

**ENGINEERED BIORETENTION DESIGN FOR CONTROL OF NUTRIENTS AND
PATHOGENS FROM AGRICULTURAL RUNOFF**

Final Report

For

Florida Department of Agriculture and Consumer Services (FDACS)

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LIST OF ACRONYMS AND ABBREVIATIONS

ADPs	Antecedent Dry Periods
BC1	Biochar 1
BC2	Biochar 2
BD	Bulk Density
BMPs	Best Management Practices
CEC	Cation Exchange Capacity
DON	Dissolved Organic Nitrogen (DON)
DOC	Dissolved Organic Carbon (DOC)
<i>E. coli</i>	Escherichia Coli
EC	Electrical Conductivity
GSD	Grain Size Distribution (GSD),
HLR	Hydraulic Loading Rate
HRT	Hydraulic Residence Time
IWSZ	Internal Water Storage Zone
K	Hydraulic Conductivity
MC	Moisture Content
N	Nitrogen
P	Phosphorous
n	Porosity
PSD	Pore Size Distribution (PSD).
S	Sand
SBC1	Sand With Biochar 1
SBC2	Sand With Biochar 2
SA	Surface Area
TAN	Total Ammonia Nitrogen
TN	Total Nitrogen
FWRA	Florida Watershed Restoration Act
FIB	Fecal Indicator Bacteria
WHC	Water Holding Capacity
SSW	Synthetic Stormwater

INTRODUCTION

Background

Florida is ranked 13th in the US for cow inventory, providing >1 million metric tons of milk (USDA-NASS 2016). Livestock operations are a major non-point source of nutrients (nitrogen [N] and phosphorus [P]) in fresh and marine waters, groundwater, and springs in Florida. Improper management of cattle manure contributes to eutrophication, resulting in harmful algal blooms, fish kills, economic losses and nitrate (NO_3^-) contamination of drinking water supplies. Runoff from cattle and dairy farms has also been shown to contaminate surface water, groundwater and crops with fecal indicator bacteria (FIB), such as *E. coli* (Lynch et al. 2009; Heiman et al., 2015).

In Florida, livestock runoff is managed by 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 ranged from 22 to 230 mg/l, with a median concentration of 160 mg/l. The Florida Watershed Restoration Act (FWRA) established both structural and non-structural best management practices (BMPs) for livestock operations. FWRA guidelines require systematic waste collection and BMP implementation, especially in Lake Okeechobee drainage basin. Alternative BMPs for managing runoff from livestock waste include constructed wetlands, vegetative buffer strips and bioretention systems (Ioannidou et al., 2020; Koelsch et al., 2006). Among these systems, bioretention is a promising technology for management of nutrients and FIB from livestock waste (Mahmoud et al., 2019; Ergas et al., 2010).

Conventional bioretention systems include a gravel drainage layer, engineered filtration medium, a planted zone with topsoil and mulch and an optional underdrain pipe (Figure 1a). In conventional bioretention systems, nitrification is promoted in the aerobic filter medium. However, total nitrogen (TN) removal is typically low because the systems lack conditions needed for denitrification (Li et al., 2014). Therefore, modified bioretention systems have been developed (Figure 1b) with an internal water storage zone (IWSZ) that may include a slow-release solid electron donor, such as wood chips, to promote denitrification (Lopez-Ponnada et al., 2020). The anoxic conditions in the IWSZ have also been shown to enhance *E. coli* removal (Ergas et al., 2010). Although these systems work well for treatment of contaminants in urban runoff, the high

concentrations of TAN, dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in dairy runoff present a challenge for these systems. During storm events, these pollutants pass through the bioretention media rapidly with the runoff, and are not retained long enough for complete biodegradation.

Biochar is a by-product of organic waste materials, such as wood chips, pyrolyzed at high temperature under oxygen limited conditions. The type of feedstock, production process and pyrolysis temperature are key factors that influence biochar properties. In general, biochar has a high cation exchange capacity (CEC), surface area (SA), porosity (n), pore size distribution (PSD), hydrophobicity, and ash content. These properties improve nutrient retention and water holding capacity (WHC) of biochar which aids plant growth. Although prior studies showed that biochar enhances the performance of bioretention systems treating urban runoff (Mohanty et al. 2014; Yao et al., 2012), this is the first study to investigate the use of biochar in bioretention systems treating runoff from dairy farms.

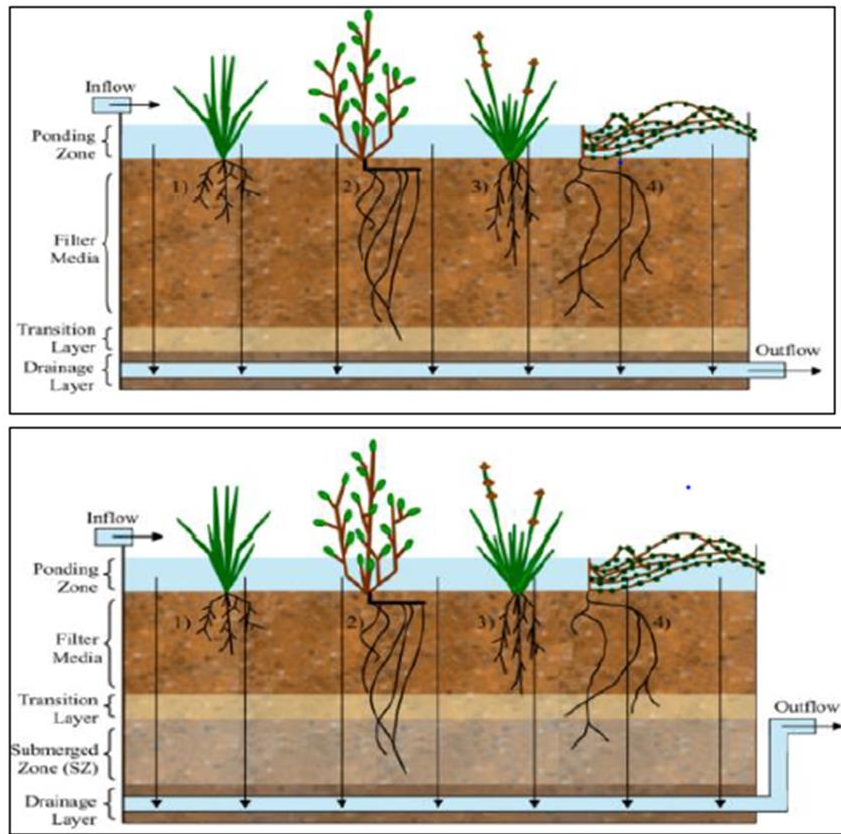


Figure 1: Schematics of bioretention systems: a) conventional and b) modified.

Objectives

The overall goal of this research was to understand total nitrogen (TN) and fecal indicator bacteria (FIB) removal mechanisms in bioretention systems amended with biochar for treatment of dairy runoff. The research was guided by the following questions:

- Are N-species and *E. coli* removals enhanced in the biochar amended bioretention systems compared with conventional sand bioretention systems?
- What are the effects of physicochemical properties of commercial biochars on removal of *E. coli* and N species?
- How do biochar amendment rates impact N-species and *E. coli* removals and hydraulic performance in bioretention systems treating dairy runoff?
- Compared with conventional bioretention, does the addition of an IWSZ and plants improve removal of FIB and TN in biochar amended bioretention systems?

MATERIALS AND METHODS

Experiments were carried out from January 2019 through May 2021 as shown in Table 1.

Table 1: Experimental design showing different deliverables and tasks.

Deliverable	Purpose	Tasks
I	Column studies for selecting biochar	• Physicochemical properties of media materials • Batch adsorption studies • Column studies with and without biochar • Hydraulic aspects of column studies
II	Column studies for selecting biochar amendment rate	• Effect of amendment rate on N-species and <i>E. coli</i> • Effect of antecedent dry period (ADP) • Effect of amendment rate on hydraulic performance

III	Pilot studies investigating effect of IWSZ and plants	• Effect of IWSZ on TN and <i>E. coli</i> removal • Effect of plants on TN and <i>E. coli</i> removal
IV	Hydraulic model	• HYDRUS-1D for simulation of breakthrough curves
V	Research dissemination	• A webinar was held to disseminate research to different stakeholders. • Research was presented at conferences and meetings of professional associations and published in journals. • The research will be the subject of one PhD dissertation.

Experimental Program

Deliverable#1

- Three different sands and two commercial biochars were characterized for pH, hydraulic conductivity (K), bulk density (BD), porosity (n), moisture content (MC), electrical conductivity (EC), grain size distribution (GSD), CEC, surface area (SA) and pore size distribution (PSD).
- Batch experiments were performed in duplicate to evaluate adsorption of NH_4^+ and NO_x by sand, BC1 and BC2 under abiotic (sterile) conditions.
- Three different columns were setup (Figure 2) with: i) sand (S), ii) sand with biochar 1 (SBC1) and iii) sand with biochar 2 (SBC2). The volumetric ratio of sand and biochar was 70:30, which corresponded to 3.10% and 4.75% of biochar by mass, for BC1 and BC2, respectively. Experiments were conducted to investigate N-species transformations and FIB removal with both urban runoff and dairy farm runoff with low and high hydraulic loading rates (HLRs) and varying antecedent dry periods (ADPs).
- Samples from S, SBC1 and SBC2 were collected from the surface, middle (15 cm from the surface) and bottom (30 cm from the surface) of each column to measure the moisture content at ADPs of 7 days and 30 days to observe the moisture retention in the mixtures.

Deliverable#2

- Two columns were setup at 20% and 50% biochar (by volume) with sand. This resulted in biochar mass fractions of 2.2% and 5.7% for SBC-20 and SBC-50, respectively.
- Experiments were conducted to investigate the effect of biochar amendment rate on N-species transformations and FIB removal at varying HLR and ADP.
- Conservative tracer studies were conducted to evaluate the influence of biochar amendment rate on HRT. Each study was carried out in duplicate at a HLR of $0.18 \text{ cm}^3/\text{cm}^2/\text{min}$ and an ADP of 7-days.

Deliverable#3

- Based on the outcomes of Deliverable #1 and #2, a pilot scale study was designed to evaluate the effect of IWSZ and plants on biochar amended bioretention systems for treatment of dairy runoff. Four pilot-scale modified bioretention systems (Figure 3) were constructed: i) sand (S), ii) sand with plants (SP), iii) biochar amended sand (B) and, iv) biochar amended sand with plants (BP).
- Experiments were conducted at a varying HLR and ADPs of 7, 10 and 30 days.

Deliverable#4

- A HYDRUS-1D model was developed and used for the simulation of tracer breakthrough curves to observe the effect of biochar amendment rates on system hydraulics.

Deliverable#5

- A webinar was organized to share the novel bioretention designs, media, plants and their effectiveness in controlling nutrients and FIB in agricultural and urban runoff on October 7th, 2020. Detailed webinar flyer, presentation and attendees' lists are provided in the Appendix.
- The research was disseminated through three journal articles (Rahman et al., 2020a; Rahman et al., 2020b; Rahman et al., 2021a) and two conference papers presented at meetings of professional associations (Rahman et al., 2019a; Rahman et al., 2019b)). An additional manuscript is currently under review for the *Journal of Sustainable Water in the Built Environment* (Rahman et al., 2021b).

- The research will be the subject of one USF Civil & Environmental Engineering PhD dissertation. Titled “Biochar amended bioretention systems for nutrient and fecal indicator bacteria control”.

