in experimental Set #3. The sulfur (International Sulfur, Inc., Mt. Pleasant, TX) was sieved into two size fractions: “large” particles, ranging from 2 to 2.36 mm, and “small” particles, ranging from 0.6 to 1.18 mm. Three variations were compared in this set: large sulfur particles alone, large sulfur particles with limestone, and small sulfur particles with limestone. The limestone (Southdown, Inc., Easton, PA) was sieved to obtain a size range from 0.6 to 1.18 mm and was added to buffer the acid production during denitrification with sulfur as the electron donor.

For each electron donor substrate, the total mass required for denitrification was calculated based on the nitrate loading for a 60-day experiment and using the appropriate reaction stoichiometry (McCarty, 1975). In the case of the organic electron donors, the total organic carbon (TOC) concentration used in the stoichiometric calculations was measured on a dry weight basis via a TOC analyzer (Shimadzu, Model 5000). In addition, the corresponding stoichiometric amount of limestone required for buffering in the 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 silica sand that had been washed to minimize effects of residual organic carbon.

The electron donor/sand mixtures were then transferred into 40 cm long by 6.4 cm inner diameter Plexiglas columns, with sampling ports that penetrated to the center installed every 10 cm along the column. A total of 4 columns were set up for each experiment including a control column, which was packed with washed silica sand only. The influent and effluent ports of the columns were separated from the packing material by two stainless steel screens. The influent screen was supported by a Plexiglas plate with 0.4 cm holes to promote even distribution of flow across the cross-sectional area of the column. The effluent screen was held in place by a rubber stopper. All four columns were operated at room temperature ( $22\pm 2^\circ\text{C}$ ).

The columns were seeded with the supernatant (settled at room temperature for 24 hours) of a secondary effluent sample from an activated sludge plant where denitrification was being performed. To inoculate the columns, the seed material was pumped into the column in an upflow mode and recycled through the column for 2 days.

After the 2-day inoculation procedure, synthetic stormwater runoff was introduced into each column in an upflow mode at a flow rate of 4 cm/hr (2.2 mL/min). The synthetic stormwater runoff was made using tap water with addition of 2.0 mg/L nitrate as N, 120 mg/L  $\text{CaCl}_2$ , 0.6 mg/L  $\text{Na}_2\text{HPO}_4$  as P, and the pH adjusted to 7 (Davis et al., 1998). The tapwater was dechlorinated with  $\text{NaHSO}_3$  and continuously purged with  $\text{N}_2$  to remove  $\text{O}_2$ , resulting in influent dissolved oxygen concentrations  $< 2$  ppm. In all experiments, samples for analysis were taken daily for nitrate, and periodically for Total Kjeldahl Nitrogen (TKN), and turbidity. In addition, during the sulfur/limestone experiments, samples were also taken for sulfate, total alkalinity, and nitrite analysis. Nitrate and sulfate concentrations were quantified via ion chromatography (Dionex DX-100) using a AS4 column with a 1.3 mM  $\text{Na}_2\text{CO}_3$ /1.5 mM  $\text{NaHCO}_3$  eluent. Nitrite

and TKN analysis were performed using Standard Methods 4500-NO<sub>2</sub><sup>-</sup> B. Colorimetric Method and 4500-N<sub>org</sub> B. Macro-Kjeldahl Method, respectively (APHA et al., 1995). Turbidity levels were quantified using a HACH 2100N turbidimeter. Alkalinity was measured following Standard Method 2320 B. Titration Method (APHA et al., 1995).

## RESULTS

The experimental columns in each set were run for 35 to 40 days. This was sufficient time for the systems to reach a quasi-steady-state condition with respect to nitrate removal and the average percent nitrate removal during this period was calculated for each experimental set (See **Figure 2 “Average Quasi-Steady-State Nitrate Removal (%)”**). In Set#1, the nitrate removals observed in the alfalfa and newspaper columns were essentially 100%, while that for the leaf mulch compost column was about 60% (See **Figure 2 “Average Quasi-Steady-State Nitrate Removal (%)”**). The removal in the control column was only about 7%. However, treated water from the alfalfa column showed some odor, increased turbidity ( $\approx 27$  NTU) and residual TKN (2-3 mg/L N), while that from the newspaper and mulch did not demonstrate any of these problems.

The Set#2 organic electron donors, sawdust, wheat straw, and wood chips, all performed well, with >95% nitrate removal, compared to <10% for the control column (See **Figure 2 “Average Quasi-Steady-State Nitrate Removal (%)”**). However, the effluent quality based on other parameters was variable. In particular, the wheat straw column had somewhat high residual TKN (0.5-1.4 mg/L N), and high turbidity (up to about 16 NTU). The sawdust and wood chips had similar TKN levels in the effluent (roughly 0.3 mg/L N) during the quasi-steady-state period. The turbidity was somewhat higher in the wood chip effluent compared to the sawdust column (average 2.4 NTU compared to 0.8 NTU); however, the wood chip system provided consistently better nitrate removal than the sawdust system throughout the course of the experiment, and showed more rapid removal of nitrate along the length of the column.

