Biochar-Amended Modified Bioretention Systems for Livestock Runoff Nutrient Management

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Florida is ranked thirteenth in the United States for cow inventory, providing more than 1 mil metric tons of milk and generating approximately 133,000 kg/year of nutrients (nitrogen [N] and phosphorus [P], USDA-NASS 2016). Livestock operations are a major nonpoint source of pollution to fresh and marine surface waters, groundwater, and springs in Florida.

Improper management of cattle manure contributes to eutrophication, excessive growth of nuisance and harmful algal blooms, fish kills, economic losses, and nitrate (NO_3^-) contamination of drinking water supplies.

The most common livestock waste management strategy in the state is treatment in settling basins or lagoons, followed by agricultural irrigation or direct discharge to surface waters (Prasad et al., 2014); however, these systems are inadequate for nutrient management. For example, a study of waste lagoons at nine dairy farms in north Florida found dissolved total ammonia nitrogen (TAN) concentrations ranging from 22 to 230 mg/l, with a median of 160 mg/l.

The Florida Watershed Restoration Act (FWRA) established both structural and nonstructural best management practices (BMPs) for livestock operations. The FWRA guidelines require systematic waste collection and BMP implementation, especially in the Lake Okeechobee drainage basin. Alternative BMPs for managing runoff from livestock waste include constructed wetlands, vegetative buffer strips, and bioretention systems (Mantovi et al., 2003; Giri et al., 2010). Among these systems, bioretention is a promising technology for nutrient management (Mahmoud et al., 2019; Ergas et al., 2010).

Conventional bioretention systems include a gravel drainage layer, engineered sand filtration medium layer, a planted zone with topsoil and mulch, and an optional underdrain pipe (Figure 1a). Nitrogen removal in these systems relies on:

- Plant uptake
- Filtration of N-containing solids
- Adsorption of NH_4^+ to negatively charged sites in the filtration medium
- Microbial N-species transformations of
  - ammonification (dissolved organic N [DON] → NH_4^+),
  - nitrification ($NH_4^+ \rightarrow NO_3^-$) in aerobic zones and
  - denitrification ($NO_3^- \rightarrow N_2$) in anoxic zones

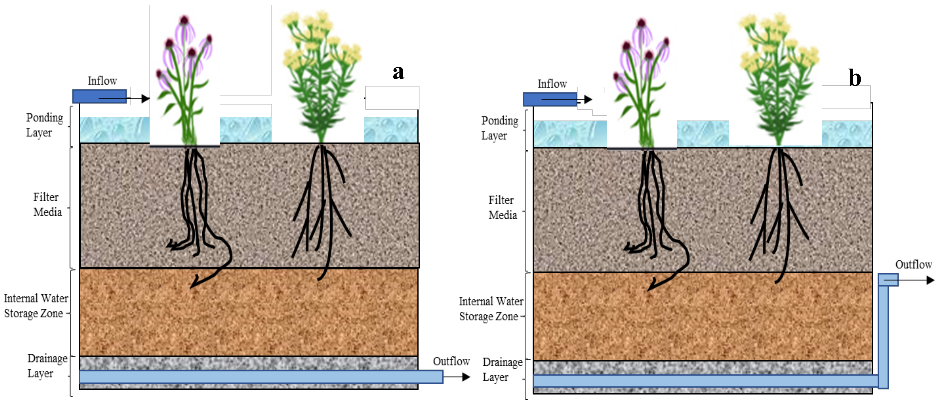

Figure 1. Schematic of two different bioretention systems: (a) conventional and (b) modified.

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In conventional bioretention systems, nitrification is promoted in the aerobic filter media layer; however, total nitrogen (TN) removal is typically low because the systems lack the conditions needed for denitrification (Li et al., 2014); therefore, modified bioretention systems have been developed (Figure 1b) that include an internal water storage zone (IWSZ), with a slow-release solid electron donor, such as wood chips, to promote denitrification (Lopez-Ponnada et al., 2020).

Although modified bioretention systems achieve high TN removals in studies with urban runoff, limited TN removal was observed in prior studies treating dairy farm runoff (Ergas et al., 2010). Dairy runoff has high DON and TAN concentrations compared with urban runoff. During storm events, these pollutants are transported through the bioretention media with the runoff and are not retained long enough for complete ammonification and nitrification; therefore, research should be carried out to overcome these limitations by amending sand-based bioretention media with adsorbent materials that have a high adsorption capacity for DON and TAN. One of the most promising low-cost adsorbent materials for this purpose is biochar (Suliman et al., 2016; Laird et al., 2010; Rahman et al., 2020).