Media Selection

Three different sands and two commercial biochars were characterized for pH, hydraulic conductivity (K), bulk density (BD), porosity (n), moisture content (MC), electrical conductivity (EC), grain size distribution (GSD), cation exchange capacity (CEC), surface area (SA) and pore size distribution (PSD). The sands were obtained from Seffner Rock & Gravel in Tampa, Florida, USA: i) concrete sand, ii) masonry sand, and iii) local sand. Masonry sand was selected because n, K and BD were consistent with recommended guidelines for the hydraulic loading rates (HLRs) used in this study (Prince George’s County Program and Planning Division, 2007). Two wood derived biochars were acquired from Biochar Supreme (Environmental Ultra, Everson, WA; (BC1)) and Biochar Now (Loveland, CO; (BC2)). Biochar Supreme (BC1) was pyrolyzed at 900–1000 °C and Biochar Now (BC2) was pyrolyzed at 550 °C. Prior to use, biochars were sieved and hand crushed to a particle size between 0.15 mm–1.00 mm to produce homogenous mixture with sand.

Runoff Preparation and Characterization

Urban stormwater runoff was prepared by adding stock solutions of *E. coli* ($\sim 10^6$ CFU/100ml), potassium nitrate (KNO₃) (1 mg/l), ammonium chloride (NH₄Cl) (1 mg/l) and DON (1 mg/l) to filtered local groundwater. Oak leaves collected from University of South Florida were used as source of DOC and DON (Lopez-Ponnada et al., 2020). Briefly, oak leaves were dried and ground to a fine powder using a coffee grinder. Subsequently, 9 gm of ground oak leaves were added to a 1x1 inch mesh bag, sealed and then submerged in 800 ml of DI water overnight. This yielded an oak leaf extract stock solution with approximately 11 mg/l of DON.

A semi-synthetic dairy runoff was prepared using dairy waste and stormwater. Prior to each experiment, fresh dairy manure was collected from South Tampa Farm, Tampa, FL and transported to the University of South Florida’s Environmental Engineering Laboratory. After collection, the manure was diluted with tap water (30% by volume), the solution was allowed to settle overnight, and the supernatant was screened through a 0.25 mm mesh. The influent was prepared by mixing 60% of the screened supernatant with 40% tap water to achieve a target

influent N-species concentration of 45 mg DON/L, 35 mg $\text{NH}_4^+\text{-N/L}$ and 1.0 mg $\text{NO}_x\text{/L}$ ($\text{NO}_x = \text{NO}_2^-\text{-N} + \text{NO}_3^-\text{-N}$). These values were consistent with concentrations observed in field studies of agricultural/feedlot runoff (Ergas et al., 2010.; Andrews et al., 1992).

Bench Scale Columns

Selection of biochar

Three different columns were setup with: i) sand (S), ii) sand with biochar 1 (SBC1) and iii) sand with biochar 2 (SBC2) (Figure 1a). The volumetric ratio of sand and biochar was 70:30, which corresponded to 3.10% and 4.75% of biochar by mass, for BC1 and BC2, respectively. Koflo 2000 ml Calibration Columns (Cary, IL) with 7.2 cm internal diameter and 50 cm height were used for the bench-scale columns. The depth of the media in each column was 30 cm. From the bottom of the column there was: i) steel mesh, ii) 7.62 cm gravel layer (#3/4 downgrade white river gravel, Seffner Rock & Gravel, Tampa, FL), iii) another steel mesh wrapped with geotextile to prevent fines from clogging the gravel, iv) 30 cm of sand or sand amended with biochar and v) 20 cm free board for ponding. SSW was applied to the surface using a peristaltic pump (Masterflex L/S, Cole-Parmer) connected to a feed container.



Figure 2: Three columns were set for the selection of biochar (Left) and two columns were set for performance evaluation of biochar amendment rates (Right).

Biochar amendment rate

Based on Phase I results, biochar 1 was selected for Phase II experiments. Two of the columns described previously were amended with 20% and 50% biochar (by volume) with sand. This

resulted in biochar mass fractions of 2.2% and 5.7% for SBC-20 and SBC-50, respectively. To seed the reactors with established microbial biofilms, the sand for Phase II was recycled from the Phase I sand column.

Pilot Scale Bioretention Systems

Four modified bioretention systems were constructed: i) sand media (S), ii) sand media with plants (SP), iii) biochar amended sand media (B) and iv) biochar amended sand media with plants (BP) (Figure 3). The total depth of each bioretention system was 102 cm. From the bottom there was: i) 7.6 cm white river gravel; ii) 30.5 cm IWSZ; iii) 45.7 cm filter medium; iv) 2.5 cm gravel layer and v) 15.2 cm free board for ponding at the top. A filter fabric was placed between the drainage layer and IWSZ layer to avoid wash out of fine particles from the system. A perforated 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 DOC content (737 ± 200 mg/l) of the dairy runoff. For the B and BP systems, the biochar fraction was 35% in the filtration media and 45% in the IWSZ. 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.

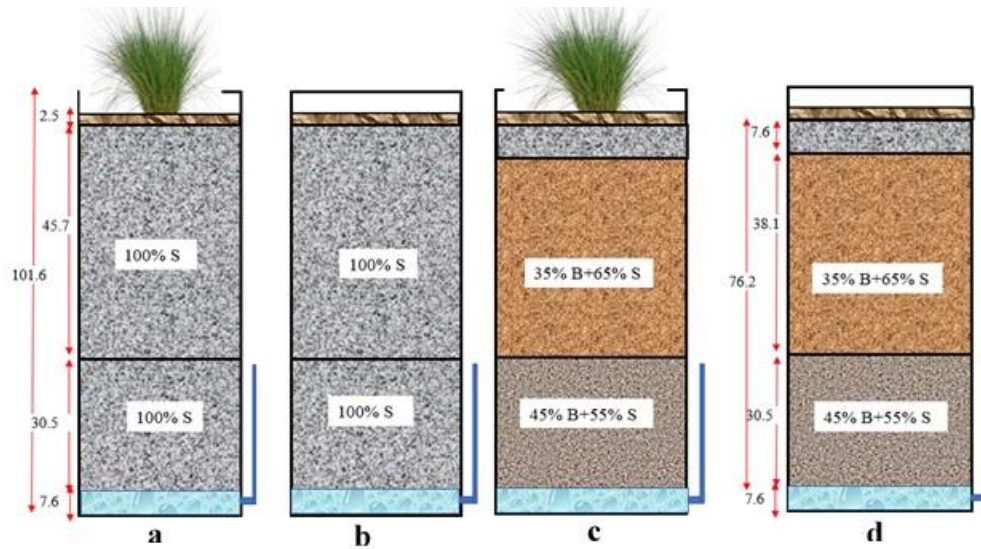


Figure 3: Diagram showing experimental design of pilot study.

Analytical Methods

GSD and MC were measured using ASTM D6913/D6913M–17 and ASTM D2974-87, respectively. Hydraulic conductivity (K) was measured by the Falling Head Test Method (ASTM D5084 – 03). The Ammonium Acetate Method (Chapman, 1965) (Method 9080) was used to measure CEC. SA and pore size distribution were measured using a Quantachrome Instrument (P/N 05061-1.5 Rev a Quantachrome Instruments, AUTOSORB-1, AS1Win Version 1.5X, 2008). SA was measured by N₂ gas adsorption-desorption using the Brunauer-Emmett- Teller (BET) method. Mesopore and micropore size distributions were measured by Barrett, Joyner and Halenda and Horvath-Kawazoe (HK) methods, respectively. A total of 20 adsorption and 20 desorption points were selected for the isotherms and degas temperature was 150 °C for 10 h.

Influent and effluent samples were collected as needed from each system to achieve the project objectives. *Standard Methods* were used for water quality analysis (APHA et al., 2018). USEPA Method 1603 was used for *E. coli* analysis (USEPA, 2014). A multi-parameter meter was used to measure pH and conductivity (*Standard Methods*, 2018; 2510 B). Total ammonia nitrogen (TAN = NH₄⁺-N + NH₃-N) and NO_x (NO_x = NO₂⁻-N + NO₃⁻-N) were measured using a Timberline Ammonia Analyzer (Timberline Instruments, Boulder, CO). Total Nitrogen (TN) and total organic carbon (TOC) were measured with a Shimadzu TOC-V CSH Total Organic Carbon/Total Nitrogen Analyzer (Shimadzu Scientific Instruments, Columbia, MD). DON was calculated by subtracting total inorganic nitrogen (TIN) from TN. The method detection limits for TAN, NO_x, TN and TOC were 0.05mg/L, 0.05mg/L, 0.03 mg/L, and 0.11 mg/L, respectively. Concentrations of anions and cations in the influent and effluent were measured using a Metrohm Peak 850 Professional AnCat ion chromatography (IC) system (Metrohm Inc., Switzerland). Samples of media material were collected for moisture content analysis (ASTM D2216).

RESULTS AND DISCUSSION

Deliverable#1

Media Properties

Physicochemical properties of the biochars are shown in Table 2. Elemental analysis revealed that BC1 had lower molar ratios of H/C, O/C and O+N/C than BC2, indicating that BC2 could be more interactive with polar compounds than BC1. BC1 had a higher pH than BC2, most likely because of the higher heating rate during pyrolysis and increased mineral ash content. Table 2 also shows that BC2 had a higher CEC than BC1. BC1 had almost four times more SA than BC2. Although both biochars were produced from wood chips, significant differences in SA can be attributed to increased carbonization at higher pyrolysis temperature for BC1.

Batch Adsorption Studies

Abiotic batch experiment results for three media materials (S, BC1 and BC2) for NH_4^+ and NO_3^- adsorption are shown in Figure 4. Significantly higher NH_4^+ adsorption was observed for biochar (3.5 mg/g) than sand (0.05 mg/g) due to higher CEC. However, differences between BC1 and BC2 were not significant. In contrast, both biochar and sand had very low NO_3^- adsorption capacity. BC1 had slightly higher NO_3^- adsorption (0.3 mg/g) compared with the other materials (~0.23 mg/g).

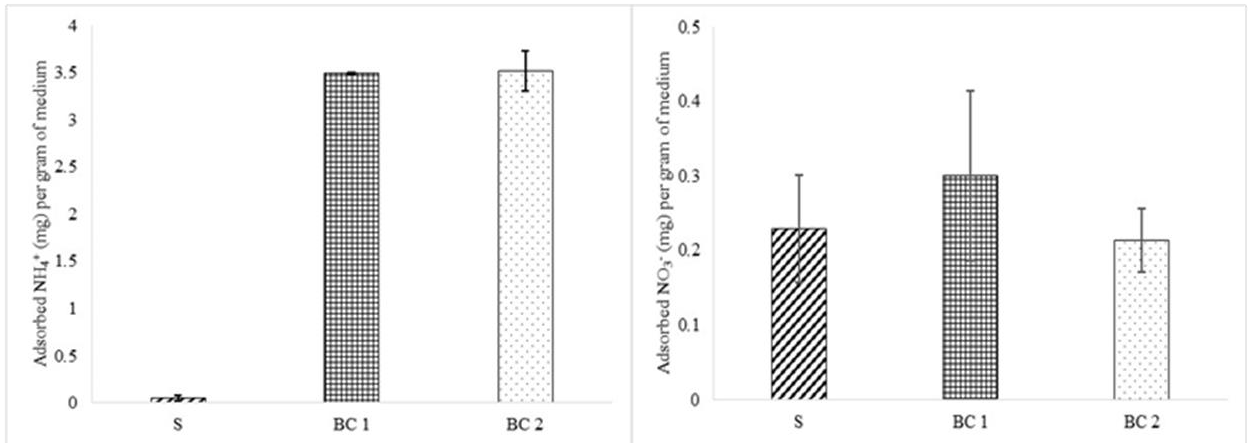


Figure 4: Batch experiment of NH_4^+ and NO_3^- adsorption for Sand (S), Biochar 1 (BC 1) and Biochar 2 (BC 2).