In Set#3, only the small sulfur particle/limestone combination performed well over the course of the experiment, with about 90% nitrate removal during the quasi-steady-state period (See **Figure 2 “Average Quasi-Steady-State Nitrate Removal (%)”**). The large sulfur only, and large sulfur/limestone columns produced only about 30% nitrate removal during the quasi-steady-state period, while the control had about 10% removal. Effluent sulfate concentrations in all three columns were approximately equal to the stoichiometric amount expected based on the nitrate removal. No clear trends were found in the alkalinity data; the buffering capacity seemed to be sufficient whether limestone was added to the columns or not, although the alkalinity levels in the sulfur-only column were generally somewhat lower. These results were expected based on the alkalinity levels in the simulated stormwater (roughly 30 mg/L as CaCO<sub>3</sub>), which should be sufficient to buffer the acid production at the tested nitrate concentration in the absence of added limestone. Interestingly, the small sulfur/limestone column effluent had relatively high nitrite levels during the quasi-steady-state period (about 0.5-0.6 mg/L N). Turbidity levels were low (<0.4 NTU) in all of the sulfur columns.

## DISCUSSION

Based on the Set#1 and Set#2 experiments for the organic substrates, alfalfa, newspaper, sawdust, wheat straw, and wood chips all appeared to be efficient electron donors and carbon sources for the removal of nitrate from stormwater runoff. However, it is also critical that the effluent water quality leaving the bioretention basin not be diminished compared to the influent and that the nitrate nitrogen removal from the system occurs via denitrification. Based on these criteria, the newspaper and wood chips are the best candidates, as they provide better effluent quality and total nitrogen removal than the other organic substrates. In the alfalfa and wheat straw systems, both of which had relatively substantial TKN in the column effluent, the nitrate was essentially completely removed from the pore water by the 20 cm height and there was qualitative evidence that sulfate reduction was occurring. One possible explanation for the high effluent TKN is that alfalfa and wheat straw have a lower C:N ratio than sawdust, wood chips, and newsprint (Rynk, 1992). Therefore, it is possible that more ammonification occurred in the alfalfa and wheat straw systems, resulting in increased TKN. It is also known that some microorganisms, including sulfate-reducing bacteria (Hansen, 1994), can reduce nitrate to ammonia in a dissimilative process, and it is possible that this is the source of the TKN in the effluent. This microbial process has been observed to be favored in anaerobic environments when carbon availability is high relative to nitrate availability (Tiedje et al., 1982), as was the case in these relatively short-term column systems. Dissimilatory reduction of nitrate to ammonia is an undesirable process in bioretention because nitrogen is conserved. This is a challenge in engineering bioretention basins for denitrification because of the relatively low nitrate levels, coupled with the need to provide suitable quantities of electron donor/carbon source to sustain the system for extended periods; however, this problem should decrease with time.

The results in Set#3 with the sulfur systems are interesting. Although the same mass of sulfur was added to all three columns, and sufficient buffering capacity was present in all three cases, significantly better nitrate removal occurred in the column with the small sulfur particles/limestone. This is probably a result of the increased number of sulfur particles and the increased surface area of the sulfur available per unit volume of reactor with the smaller sulfur particles. Thus, with the smaller particles, more surface area was available for contact with the nitrate-laden water, and for growth of the denitrifying microorganisms (Liu, 1992, referenced in Zhang and Shan, 1999). It is possible that with longer hydraulic retention times, the large sulfur particle systems would demonstrate improved nitrate removal efficiency (e.g., Koenig and Liu, 1996). Based on this evaluation, the small sulfur/limestone combination appears to be a good candidate system, although there is some concern at this point that relatively high levels of nitrogen may be leaving the system in the form of nitrite. This is being further investigated. Accumulation of nitrite is a characteristic of the chemolithotrophic denitrifying bacterium *Thiobacillus denitificans* (Baalsrud and Baalsrud, 1954). It may be that nitrite concentration levels can be decreased with longer residence times (e.g., Sikora and Keeney, 1976).

One interesting finding from these experiments is that a suitable inoculum was provided in all cases by the settled supernatant of a secondary effluent sample. For example, in the case of the

organic substrates, which are all complex, cellulose-rich, carbon sources, no steps were taken to select for a cellulose-degrading inoculum. In addition, in the case of sulfur, a sufficient inoculum of chemolithotrophic denitrifying bacteria was provided in the secondary effluent. This 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)

## CONCLUSIONS

Based on the experiments performed, excellent nitrate removal from synthetic stormwater runoff was observed in anoxic sand-packed columns containing alfalfa, newspaper, wheat straw, wood chips, and sawdust. However, based on total nitrogen removal and other water quality characteristics, newspaper and wood chips are the best candidates out of these sets for providing the electron donor/carbon source in bioretention basins engineered for nitrate removal. These substrates are also attractive for other reasons as well. For example, they are both waste products that are readily available in many areas. Furthermore, these are both cellulose-rich substrates, and cellulose is an abundant renewable resource.