Biochar is the byproduct of pyrolysis of waste organic materials, such as wood waste, rice hulls, grasses, or manure, at temperatures

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between 300 and 1000°C in an oxygen-limited environment. Properties of biochar include a high specific surface area (SA), cation exchange capacity (CEC), porosity, and water-holding capacity. Biochar has been widely used as an agricultural soil amendment (Laird et al., 2010) and for water treatment (Mukherjee et al., 2011). Several prior studies showed that amendment of bioretention media with biochar improved their performance for treatment of urban runoff (Tian et al., 2016; Afrooz et al., 2017; Rahman et al., 2020). The high SA and CEC of biochar help to retain DON and NH_4^+, allowing a longer residence time for microbial transformations (Tian et al., 2016). In addition, the higher water and nutrient retention capacity of biochar-amended bioretention media enhances microbial activity and plant growth.

The overall goal of this research is to understand N removal mechanisms and develop guidelines for amending modified bioretention systems, with biochar for treatment of dairy runoff. Four pilot-scale modified bioretention systems were set up in the botanical gardens at the University of South Florida (USF), with and without biochar, and with and without plants. The systems were operated with semisynthetic dairy runoff and monitored for N-species and organic carbon transformations.

Materials and Methods

Dairy Runoff Preparation

Fresh liquid dairy manure was collected from South Tampa Farm in Tampa. Manure was mixed with stormwater from a stormwater pond on the USF campus in a 200-L tank and allowed to settle overnight. Supernatant was screened through a 0.25 mm mesh, mixed with additional pond water (60 percent supernatant/40 percent pond water) and stored in a 250-L rain barrel. Target concentrations of N-species and *E. coli* were 35 mg/l NH_4^+-N, 1 mg/l NO_3^--N, 45 mg/l DON, and 1x106 colony-forming units (CFU) *E. coli*/100 ml, which was similar to livestock runoff composition in prior studies (Ergas et al., 2010; Hu et al., 2011; Andrews, 1992).

Porous Media

Detailed information on the sand and biochar used in this study was published previously (Rahman et al., 2020). Briefly, masonry sand, with a hydraulic conductivity of 13.2 cm/hour, was purchased from Seffner Rock and Gravel in Tampa. Biochar was generously donated by Biochar Supreme (Loveland, Colo.). Physicochemical properties of biochar, including SA, CEC, pore volume, bulk density, and porosity are presented in the results section.

Modified Bioretention Systems

Four modified bioretention systems were constructed (Figure 2):

- Sand media (S)
- Sand media with plants (SP)
- Biochar-amended sand media (B)
- Biochar-amended sand media with plants (BP)

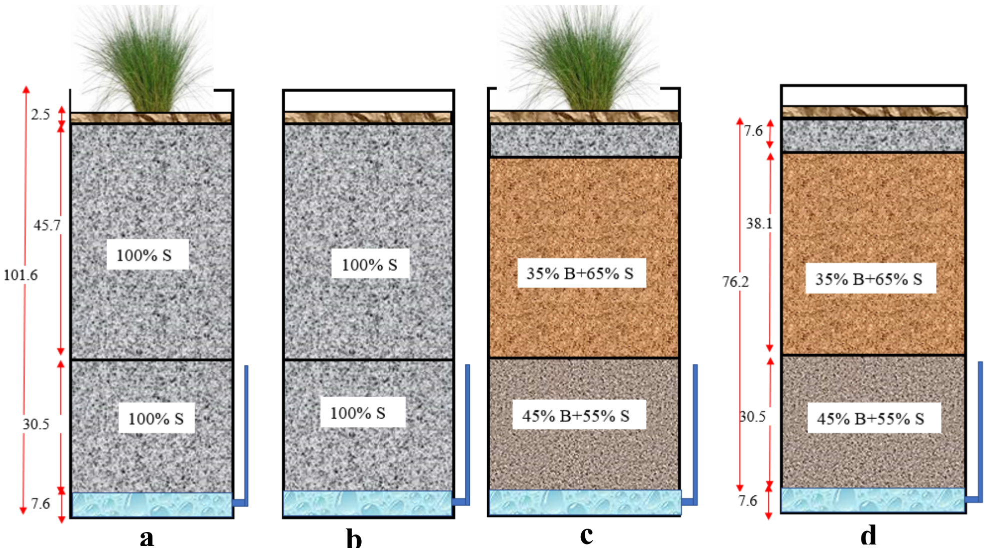

Figure 2. Cross-sectional diagrams of (a) sand modified bioretention cell with plants (SP), (b) sand modified bioretention cell (S), (c) biochar-amended sand modified bioretention cell with plants (BP), and (d) biochar-amended sand modified bioretention cell (B). Units are in cm.