Bench-Scale Columns: Water Quality

Overall removal performances for TAN, NO_x , DON, TN, DOC and *E. coli* for 18 urban stormwater experiments are shown in Table 3. Both biochar amended columns had significantly

higher TAN removals compared with sand ($p < 0.05$), indicating that biochar amendment enhanced NH_4^+ adsorption. Although BC2 had a higher CEC, TAN mass removals for biochar amended columns were not significantly different from each other ($p < 0.05$). The results indicate that 30% (v/v) (5% w/w) biochar amendment is adequate for TAN removal from urban stormwater.

No significant differences were observed for overall NO_x , DON or TN mass removals between columns. However, a slightly higher effluent NO_x mass was observed for the biochar amended columns compared with the sand column (Table 3). This was likely due to the lower hydraulic conductivity (K) of the biochar amended columns, which reduces the flow velocity and increases HRT. The longer HRT provides greater opportunity for nitrifying bacteria to convert TAN to NO_x . TAN adsorption by biochar also provides opportunities for nitrification during the ADP. Biochar addition also increased effluent pH (biochar: 9.5-10.2, sand: 7.9), which favors nitrification.

DOC removals were significantly higher ($p < 0.05$) in biochar amended columns than sand. Significantly higher DOC removal was observed in SBC1 than SBC2, most likely due to greater SA and pore volume of BC1. DON removal mainly occurs due to surface adsorption and ammonification; however, no significant differences were observed in DON removal between the three columns.

E. coli removals were significantly different in all three columns ($p < 0.05$). Throughout the course of experiments, effluent *E. coli* concentrations from SBC1 were below detection limits (< 30 CFU/100 ml), therefore log removals could not be calculated. SBC2 had an order of magnitude higher *E. coli* removal than S (4.23 $\pm$ 0.61 vs. 3.43 $\pm$ 1.05 log removal). The higher SA of SBC1 was the most likely reason for the increased *E. coli* attachment compared with SBC2 or sand.

Bench-Scale Columns: Hydraulics

Moisture content (MC) for the three columns (S, SBC1 and SBC2) for 7- and 30-day ADPs are shown in Figure 5. As expected, as ADPs increased, MC of all columns decreased due to drainage and evaporation. Evaporation and drainage increase air and oxygen availability in pore space, thus promoting nitrification of adsorbed NH_4^+ . MC data also revealed that saturated conditions prevailed toward the bottom of the biochar amended columns compared to the sand

column, which persisted for several days (ADP7), thus promoting denitrification at the bottom of the column (Figure 5). Most likely, higher fraction of micropores in SBC1 retained more infiltrated water compared to meso- or macro-pores due to capillary, thus providing a higher MC even for an ADP of 30-days.

Figure 6 shows the average percent water retention for eighteen simulated storm events for the three columns. An overall comparison shows that biochar increased water retention compared with sand. The average water retention was 0.036, 0.059 and 0.053 g of infiltrated stormwater per gram of S, SBC1 and SBC2 media, respectively. A comparison of SBC1 and SBC2 (Figure 6b) showed that BC1 had a higher water holding capacity (0.79 g of infiltrated water/g of biochar) compared with BC2 (0.37 g of infiltrated water/g of biochar), resulting in saturated media conditions. The higher pyrolysis temperature of BC1 increased micropores fraction and water holding capacity compared with BC2.

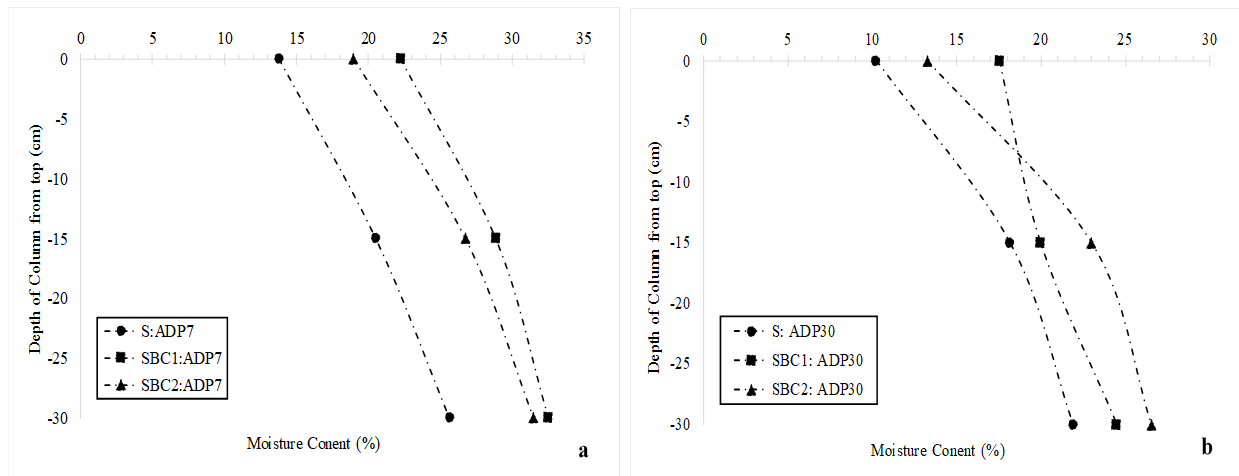


Figure 5: Moisture content at three different depths (i. surface, ii. mid depth: 15 cm from the top surface and iii. bottom depth: 30 cm from the surface) of the three columns (i. Sand, ii. SBC1 and iii. SBC2) for 7- and 30-days ADPs.

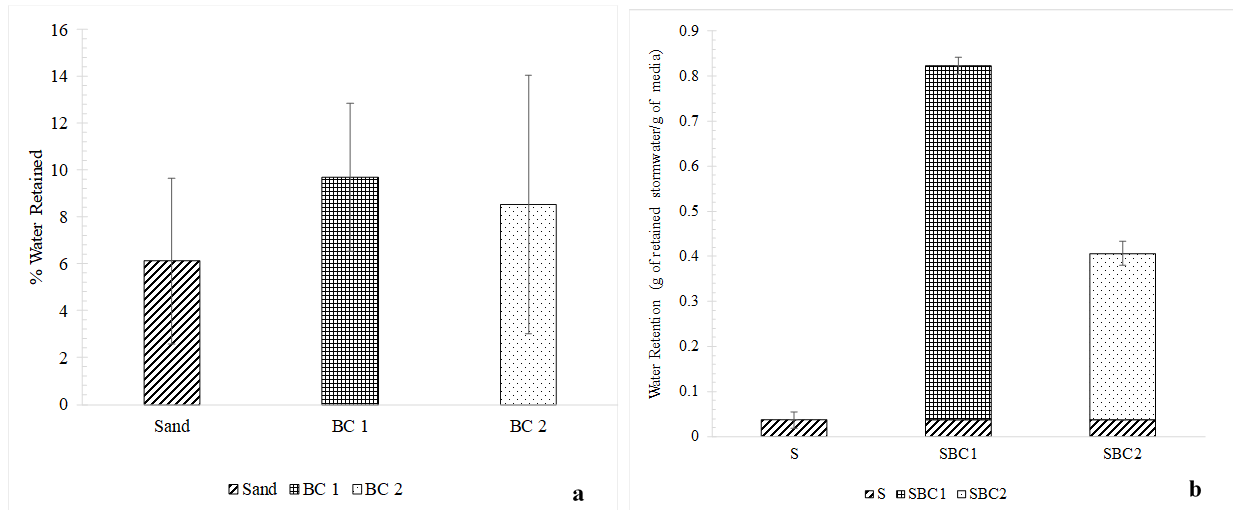


Figure 6: a) Percent water retention with error bars for the three columns over eighteen storm events. b) Average water retention of three porous media in the three columns.

Table 2: Physicochemical characterization of two biochars used in this study.

	Organic carbon	Ash	H/C	O/C	(O+N)/C	pH	CEC	SA	Mesopore	Micropore	Pore Volume	BD
	(%)	(%)					cmol/kg	m ² /g	cc/g	cc/g	cc/g	g/cc
Biochar 1	80.1	5.8	0.56	0.09	0.09	10.12 ± 0.2	10.57	537 ± 60	0.15	0.19	0.36	0.10
Biochar 2	81.7	1.2	0.7	0.106	0.11	8.5 ± 0.3	13.63	136 ± 46	0.062	0.061	0.13	0.19

*CEC: Cation Exchange Capacity; SA: Surface Area; BD: Bulk Density

Table 3: Overall mass contaminant removal performance for the three columns

	Influent		S		SBC1		SBC2			
Pollutant	Concentration (mg/)	% Mass Removal (Avg.± Std.)	Med.	Total Effluent Mass (mg)	% Mass Removal (Avg.± Std.)	Med.	Total Effluent Mass (mg)	% Mass Removal (Avg.± Std.)	Med.	Total Effluent Mass (mg)
TAN	1.00 ± 0.4	78.3 ± 13.1 ^a	76.3	6.7	99.2 ± 1.3 ^b	100	0.2	99.5 ± 0.7 ^b	99.9	0.1
NOx	0.98 ± 0.5	-14.5 ± (-41.2) ^d	-0.6	17.6	-36.7 ± (-62.8) ^d	-13.3	20.2	-27.9 ± (-47.2) ^d	-12.2	19.4
DON	1.16 ± 0.2	41.0 ± 20.5 ^d	38.6	12.5	46.8 ± 26.5 ^d	43.9	11.8	50.2 ± 24.9 ^d	52.4	11.2
TN	3.14 ± 0.4	39.4 ± 10.1 ^d	39.3	36.9	44.6 ± 14.1 ^d	40.5	31.6	47.6 ± 11.6 ^d	46.3	30.4
DOC	19.93 ± 8.1	74.7 ± 10.8 ^a	75.1	91.5	92.5 ± 5.1 ^b	93.4	22.4	86.3 ± 7.8 ^c	88.9	39.1
<i>E. coli</i> *	2.24x10 ⁷ ± 1.80x10 ⁷	3.4 ± 1.1 ^a	3.0	N/A	BDL ^b	-	N/A	4.2 ± 0.6 ^c	4.3	N/A

Values across a row followed by a different superscripted letter are significantly different ($p < 0.05$) among the three columns using Tukey tests. BDL=Below Detection Limit.

**E. coli* influent concentration unit: CFU/100 ml; Mass Removal and median in log10 scale.

*S: Sand column; SBC1: Sand amended Biochar 1 column; SBC2: Sand amended Biochar 2 column.

Deliverable#2

Effect of Amendment Rate on N-species and TOC

Average N-species and TOC removals for ten experiments with SBC-20 and SBC-50 columns are summarized in Table 4. TAN removal was significantly ($p < 0.05$) higher for SBC-50 (71%) compared to SBC-20 (34%). The higher biochar amendment rate in SBC-50 increased the surface charge availability for NH_4^+ adsorption. Preliminary laboratory results showed that dairy runoff contains Ca^{2+} (17.01 mg/l), Mg^{2+} (13.1 mg/l), Al^{3+} (19.2 mg/l) and Fe^{2+} (15.7 mg/l) ions that compete with NH_4^+ for surface sites, resulting in a lower TAN removal for SBC-20. As discussed previously, biochar addition favors denitrification, which led to TN removal.