The results with the sulfur and sulfur/limestone systems indicate that sulfur also holds promise as a electron donor for denitrification in engineered bioretention, in particular, with small sulfur particle sizes. Importantly, as discussed by others (Zhang and Shan, 1999), sulfur is also a relatively inexpensive resource (\$0.018/kg; \$16/ton).

The next stage in this work includes the optimization of the anoxic zone (e.g., sizing, porous medium). This will be performed using the electron donors that gave the best nitrate removal efficiency and effluent quality in the experiments reported here: newspaper, wood chips, and small sulfur particles/limestone. In addition, the performance of the optimized system will be evaluated under conditions of intermittent loadings, such as are expected in the field. This is a unique challenge of bioretention that distinguishes it from many other engineered systems for biological denitrification.

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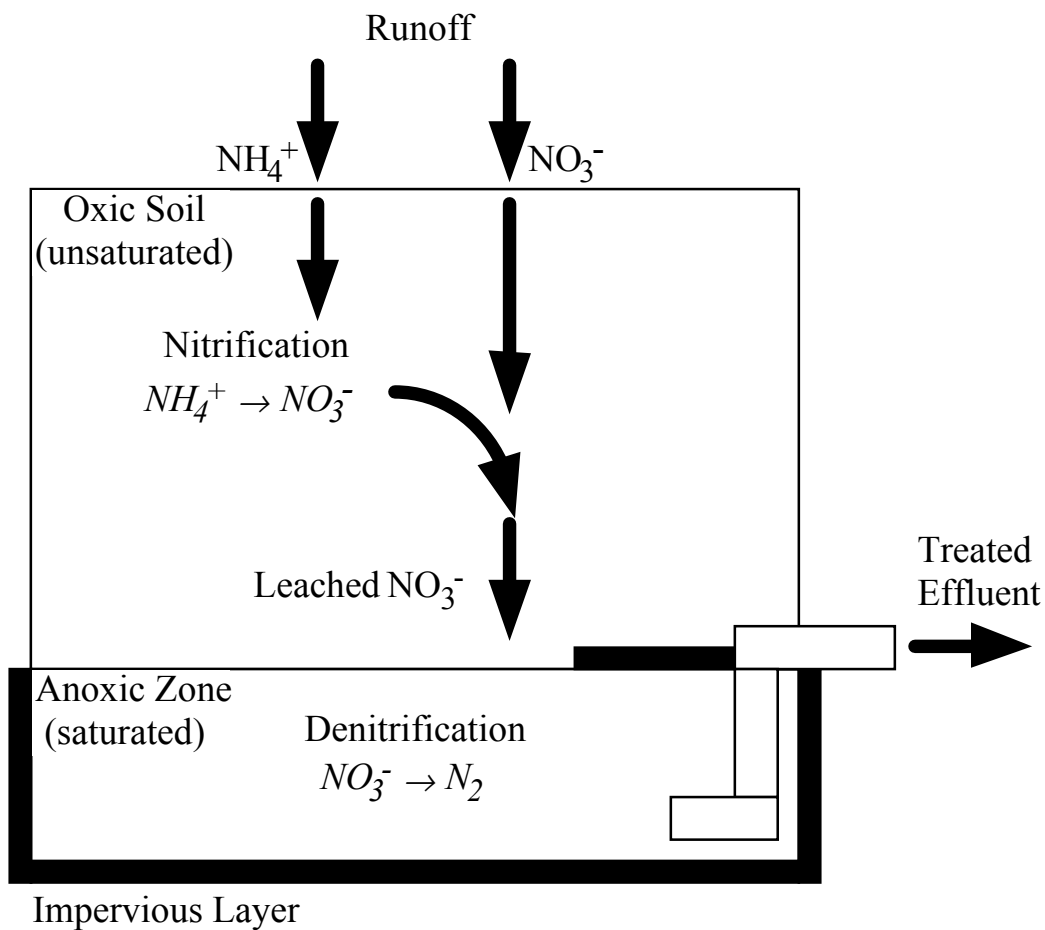
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Figure 1. Diagram of Modified Bioretention for Denitrification.



**Figure 2. Average Quasi-Steady-State Nitrate Removal (%): (a) Set #1 Data, (b) Set #2 Data, and (c) Set #3 Data. Error Bars Represent  $\pm$  One Standard Deviation.**