The total depth of each bioretention system was 102 cm. From the bottom there was:

- 7.6 cm downgraded white river gravel (3/4 in.)
- 30.5 cm IWSZ
- 45.7 cm filter medium
- 2.5 cm gravel layer (½ in.)
- 15.2 cm free board as a ponding layer at top

A filter fabric was placed in between the drainage layer and IWSZ layer to avoid washout of fine particles from the system. A perforated polyvinyl chloride (PVC) underdrain pipe, with an upturned outlet elbow, was used to create an IWSZ. Note that the IWSZ did not contain wood chips due to the high dissolved organic carbon (DOC) content (737±200 mg/l) of the dairy runoff. For the B and BP systems, the biochar fraction was 35 percent in the filtration media and 45 percent in the IWSZ.

The SP and BP systems were planted with *Muhlenbergia* (Muhly grass), which was purchased from a local nursery. Muhly grass is a native Florida perennial that attracts wildlife and has favorable light and moisture requirements, growth rate, and mature plant height and spread. After planting, the systems were watered periodically for three months for the growth of roots and biomass before performing dairy runoff experiments.

Experimental Design

Dairy runoff experiments reported in this article were performed at a hydraulic loading rate (HLR) of 0.98 cm/minute (flow rate of 222 ml/minute). This HLR was selected by assuming a 0.25-in. rainfall event over four hours and that the bioretention surface occupied 5 percent of the drainage area. All experiments reported were carried out at a seven-day antecedent dry period (ADP), which is the time between two successive runoff events.

Water Quality Analysis

Influent and effluent samples were analyzed using *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2018). The TAN and NOx (NO_3^--N+NO_2^--N) were measured using a Timberline Ammonia Analyzer (Timberline Instruments; Boulder, Colo.). The TN and total organic carbon (TOC) were measured with a Shimadzu TOC-V CSH TOC/TN Analyzer (Shimadzu Scientific Instruments; Columbia, Md.). The DON was calculated by subtracting total inorganic nitrogen (TIN = TAN+NOx) from TN. Method detection limits for TAN, NOx, TN, and TOC were 0.05 mg/l, 0.05 mg/l, 0.03 mg/l, and 0.11 mg/l, respectively. The pH and conductivity were measured using a multiparameter meter and calibrated probes. Effluent flow rates were measured volumetrically to assess the hydraulic performance.