DON removal was significantly ($p < 0.05$) higher in SBC-50 than SBC-20 due to greater adsorption capacity, which resulted in greater ammonification and nitrification-denitrification. Hence, enhanced adsorption, ammonification, nitrification and denitrification resulted in higher TN removals for SBC-50 compared with SBC-20 ($p < 0.05$).

N-species and TOC concentration profiles for SBC-20 and SBC-50 are shown in Figure 7. The experiment was performed at a $0.10 \text{ cm}^3/\text{cm}^2/\text{min}$ HLR and 12-day ADP. After the first pore volume was flushed from the column (≈ 60 minutes), effluent concentrations slowly increased over time. For the first 2 pore volumes (≈ 120 minutes) both columns had similar low effluent TAN concentrations, but afterward effluent TAN concentrations increased in SBC-20, while steady performance was observed in SBC-50. Effluent NO_x concentrations were high in the initial soil pore water because of flushing of NO_x that had been generated by nitrification during the long ADP of 12-days between infiltration experiments. After 60 minutes, effluent NO_x concentrations in SBC-20 decreased until the experiment ended, possibly due to saturated media conditions resulting in denitrification or shorter HRT than needed to convert TAN to NO_x . In SBC-50, once the initial pore water was flushed from the column, effluent NO_x concentrations increased (≈ 90 minutes) possibly due to further nitrification of adsorbed TAN during the initial stage of the experiment. After 150 minutes, effluent concentrations decreased due to the anoxic conditions that developed in the media, which favored denitrification. Until 1.5 pore-volume, both columns leached the DON, which was captured in porewater and media surface during the previous experiment. Once the trapped porewater was released, effluent DON concentrations gradually decreased until the experiment was completed due to adsorption of DON in available

biochar surface. Effluent TN concentrations followed a similar pattern. As expected, SBC-50 had lower effluent TOC concentrations at the end of the experiment due to higher TOC adsorption compared to SBC-20 and TOC acting as carbon source and electron donor for denitrification.

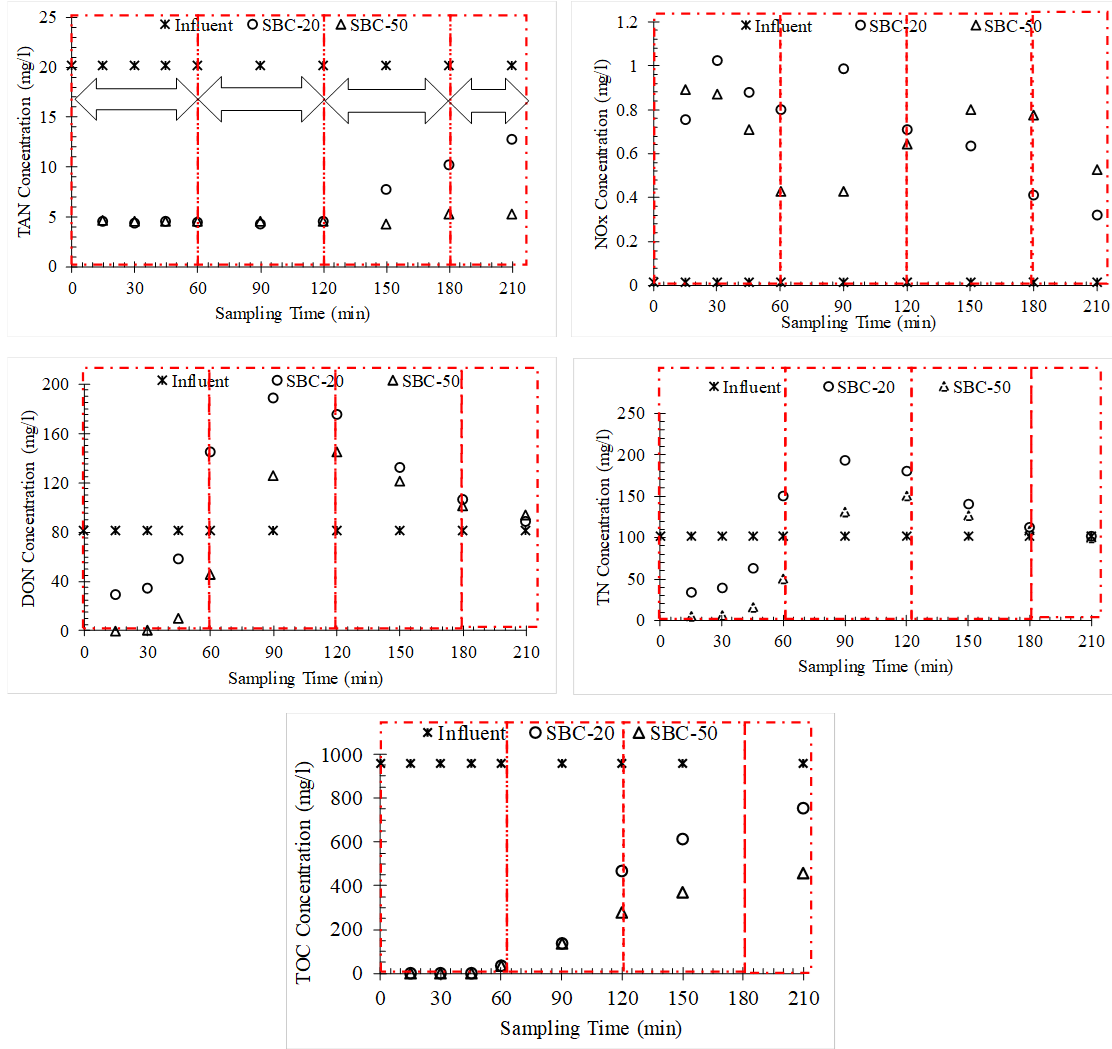


Figure 7: Pollutant concentration profiles (a: TAN; b: NO₃⁻; c: DON, d: TN, and e: TOC) for SBC-20, and SBC-50 bioretention systems with 12-day ADP and high HLR. The red lines indicate the number of pore volumes

Effect of Amendment Rate on FIB removal

A summary of overall *E. coli* and *Enterococci* removal performance for SBC-20 and SBC-50 is shown in Table 5. Better removal was observed in SBC-50 than SBC-20 for both FIB. Significantly higher removals of *E. coli* were observed than *Enterococci*, indicating a greater

attachment affinity to the biochar surface for *E. coli*. Differences in *E. coli* and *Enterococci* transport in biochar amended media are attributable to their unique microbial properties, including cell membrane composition, motility, shape, surface charge and hydrophobicity (Becker et al., 2004; Silliman et al., 2001). Although SBC-50 had a higher SA and hydrophobicity than SBC-20, there was no significant difference in *E. coli* or *Enterococci* removals between the two columns. This could possibly be due to the complex dairy runoff matrix, which contains high levels of TOC and DON, which have a high affinity for surface attachment to biochar.

E. coli breakthrough profiles for SBC-50 and SBC-20 for experiments conducted with 7-day and 28-day ADPs at a HLR of $0.18 \text{ cm}^3/\text{cm}^2/\text{min}$ are shown in Figure 8. For 7-day ADP, SBC-50 showed slightly lower log removal for the first PV (SBC-20: $\log 2.07 \pm 0.24$ and SBC-50: $\log 1.94 \pm 0.18$). This might be due to the greater MC of SBC-50, which provided favorable conditions for the survival or regrowth of *E. coli* compared with SBC-20. However, considering the entire course of the experiment at 7-days ADP, greater log removal was observed with SBC-50 ($\log 1.52 \pm 0.42$) compared with SBC-20 ($\log 1.47 \pm 0.53$). Biochar has a high adsorption affinity for TOC and competition between *E. coli* and TOC on the biochar surface may have resulted in decreased *E. coli* removal from SBC-50. For shorter ADPs, adsorbed TOC might not be completely biodegraded prior to the next storm event or there might be competition with other microbes, resulting in reduced *E. coli* removal.

For 28-day ADP, SBC-50 had higher *E. coli* log removal ($\log 1.63 \pm 0.37$) compared to SBC-20 ($\log 1.27 \pm 0.34$). Until the first PV (60 minutes), SBC-50 had 17% higher log removal compared to SBC-20. This might be due either to higher *E. coli* die off compared with other microbes or less remobilization of attached *E. coli* during the first flush of pore water. A similar laboratory study by Mohanty and Boehm (2014) showed that only 2% of the deposited *E. coli* remobilized from biochar-amended sand filters treating urban runoff. Therefore, due to the higher biochar amendment rate in SBC-50, lower remobilization was observed in SBC-50 for the first PV.

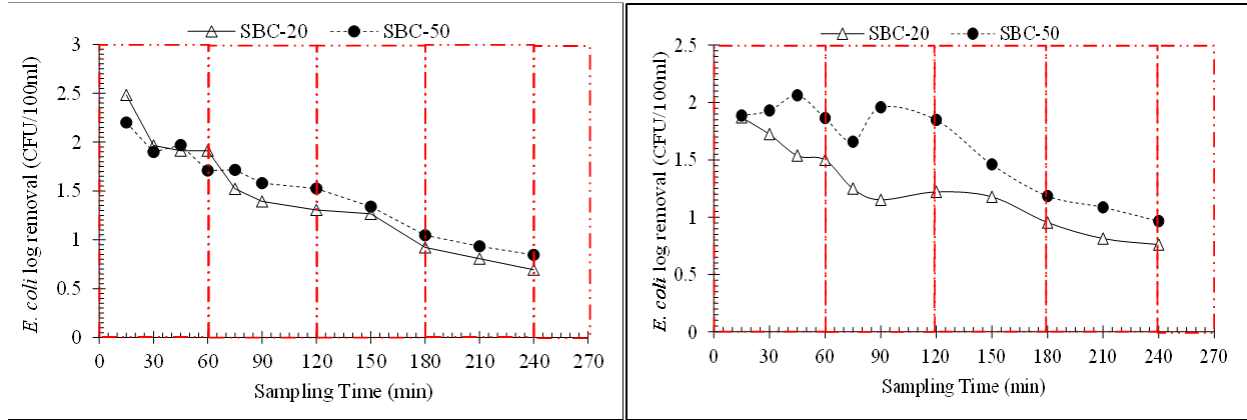


Figure 8: *E. coli* removal in effluent for SBC-20 and SBC-50 columns for a) 7-days and b) 28-days ADPs.

Effect of Amendment Rate on Hydraulic Performance

Volumetric moisture content measurements at different depths are shown in Figure 9 for ADPs of 1, 2, 3, 11 and 15-days. Moisture content increased with depth in both columns due to gravitational drainage. As expected, higher MCs were observed in SBC-50 than SBC-20. Following the drainage phase, the volumetric moisture content in SBC 20 was $\sim 0.24 \text{ cm}^3/\text{cm}^3$ at the surface but increased to $0.51 \text{ cm}^3/\text{cm}^3$ (60%) at the bottom of the column. Similarly, the moisture content was $0.16 \text{ cm}^3/\text{cm}^3$ at the top of SBC-50, which was lower by a factor of 3.3 compared to bottom surface ($0.58 \text{ cm}^3/\text{cm}^3$). Near-saturation condition at the bottom of the column favors denitrification. Close to the surface, however, drainage and evaporation allowed air entry to the medium during ADP, which facilitated nitrification of adsorbed NH_4^+ . A 33% higher evaporation rate was observed for SBC-50 compared with SBC-20.