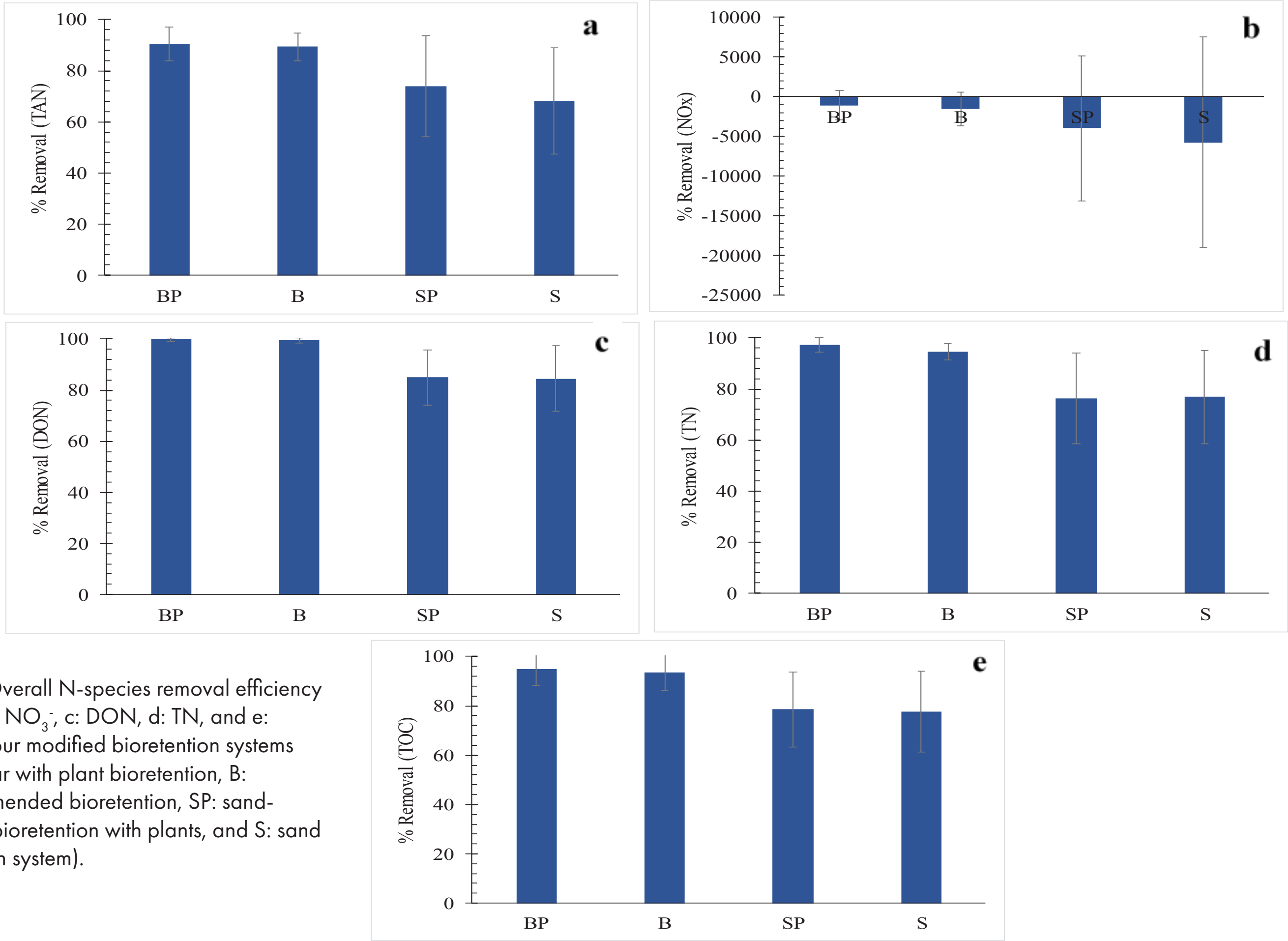

Figure 3. Overall N-species removal efficiency (a: TAN, b: NO_3^-, c: DON, d: TN, and e: TOC) for four modified bioretention systems (BP: biochar with plant bioretention, B: biochar-amended bioretention, SP: sand-amended bioretention with plants, and S: sand bioretention system).

Results and Discussion

Biochar Characteristics

The feedstock used for biochar production was shredded wood chips, which was pyrolyzed at ~900ºC. Analysis of the biochar elemental composition showed that it was composed of 80 percent carbon, 0.4 percent nitrogen, and 9.6 percent oxygen. Due to its high ash content (5.8 percent), the biochar had a high pH (10.12±0.2), which is favorable for nitrification. The biochar had high surface area (537±60.15 m^2/g) and CEC (10.57 cmol/kg), which favors DON and NH_4^+ adsorption. It also had a low bulk density (0.10 g/cm^3) and high water holding capacity (874 gH_2O/100 g biochar). The high pore volume 0.36 cm^3/g included 0.19 cm^3/g micropore volume and 0.15 cm^3/g mesopore volume.

Overall Performance of Modified Systems

Average influent concentrations of N-species in semisynthetic dairy runoff were:

- TAN: 26.1±9.5 mg/l
- NOx: 0.063±0.04 mg/l
- DON: 42.7±18.1 mg/l
- TN: 68.8±19.2 mg/l

Relatively higher influent TOC concentrations (737.5±199.4) were observed, compared to prior studies. The N-species removal efficiencies for the four modified bioretention systems are shown in Figure 3. Higher TAN removal was observed in biochar-amended systems, compared with unamended systems, with the highest (90.6 percent±6.5) and lowest (68.2 percent±20.8) removal efficiencies observed in BP and S systems, respectively. The high CEC of biochar likely resulted in TAN retention, allowing more time for nitrification when compared with the unamended systems. Lower average effluent NOx concentrations were observed for biochar-amended systems (0.72-1.18 mg/l) than for sand systems (2.09-3.15 mg/l). As influent dairy runoff had high organic carbon content, it was hypothesized that TOC retained in the IWSZ due to adsorption onto biochar was utilized as an electron donor for denitrification. In S and SP, the lack of adsorbed TOC in the IWSZ likely limited denitrification.

The DON removal largely depends on either adsorption or ammonification, followed by nitrification. As biochar enhances soil microbial activity due to its high surface area and porosity (Anderson et al., 2011), enhanced adsorption and ammonification resulted in higher DON (<99 percent) removal in B and BP. Average effluent DON concentrations for biochar-amended bioretention systems were 0.07-0.16 mg/l, which was lower than unamended systems (5.03-5.67 mg/l). The N removal was limited in S (76.89 percent±18.2) and SP (76.26 percent±17.72) bioretention systems compared to B and BP due to low TAN and DON adsorption and limited denitrification.

Pollutant Breakthrough During Storm Events

Effluent TAN and TN concentration profiles over time for the four bioretention systems for a four-and-a-half-hour storm event are shown in Figure 4. As discuss previously, TAN removal mainly depends on media adsorption, nitrification, and plant uptake. During the dry days between successive runoff events, pore water was replaced by oxygen in the unsaturated zone of the bioretention systems; thus, the adsorbed TAN was nitrified to NO_3^-, resulting in low effluent TAN concentrations. During the first 90 minutes, both B and BP had low average effluent TAN concentrations (0.93-0.97 mg/l) compared with S (17.3 mg/l) and SP (2.02 mg/l).

Ergas et al. (2010) also observed limited nitrification in modified sand bioretention systems treating dairy runoff that included a sand-based unsaturated zone. Once the pore water in the IWSZ was flushed from the systems (90-270 minutes), effluent TAN concentrations in SP

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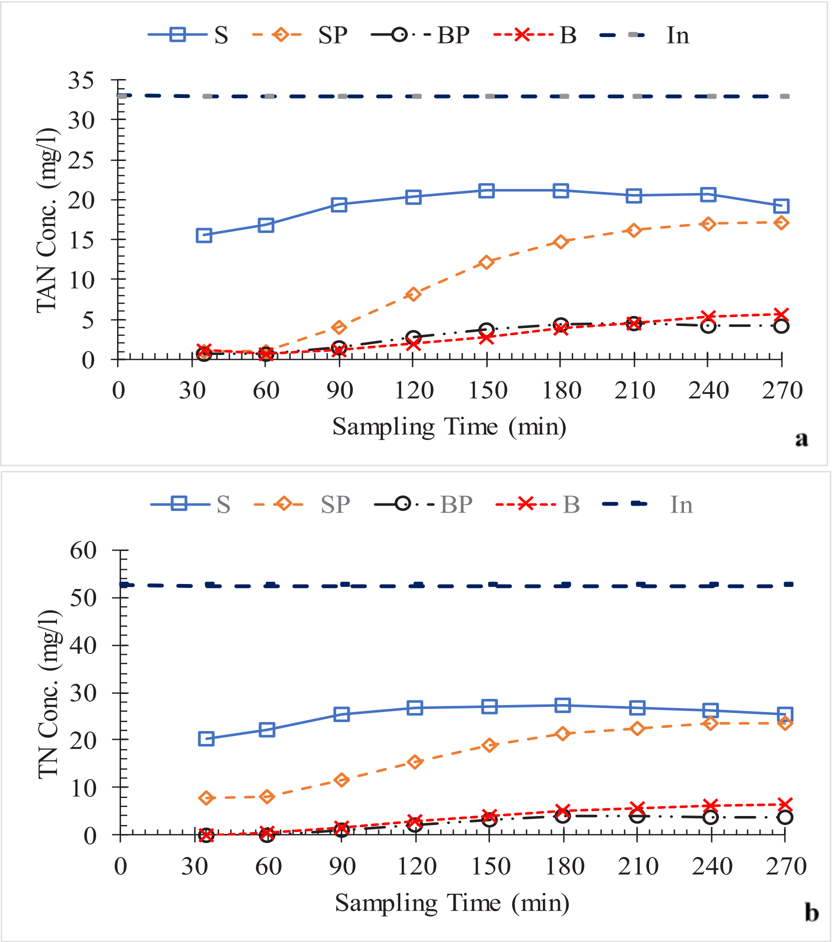

Figure 4. Pollutant breakthrough curve of (a) TAN and (b) TN for four modified bioretention systems considering 222 ml/minute flow rate for four-and-a-half hours of dairy runoff experiment.