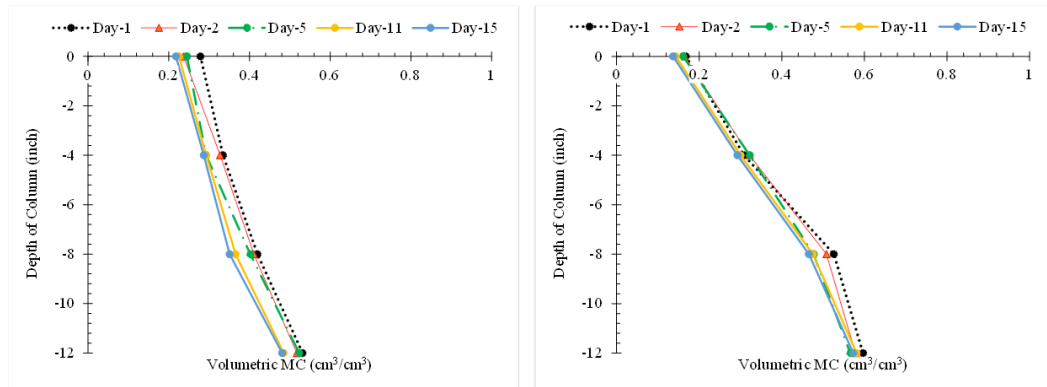


Figure 9: Volumetric moisture content (cm^3/cm^3) with depth for varying ADPs: a) SBC-20 and b) SBC-50.

Table 4: Overall N-species and organic carbon removal for SBC-20 and SBC-50 columns.

Parameter	Influent (mg/L)	SBC-20		SBC-50	
		Effluent (mg/L)	% Removal	Effluent (mg/L)	% Removal
TAN	30.75±14.56	20.23±17.19	33.61±53.31 ^a	8.94±6.20	71.20±20.40 ^b
NO _x	0.03±0.08	0.23±0.38	-765.87±1396 ^c	0.38±0.80	-779.38±1422 ^c
DON	57.17±29.36	30.86±38.14	38.19±56.53 ^a	19.02±24.71	67.40±28.68 ^b
TN	88.33±36.84	45.81±38.77	39.34±50.73 ^a	28.72±23.16	65.10±24.34 ^b
TOC	761.83±468.59	180.62±85.72	71.04±17.98 ^a	127.99±98.90	83.84±6.21 ^b

Table 5: Overall *E. coli* and *Enterococci* removal performance for for SBC-20 and SBC-50 columns.

Column	Influent <i>E. coli</i> (CFU/100 mL)	Effluent <i>E. coli</i> (CFU/100 mL)	Log removal	Influent <i>Enterococci</i> (CFU/100 mL)	Effluent <i>Enterococci</i> (CFU/100 mL)	Log Removal
SBC-20	8.63*10 ⁶ ± 7.07*10 ⁶	3.71*10 ⁵ ±	1.72±	5.63*10 ⁶ ± 4.07*10 ⁶	4.57*10 ⁵ ±	1.09±
		2.52*10 ⁵	0.32		2.57*10 ⁵	0.24
SBC-50	7.07*10 ⁶	3.12*10 ⁵ ±	1.76±	4.07*10 ⁶	3.47*10 ⁵ ±	1.21±
		2.50*10 ⁵	0.29		2.17*10 ⁵	0.39

Deliverable#3

Pilot System Water Quality Performance

N-species removal efficiencies for the four modified bioretention systems are shown in Figure 10. Higher TAN removal was observed in biochar amended systems compared with un-amended systems, with the highest ($90.6\% \pm 6.5$) and lowest ($68.2\% \pm 20.8$) removal efficiencies observed in BP and S systems, respectively. The high CEC of biochar likely resulted in TAN retention, allowing more time for nitrification compared with the un-amended systems. Lower average effluent NO_x concentrations were observed for biochar amended systems (0.72-1.18 mg/l) than 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 electron donor for denitrification. In S and SP, the lack of adsorbed TOC in the IWSZ likely limited denitrification.

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), therefore, enhanced adsorption and ammonification resulted in higher DON (<99%) 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 un-amended systems (5.03-5.67 mg/l). TN removal was limited in S ($76.89\% \pm 18.2$) and SP ($76.26\% \pm 17.72$) bioretention systems compared with B and BP due to low TAN and DON adsorption and limited denitrification.

Effluent TAN and TN concentration profiles over time for the four bioretention systems for a 4.5-hour storm event are shown in Figure 11. TAN removal mainly depends on i) media adsorption, ii) nitrification and iii) 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 NO₃⁻, resulting 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). Once the pore water in the IWSZ was flushed from the systems (90-270 minutes), effluent TAN concentrations in SP increased and were almost the same as S by the end of the experiment. 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. However, B and BP systems maintained relatively low effluent TAN concentrations throughout the experiment due to the high affinity of biochar to 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. 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.

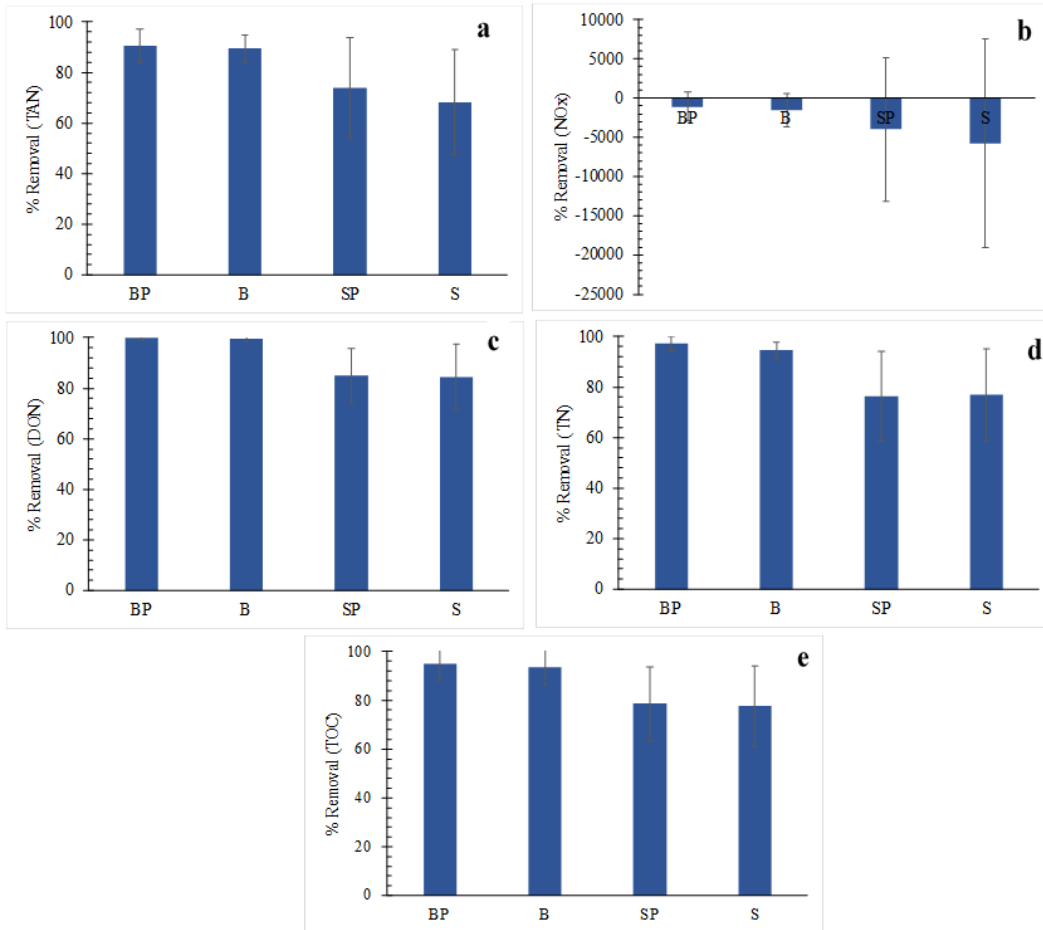


Figure 10: Overall N-species removal efficiencies (a: TAN; b: NO_3^- ; c: DON; d: TN and e: TOC) for four modified bioretention systems (BP: biochar with plant bioretention; B: biochar amended bioretention; SP: sand amended bioretention with plant and S: sand bioretention system).

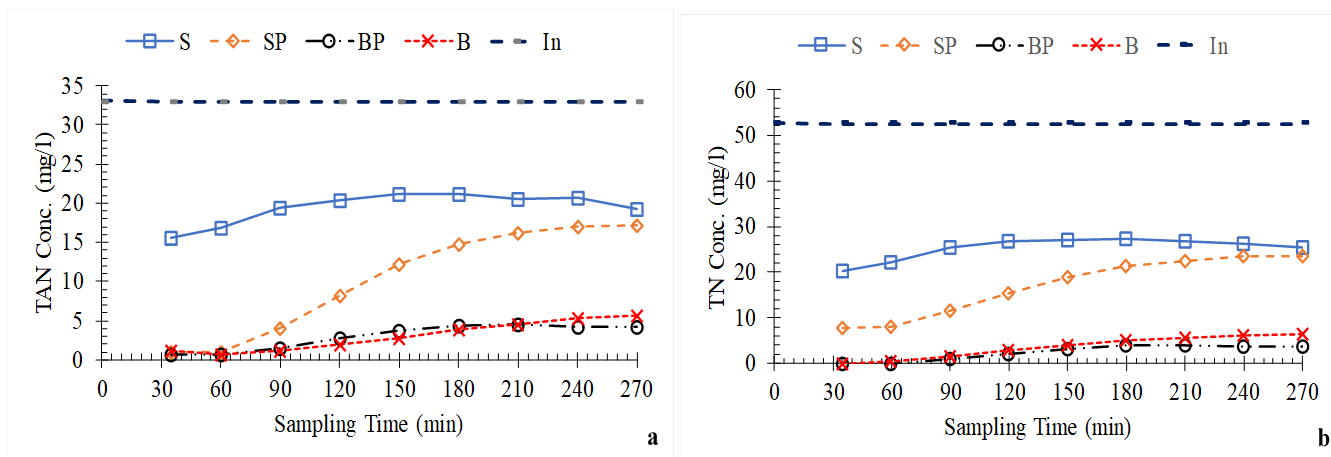


Figure 11: Pollutant breakthrough curves for (a) TAN and (b) TN for four modified bioretention systems considering 222 ml/min flow rate for 4.5 hours dairy runoff experiment.

Effect of IWSZ on E. coli Removal

Log *E. coli* removals for the pilot-scale bioretention systems are shown in Table 6. Inclusion of the IWSZ resulted in a 40% higher log *E. coli* removal than the column studies for experiments carried out with the same ADP and HLR. Higher *E. coli* removals in pilot units with an IWSZ may have been due to the longer retention times and/or the anoxic conditions present in the IWSZ. The first PV, retained in the IWSZ showed higher *E. coli* log removal compared to greater than 1st PV of infiltrated water.

Effects of Plants on TN removal

The effects of plants on NH_4^+ removal was not significant for biochar amended systems compared with unamended systems. For NH_4^+ , BP showed 1% greater removal efficiency compared to B; however, the unamended system with plants (SP) had 6% higher NH_4^+ removal compared to sand system without plant (S) (Figure 11). Mean NO_x leaching decreased for the planted systems (BP or SP) compared with unplanted systems, both with or without biochar amendment (B or S). In both cases, NO_x export decreased by 30% due to the presence of plants. Plants enhance denitrification due to greater microbial activity and the presence of bioavailable organic carbon in the rhizosphere from root exudates and sloughed-off root tissue. Even if the sand layer is well-oxygenated compared to the anoxic conditions of the IWSZ layer, the microbiome of the rhizosphere allows for denitrifiers to occur near plant roots and thrive in anoxic microsites where oxygen diffusion is reduced. This may explain the enhanced denitrification observed in the planted

systems. TN removal was not significantly higher when the systems were planted. Biochar with plant (BP) had 3% higher TN removal compared to biochar without plant system (B). No significant differences were observed for DON removal in planted and unplanted systems.

Effects of Plants on E. coli Removal

Biochar amended systems had better *E. coli* removal performance compared with unamended systems (Figure 12). Systems planted with *Muhlenbergia*, which has an extensive root system, had better performance than the corresponding systems without plants. The best performance was observed in the bioretention system with both biochar and plants. The quantity of microorganisms living in the rhizosphere is several orders of magnitude higher than that in bulk soils (Mukerji et al., 2006). It is well known that addition of biochar to soil aids in plant growth by retaining water and nutrients and providing a good habitat for beneficial microbes in the rhizosphere (Werner et al., 2018; Ippolito et al., 2012). Plants can improve FIB removal through predation and competition by rhizosphere microbes or inactivation by antimicrobial compounds from root exudates (Chandrasena et al., 2014; 2017). However, plant roots can also increase FIB transport by creating preferential flow paths through the media (Clothier et al., 2008).

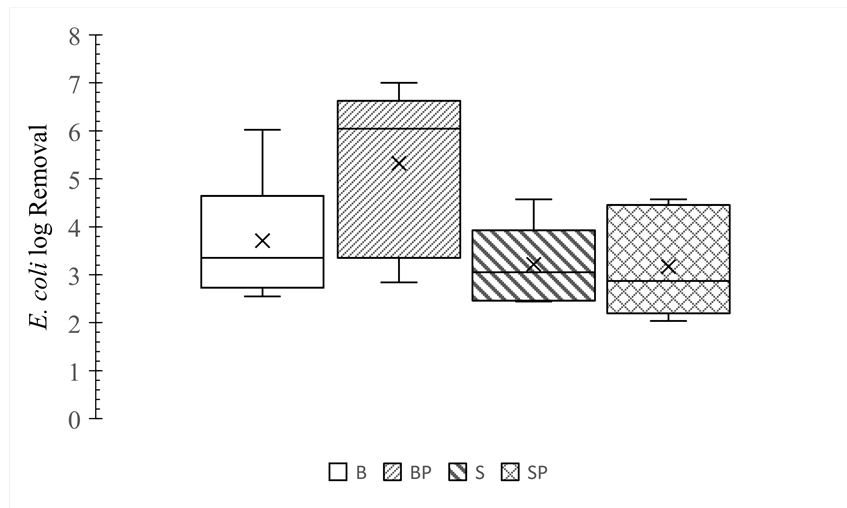


Figure 12: Overall performance of *E. coli* removal for pilot studies for four modified bioretention systems.

Table 6: *E. coli* removal performance for pilot studies for four bioretention systems considering different pore water infiltration with 7-days ADPs and 0.10 cm³/cm²/min HLR

System	Log Removal		
	<1 PV (Time <90 minutes)	1<PV<2 (90 <Time<180 minutes)	PV>2 (180 <Time<240 minutes)
B	3.24±0.52	2.18±0.13	2.05±0.06
BP	4.22±1.99	2.24±0.15	1.65±0.11
S	2.84±0.33	2.29±0.04	2.17±0.0
SP	2.52±0.44	1.78±0.05	1.71±0.03

Deliverable#4

Mathematical Model

Experimental and simulated breakthrough curves for a 4-hour tracer experiment with a 0.18 cm³/cm²/min HLR and ADP of 3-days are shown in Figure 13. Inspection of the breakthrough curves shows that the effluent tracer concentration was equal to the influent concentration at 120 minutes for SBC-20 and 165 minutes for SBC-50, indicating a longer HRT with a higher biochar fraction. After an initial lag period, concentrations started to increase at 30 minutes for SBC-20 and 45 minutes for SBC-50. These findings were corroborated with the effluent flow rate data, where SBC-20 had shorter HRT compared with SBC-50.

Figure 14 shows simulated MC in the columns at different media depths at different time intervals during the experiment. Collected media samples showed a lower initial MC for SBC-20 (0.26 cm³/cm³) compared with SBC-50 (0.40 cm³/cm³) at a depth of 6 cm. The calibrated model showed that within 30 minutes of infiltration, SBC-20 reached full saturation (saturated water content=0.41 cm³/cm³) whereas SBC-50 reached 83% saturation (saturated water content= 0.54 cm³/cm³) at that time. During dry days, pore water was replaced by air due to evaporation because of the higher porosity of SBC-50 (0.535 cm³/cm³) compared with SBC-20 (0.41cm³/cm³), resulting in a longer time period needed to reach the saturation in the column with more biochar. Based on the input parameters and calibration, it can be concluded that increasing the biochar fraction increases porosity (especially micro-porosity) and slightly reduces saturated conductivity. The changes in hydraulic properties impacted the HRT, the length of time the solution is in contact with the treatment media.

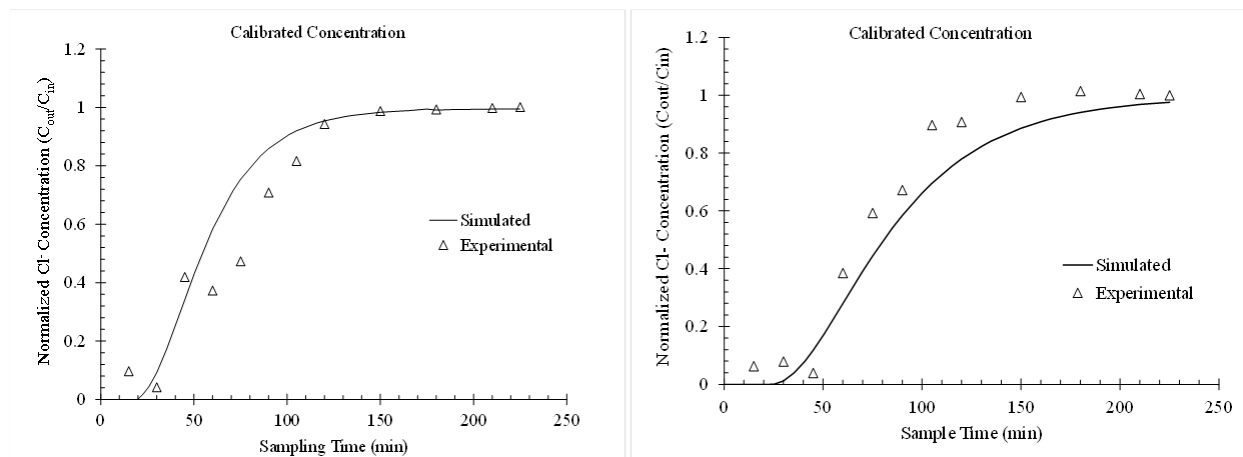


Figure 13: Tracer breakthrough curves and model simulations for: a) SBC-20 and b) SBC-50.

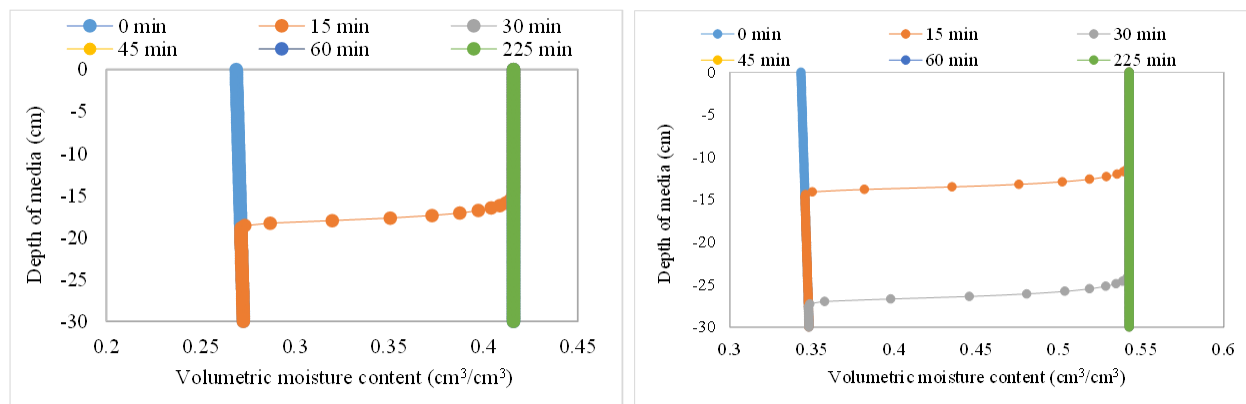


Figure 14: Vertical profile of a) moisture content of the SBC-20 and SBC-50 columns at different time intervals.

Deliverable#5

Research Dissemination

An educational webinar was presented by the research team on October 7, 2020. FDACS OAWP advertised the webinar through their networks. The webinar was also advertised to staff at the Florida Department of Environmental Protection, City of Tallahassee and City of Winter Haven, FL. The webinar was attended by 38 participants. It covered the following topics: 1) importance of green infrastructure, 2) bioretention systems and its application, 3) design of bioretention systems, 4) bench and pilot studies of biochar enhanced bioretention systems. Additional publications and presentations resulting from this project are shown in Table 7.

Table 7: Publications and presentations resulting from this project.

Peer reviewed journal articles	1. Rahman, M. Y. A., Nachabe, M. H., & Ergas, S. J. (2020a). Biochar amendment of stormwater bioretention systems for nitrogen and Escherichia coli removal: Effect of hydraulic loading rates and antecedent dry periods. <i>Bioresource technology</i> , 310, 123428.	2020
	2. Rahman, M.Y.A., Truong, N., Ergas, S.J., Nachabe, M. (2020b) Biochar amended modified bioretention systems for livestock runoff nutrient management, <i>Florida Water Resources Journal</i> , Sept. 2020.	2021
	3. Rahman, M.Y.A., Cooper, R., Truong, N., Ergas, S.J. Nachabe, M. (2021a) Water quality and hydraulic performance of biochar amended biofilters for management of agricultural runoff, <i>Chemosphere</i> , in press.	2020
	4. Rahman, M.Y.A., Truong, N., Nachabe, M., Ergas, S.J. (2021b) Removal of fecal indicator bacteria from dairy runoff using biochar amended bioretention, <i>J. Sustainable Water in the Built Environment</i> , in review.	Submitted
Conference presentations	1. Rahman, M.Y.A.; Ergas, S. J., Nachabe, M.H. (2019) Biochar Amended Bioretention for <i>E. coli</i> and Nitrogen Removal from Urban Stormwater Runoff. <i>Florida Water Resource Conference (FWRC 2019)</i> , Tampa, FL, USA, April 2019.	April, 2019
	2. Rahman, M.Y.A.; Ergas, S. J., Nachabe, M.H. (2019) Efficacy of Biochar Amended Bioretention for <i>E. coli</i> and Nitrogen Removal from Urban Runoff. <i>Water Environment Federation Stormwater and Green Infrastructure Symposium (SWG1-19)</i> , Fort Lauderdale, FL, USA, May 2019.	May, 2019
Dissertation	3. Rahman, M.Y.A. (2021) Biochar amended bioretention systems for nutrient and fecal indicator bacteria control, <i>PhD Dissertation</i> , Department of Civil & Environmental Engineering, University of South Florida	2021
Webinar	4. Ergas, S.J., Nachabe, M., Rahman, M.Y.A., Cooper, R. (2020) Biochar Amended Bioretention Systems for Nutrient & Pathogen Management from Agricultural & Urban Runoff, <i>Webinar presented for FDACS Office of Agricultural Water Policy</i> , October 7, 2020.	2020

CONCLUSIONS

The overall goal of this research was to understand N-species and FIB removal mechanisms in bioretention systems amended with biochar for treatment of dairy runoff. The research was carried out through carefully controlled bench-scale and pilot-scale studies with urban and agricultural runoff. The research team also developed a HYDRUS-1D model to elucidate hydraulic performance of the biochar amended systems. The research was disseminated to water managers, engineers, farmers, researchers, students, and other stakeholders through presentations and publications. The following are the major findings of this research:

Biochar characterization and batch adsorption studies:

- Biochar produced at a higher pyrolysis temperature had a lower cation exchange capacity due to the loss of volatile matter with negatively charged functional groups during pyrolysis.
- Biochar produced at higher pyrolysis temperature had almost four times higher surface area. Although both biochars were produced from wood chips, significant differences in surface area can be attributed to increased carbonization at higher pyrolysis temperature.
- Abiotic batch experiments showed that significantly higher NH_4^+ adsorption was observed for biochar (3.5 mg/g) than sand (0.05 mg/g) due to higher cation exchange capacity. NO_3^- adsorption capacity of biochar was low.