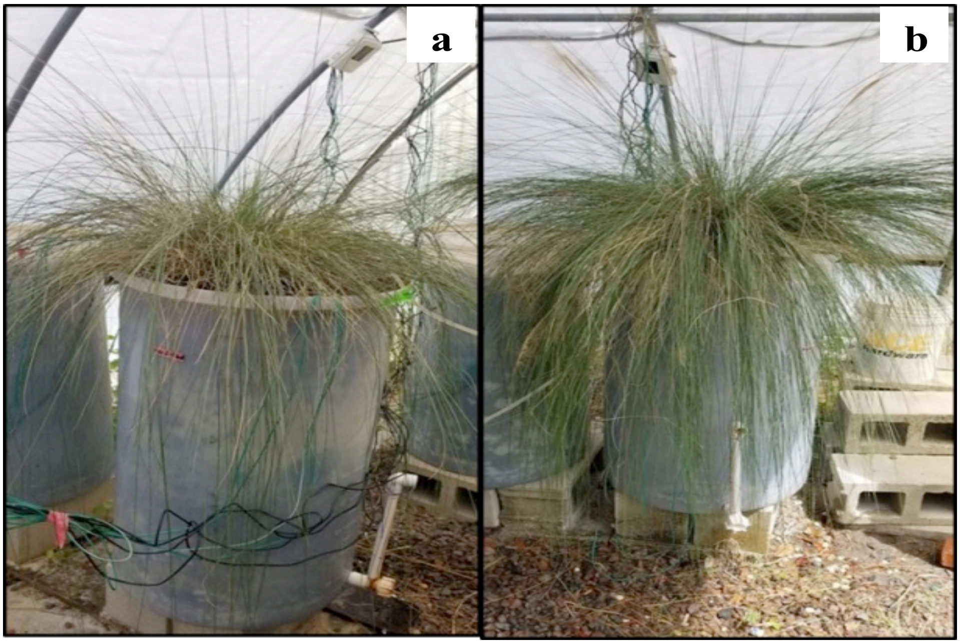

Figure 5: Two modified bioretention systems: (a) sand with plant, and (b) biochar with plant after twelve runoff experiments.

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increased and were almost similar to S by the end of the experiment. The saturated condition that developed in the aerobic layer for the last hour of the runoff experiments due to water accumulation in the ponding zone resulted in limited nitrification, and therefore, higher effluent TAN concentrations were observed in S and SP. The B and BP systems, however, maintained relatively low effluent TAN concentrations throughout the experiment due to the high affinity of biochar to adsorb positively charged NH_4^+ ions.

Effluent TN concentrations for B and BP systems followed the same breakthrough trends. During the ADP between two rain events, adsorbed TOC was bioavailable in the IWSZ and denitrifying bacteria utilized the desorbed TOC for denitrification; hence, in B and BP during the first 90 minutes, effluent TN concentrations were low and then slowly increased until the end of the experiment. The S and SP had higher effluent TN concentrations from the beginning of the experiment, indicating that limited TOC availability in the IWSZ resulted in lower NO_3^- removal. In addition, DON adsorption and ammonification were low (data not shown).

Effect of Plants

The effect of plants on N-species removal for bioretention systems, with or without plants, can be seen in Figures 3 and 4. Both systems with plants achieved higher N-species removal efficiencies, compared to systems without plants. Prior research with planted and unplanted bioretention systems also showed that both TAN and NO_3^- are taken up by plants (Zhang et al., 2011; Lea et al., 2001). Denitrification is also favored by enhanced microbial activity and the availability of organic carbon in the rhizosphere due to the presence of root exudates and sloughed-off root tissues (Havlin, 2013).

As shown in Figure 5, after 10 months of operation, the biochar-amended BP had higher biomass growth compared to SP. It has been shown in prior agricultural studies (Karhu et al., 2011) that biochar helps to promote plant growth by retaining moisture and nutrients and stimulating the activity of beneficial microorganisms. Future studies will be carried out to quantify the plant biomass and root growth after dismantling the bioretention systems.

Conclusions

Nitrogen removal mechanisms were investigated in modified bioretention systems, with and without biochar amendment and with and without plants. Addition of biochar enhanced the TAN and DON removal during infiltration. Higher TOC adsorption in the IWSZ in systems with biochar favored denitrification, resulting in higher TN removal. Due to high moisture and nutrient retention, better plant growth was observed in the biochar-amended system with plants, which also influences N-species removal. Current research is focused on investigating N-species and *E. coli* removal in these systems under varying HLR and ADP.

Acknowledgments

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