Column studies with and without biochar:

- Biochar addition increased NH_4^+ adsorption during the wetting period, providing substrate for nitrification during the drainage period.
- The higher moisture content and presence of adsorbed dissolved organic carbon in biochar amended columns favored denitrification, resulting in higher total nitrogen removals.
- *E. coli* removal was a strong function of surface area; greater than 6 log *E. coli* removal was observed in the column amended with high surface area biochar.

Column studies with varying biochar amendment rates:

- Higher amendment rates increased the surface charge availability for NH_4^+ and DON adsorption.

- Favorable condition for denitrification developed near the bottom of the biochar amended columns due to increased moisture content and adsorbed dissolved organic carbon, resulting in higher TN removal in the column with higher biochar content.
- The column with the higher amendment rate also had a higher hydraulic residence time due to the increased porosity and greater microporous structure.
- Significantly higher removals of *E. coli* were observed than *Enterococci* in biochar amended columns regardless of amendment rates, indicating a greater attachment affinity to the biochar surface for *E. coli*.
- There were no significant differences in *E. coli* or *Enterococci* removals between columns with different biochar amendment rates. This might be due to complex dairy runoff matrix, which contains high levels of dissolved organic carbon and nitrogen, which have a high affinity for surface attachment to biochar.

Pilot bioretention studies with plants and internal water storage zones (IWSZ):

Summary data from the pilot studies are shown in Table 8. Major findings from the pilot-scale studies are summarized below.

Table 8: Summary data from pilot study showing removal efficiency for N-species, total organic carbon (TOC) and log *E. coli* removal in bioretention systems with and without biochar and with and without plants.

Parameter	Units	Sand	Sand/Plant	Biochar	Biochar/Plant
Total N	% removal	76.9 ± 18.2	76.3 ± 17.7	94.5 ± 2.9	97.2 ± 2.9
Ammonia	% removal	68.2 ± 20.9	73.9 ± 19.7	89.3 ± 5.4	90.6 ± 6.5
Org-N	% removal	84.6 ± 12.8	84.9 ± 10.9	99.5 ± 0.95	99.8 ± 0.5
TOC	% removal	77.8 ± 16.5	78.6 ± 15.2	93.4 ± 7.3	94.8 ± 6.6
<i>E. coli</i>	Log removal	3.2 ± 0.9	3.2 ± 1.1	3.7 ± 1.3	5.3 ± 1.7

- Similar to the column studies, biochar significantly improved total nitrogen and total organic carbon removals compared with unamended bioretention systems. Our research shows that this is due to the uncoupling of hydraulic and pollutant retention times due to the high surface area and cation exchange capacity of biochar. This allows ammonium, dissolved organic

nitrogen and dissolved organic carbon more time for aerobic degradation during the antecedent dry periods between storm events.

- Dissolved organic carbon adsorption and anoxic conditions in the IWSZ favored denitrification of nitrate produced in the unsaturated layer, resulting in higher TN removal in bioretention systems amended with biochar compared with unamended systems.
- The inclusion of plants, biochar and an IWSZ in pilot-scale systems resulted in the best *E. coli* removal performance, most likely due to adsorption and subsequent die-off of attached microorganisms.
- Due to high moisture and nutrient retention, better plant growth was observed in the biochar amended systems. Greater plant growth improves TN removal through plant uptake and greater activity of rhizosphere microorganisms.
- Greater plant growth in biochar amended bioretention systems also improves FIB removal through predation and competition by rhizosphere microbes or inactivation by antimicrobial compounds from root exudates.
- Higher *E. coli* removals in pilot units with an IWSZ may have been due to the longer retention times and/or the anoxic conditions present in the IWSZ.

REFERENCES

- Anderson, C. R., Condon, L. M., Clough, T. J., Fiers, M., Stewart, A., Hill, R. A., Sherlock, R. R. (2011) Biochar induced soil microbial community change: Implications for biogeochemical cycling of carbon, nitrogen and phosphorus. *Pedobiologia*. 54(5-6):309-320.
- Andrews, W.J. (1992) *Reconnaissance of water quality at nine dairy farms in north Florida, 1990-91*. US Department of the Interior, US Geological Survey, 1992.
- APHA, AWWA, WEF (2018) *Standard Methods for the Examination Water and Wastewater* 23rd Ed. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Washington D.C.
- Becker, M.W., Collins, S.A., Metge, D.W., Harvey, R.W., Shapiro, A.M. (2004) Effect of cell physicochemical characteristics and motility on bacterial transport in groundwater, *J. Contaminant Hydrology*. 69: 195–213.
- Chandrasena, G.I., Shirdashtzadeh, M., Li, Y.L., Deletic, A., Hathaway, J.M., McCarthy, D.T. (2017) Retention and survival of *E. coli* in stormwater biofilters: Role of vegetation, rhizosphere microorganisms and antimicrobial filter media. *Ecological Engineering*, 102:166-177.
- Chandrasena, G.I., Deletic, A., McCarthy, D.T. (2014) Survival of *Escherichia coli* in stormwater biofilters. *Environmental Science & Pollution Research*, 21:5391–5401.
- Chapman, H.D. (1965) Cation-exchange capacity, in C.A. Black (ed.), *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, American Society of Agronomy, Madison, Wisconsin.
- Clothier, B.E., Green, S.R., Deurer, M. (2008) Preferential flow and transport in soil: Progress and prognosis. *European Journal Soil Science*, 59(1): 2-13.
- Ergas, S.J., Sengupta, S., Siegel, R., Yao, Y., Pandit, A., Yuan, X. (2010) Denitrifying bioretention systems for control of non-point nitrogen sources, *J. Environmental Engineering-ASCE*, 136(10):1105-1112.
- Heiman, K.E., Mody, R.K., Johnson, S.D., Griffin, P.M., Gould, L.H. (2015) *Escherichia coli* O157 outbreaks in the United States, 2003–2012, *Emerging Infectious Diseases*, 21(8): 1293–1301.

- Ioannidou, V., Stefanakis, A.I. (2020) The use of constructed wetlands to mitigate pollution from agricultural runoff. In *Contaminants in Agriculture* (pp. 233-246). Springer, Cham.
- Ippolito, J.A., Laird, D.A., Busscher, W.J. (2012) Environmental benefits of biochar. *J. Environmental Quality*, 41(4): 967-972.
- Koelsch, R.K., Lorimor, J.C., Mankin, K.R. (2006) Vegetative treatment systems for management of open lot runoff: Review of literature. *Applied Engineering in Agriculture*, 22(1):141–153.
- Li, L., Davis, A.P. (2014). Urban stormwater runoff nitrogen composition and fate in bioretention systems. *Environmental Science & Technology*, 48(6): 3403–3410.
- Liu, Z., Dugan, B., Masiello, C.A., Barnes, R.T., Gallagher, M.E., Gonnermann, H. (2016) Impacts of biochar concentration and particle size on hydraulic conductivity and DOC leaching of biochar-sand mixtures. *J. Hydrology*, 533:461-472.
- Lopez-Ponnada, E.V., Lynn, T.J., Ergas, S.J., Mihelcic, J.R. (2020) Long-term field performance of a conventional and modified bioretention system for removing dissolved nitrogen species in stormwater runoff. *Water Research*, 170: 115336.
- Lynch, M.F., Tauxe, R.V., Hedberg, C.W. (2009) The growing burden of foodborne outbreaks due to contaminated fresh produce: Risks and opportunities, *Epidemiology & Infection*, 137(3):307–315.
- Mahmoud, A., Alam, T., Rahman, M.Y.A., Sanchez, A., Guerrero, J., Jones, K.D. (2019) Evaluation of field-scale stormwater bioretention structure flow and pollutant load reductions in a semi-arid coastal climate. *Ecological Engineering*. 1(2019): 100007.
- Mohanty, S.K., Boehm, A.B. (2014) *Escherichia coli* removal in biochar-augmented biofilter: effect of infiltration rate, initial bacterial concentration, biochar particle size, and presence of compost. *Environmental Science & Technology*, 48: 11535–11542.
- Mohanty, S.K., Cantrell, K.B., Nelson, K.L., Boehm, A.B. (2014) Efficacy of biochar to remove *Escherichia coli* from stormwater under steady and intermittent flow. *Water Research*, 61: 288–296.

- Mukerji, K.G., Manoharachary, C., Singh, J. (2006) *Microbial Activity in the Rhizosphere*. Springer, Berlin.
- Prasad, R., Hochmuth, G., Wilkie, A.C. (2014) *Anaerobic Digesters for Manure Management at Livestock Operations*; EDIS #SL402; UF/IFAS Extension: Gainesville, FL, USA.
- Prince George's County (PGC) (2007) *Bioretention Manual*, PGC, Maryland, Dept. of Environmental Resources, Environmental Services Div., Landover, Md
- Rahman, M.Y.A.; Ergas, S. J., Nachabe, M.H. (2019a) Biochar amended bioretention for *E. coli* and nitrogen removal from urban stormwater runoff. *Florida Water Resource Conference (FWRC 2019)*, Tampa, FL, USA, April 2019.
- Rahman, M.Y.A.; Ergas, S. J., Nachabe, M.H. (2019b) Efficacy of biochar amended bioretention for *E. coli* and nitrogen removal from urban runoff. *Water Environment Federation Stormwater and Green Infrastructure Symposium (SWG-I-19)*, Fort Lauderdale, FL, USA, May 2019.
- Rahman, M. Y. A., Nachabe, M. H., & Ergas, S. J. (2020a). Biochar amendment of stormwater bioretention systems for nitrogen and *Escherichia coli* removal: Effect of hydraulic loading rates and antecedent dry periods. *Bioresource Technology*, 310, 123428.
- Rahman, M.Y.A., Truong, N., Ergas, S.J., Nachabe, M. (2020b) Biochar amended modified bioretention systems for livestock runoff nutrient management, *Florida Water Resources Journal*, Sept. 2020.
- Rahman, M.Y.A., Cooper, R., Truong, N., Ergas, S.J. Nachabe, M. (2021a) Water quality and hydraulic performance of biochar amended biofilters for management of agricultural runoff, *Chemosphere*, in press.
- Rahman, M.Y.A., Truong, N., Nachabe, M., Ergas, S.J. (2021b) Removal of fecal indicator bacteria from dairy runoff using biochar amended bioretention, *J. Sustainable Water in the Built Environment*, in review.
- Silliman, S., Dunlap, R., Fletcher, M., Schneegurt, M. (2001) Bacterial transport in heterogeneous porous media: Observations from laboratory experiments. *Water Resources Research*, 37: 2699–2707.

- USDA-NASS (2016) *Florida Cattle Facts*, Mark Hudson, State Statistician, Southern Region, United States Department of Agriculture, National Agricultural Statistics Services, Maitland FL 32751. www.nass.usda.gov/fl.
- USEPA (2014) Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (Modified mTEC), EPA-821-R-14-010, United States Environmental Protection Agency, Washington DC.
- Werner, S., Kätzl, K., Wichern, M., Buerkert, A., Steiner, C., Marschner, B. (2018) Agronomic benefits of biochar as a soil amendment after its use as wastewater filtration medium. *Environmental Pollution*, 233: 561-568.
- Yao, Y., Gao, B., Zhang, M., Inyang, M., Zimmerman, A.R. (2012) Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere*, 89: 1467–1471.

APPENDICES



Figure 15: Experimental Setup for stormwater runoff experiment for three columns.

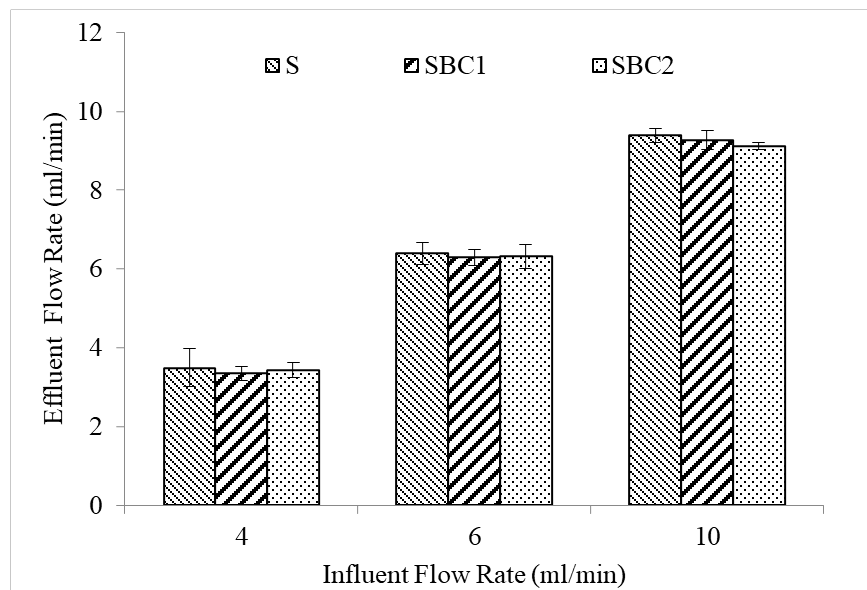


Figure 16: Influent and Effluent Relationship for three different HRTs for three columns.

Table 9: Effect of three different flow rates/HRTs of three different columns for contaminant removal based on mass removal

		TAN	NOx	Org-N	TN	<i>E. coli</i>	DOC
		Mean $\pm$ std.	Mean $\pm$ std.	Mean $\pm$ std.	Mean $\pm$ std.	Mean $\pm$ std.	Mean $\pm$ std.
High HRT	SAND	98.59 $\pm$ 0.1 ^b	14.10 $\pm$ 13.22 ^d	42.21 $\pm$ 10.87 ^{bc}	43.17 $\pm$ 6.77 ^d	99.9057 $\pm$ 0.077 ^{bc}	73.94 $\pm$ 2.63 ^{bc}
	SBC1	99.77 $\pm$ 0.34 ^a	1.74 $\pm$ 9.39 ^d	61.90 $\pm$ 9.65 ^a	44.49 $\pm$ 6.59 ^d	100 $\pm$ 0 ^{ac}	88.99 $\pm$ 1.09 ^{ac}
	SBC2	99.51 $\pm$ 0.86 ^d	8.03 $\pm$ 17.49 ^d	63.58 $\pm$ 5.15 ^a	49.01 $\pm$ 7.49 ^d	99.9799 $\pm$ 0.033 ^{ab}	83.86 $\pm$ 1.49 ^{ab}
Medium HRT	SAND	87.32 $\pm$ 6.84 ^{bc}	17.36 $\pm$ 24.99 ^d	43.70 $\pm$ 11.09 ^{bc}	41.43 $\pm$ 14.74 ^d	99.6986 $\pm$ 0.219 ^{bc}	77.75 $\pm$ 5.38 ^{bc}
	SBC1	98.76 $\pm$ 2.07 ^a	15.31 $\pm$ 7.99 ^d	61.02 $\pm$ 3.57 ^a	50.13 $\pm$ 2.92 ^d	100 $\pm$ 0 ^a	92.30 $\pm$ 3.45 ^a
	SBC2	98.85 $\pm$ 1.77 ^a	11.03 $\pm$ 11.27 ^d	55.60 $\pm$ 8.57 ^a	46.35 $\pm$ 7.41 ^d	99.9447 $\pm$ 0.036 ^a	90.24 $\pm$ 1.23 ^a
Low HRT	SAND	66.572 $\pm$ 35.20 ^{bc}	-13.78 $\pm$ 33.93 ^{bc}	25.94 $\pm$ 19.92 ^d	33.56 $\pm$ 10.20 ^d	99.7259 $\pm$ 0.214 ^{bc}	66.73 $\pm$ 7.88 ^{bc}
	SBC1	98.78 $\pm$ 2.23 ^a	-47.10 $\pm$ 17.75 ^a	27.68 $\pm$ 8.59 ^d	40.96 $\pm$ 3.42 ^d	100 $\pm$ 0 ^a	92.16 $\pm$ 1.35 ^{ac}
	SBC2	99.60 $\pm$ 0.83 ^a	-42.70 $\pm$ 22.94 ^a	32.85 $\pm$ 16.57 ^d	43.54 $\pm$ 10.32 ^d	99.9592 $\pm$ 0.031 ^a	83.90 $\pm$ 2.29 ^{ab}



Figure 17: Experimental Setup for dairy runoff experiment

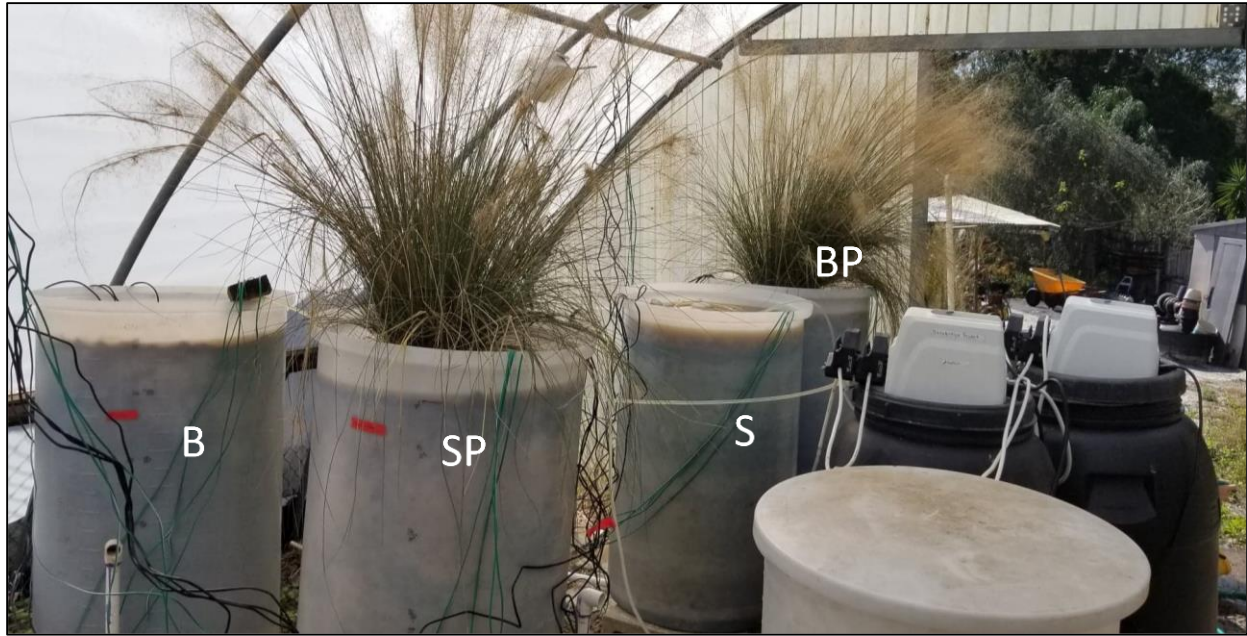


Figure 18: Experimental Setup on pilot studies for dairy runoff experiments.

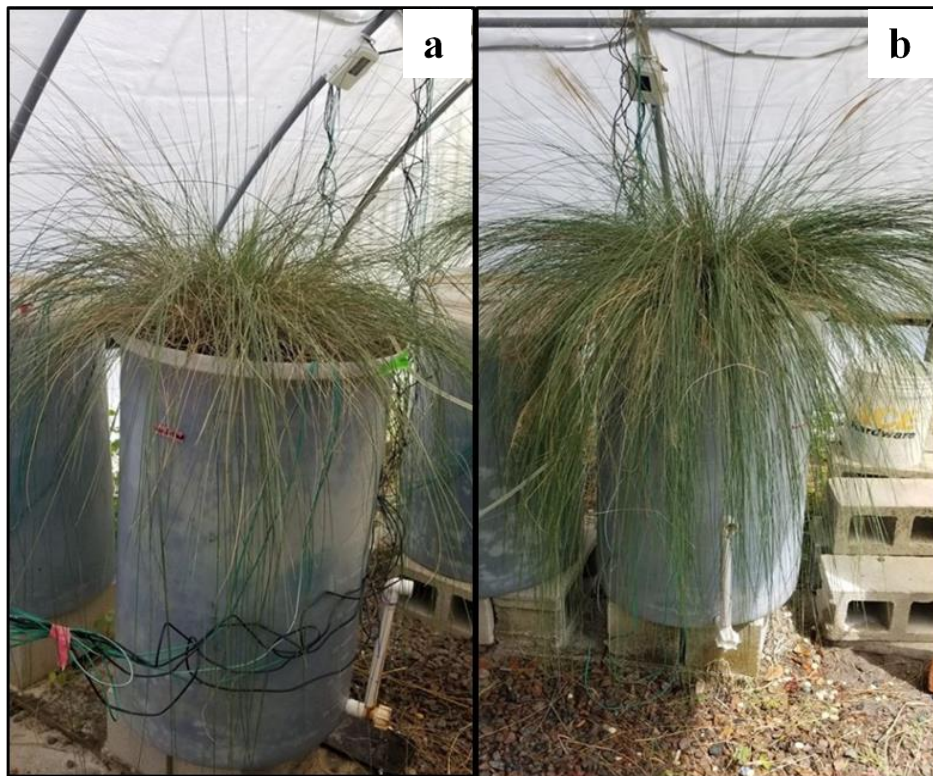


Figure 19: Plant biomass growth in sand with plant (left) and biochar amended planted bioretention (Right).