DCT 279

Evaluating Biochar Amendment of DNREC Biosoil-14 Bioretention Medium

By

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EVALUATING BIOCHAR AMENDMENT OF DNREC BIOSOIL-14 BIORETENTION MEDIUM

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Table of Contents

List of Figures

List of Tables

1. Problem Statement

In field tests conducted previously at the University of Delaware, biochar amendment to standard bioretention media showed dramatic improvement in removal of nutrients, particularly nitrate. Biochar addition removed between 30-83% of the nitrate in stormwater, while a control cell with a standard bioretention mix exhibited much poorer performance. In order to incorporate biochar in bioretention media in DelDOT facilities in the state of Delaware, it is necessary to conduct additional tests with the standard bioretention mix accepted by the Delaware Department of Natural Resources and Environmental Control (DNREC). The PI met with DNREC representatives in March 2017, and with their guidance developed an experimental plan to provide the necessary data to satisfy DNREC requirements. DNREC requested laboratory tests comparing DNREC Biosoil-14 bioretention medium with and without biochar amendment. DNREC also requested data evaluating the impact of biochar on plant growth.

The objective of this study was to address DNREC's requirements by conducting laboratory experiments to evaluate the impact of biochar amendment on nutrient removal in the DNREC Biosoil-14 medium as well as the North Carolina bioretention medium previously used in University of Delaware field tests. Laboratory experiments with the North Carolina medium provide a benchmark for comparison to previous field tests. In addition to nutrient removal experiments, laboratory tests were also conducted to evaluate the impact of biochar amendment on plant growth in these two bioretention media.

2. Experimental Methods

a. Bioretention Media

Six types of mixed filter media were tested in this study. The mixture description and characteristic are listed in Table 1. The biochar was commercially produced by The Biochar Company (Berwyn, PA) through pyrolysis of Southern Yellow Pine at 550℃ (Soil Reef™ biochar). The sand in the North Carolina bioretention media (NC-mix and NC-4B) was C33 concrete sand from Mason-Dixon Sand & Gravel (Port Deposit, MD). The fines in the North Carolina bioretention media consisted of 63% clay, 12% silt and 25% sand by mass, also from Mason-Dixon Sand & Gravel. The sawdust in the North Carolina bioretention media was obtained from Second Chance Hard-wood (Elkton, MD) and derived from white oak and white cedar wood.

The sand, mulch and compost in the Delaware bioretention media (DE-mix, DE-4B, DE-SMB, and DE-SMC) were obtained from DNREC approved Biosoil-14 supplier Holland Mulch, Inc. (Edgemoor, DE). The sand from Holland Mulch, Inc. was concrete sand and had similar properties as the sand from Mason-Dixon Sand & Gravel. All components were sieved to pass the 2 mm sieve, oven-dried at 65 ℃ for 48 hours before mixing, and then stored in sealed 5-gal buckets. For each component and their mixtures, bulk density was measured following ASTM D2854 with air-dried media; pH and organic matter (OM) were measured following ASTM D4972 and ASTM d2974, respectively; total carbon (TC) and total nitrogen (TN) were measured by combusting using an Elementar VarioMax CN Analyzer (Elementar Americas, Mt. Holly, NJ); extractable phosphorus (M3-P) was extracted using the Mehlich 3 soil test extractant and analyzed by a Thermo Iris Intrepid II XSP Duo View ICP (Thermo Elemental, Madison, WI). The properties of mixtures and each component are showed in Table 1 and Figure 1. Note that if a mixture has a biochar content that is 18% by volume this is approximately 4% by mass (dry mass).

Table 1. Description of bioretention media and properties for column experiments.

Columns	Description	Abbr.	Composition (by volume)	Bulk density (g/cm3)	Total mass in column (g)	Mass of individual component (g)						pH (1:1)	Organic matter (%)
						Sand	Fines	Sawdust	Biochar	Compost	Mulch		
#1, #2	NCDWQ bioretention filter media	NC-mix	62% Sand, 11% Fines, 27% Sawdust	1.40	1807	1590	145	72	--	--	--	4.9	3.6±0.1
#3, #4	NC with 18% biochar	NC-4B	52% Sand, 9% Fines, 21% Sawdust, 18% Biochar	1.24	1602	1362	124	62	54	--	--	6.7	6.7±0.5
#5, #6	DNREC Biosoil-14	DE-mix	60% Sand, 30% Mulch, 10% Compost	1.32	1694	1498	--	--	--	86	110	7.1	4.9±0.1
#7, #8	SMC with 18% biochar	DE-4B	49% Sand, 25% Mulch, 8% Compost, 18% Biochar	1.14	1471	1246	--	--	61	70	93	7.2	8.6±1.0
#9, #10	Remove compost from SMCB	DE-SMB	60% Sand, 22% Mulch, 18% Biochar	1.28	1670	1527	--	--	61	--	82	7.6	5.2±0.4
#11, #12	Remove mulch from SMCB	DE-SCB	60% Sand, 22% Compost, 18% Biochar	1.25	1610	1381	--	--	55	174	--	7.3	8.9±1.3

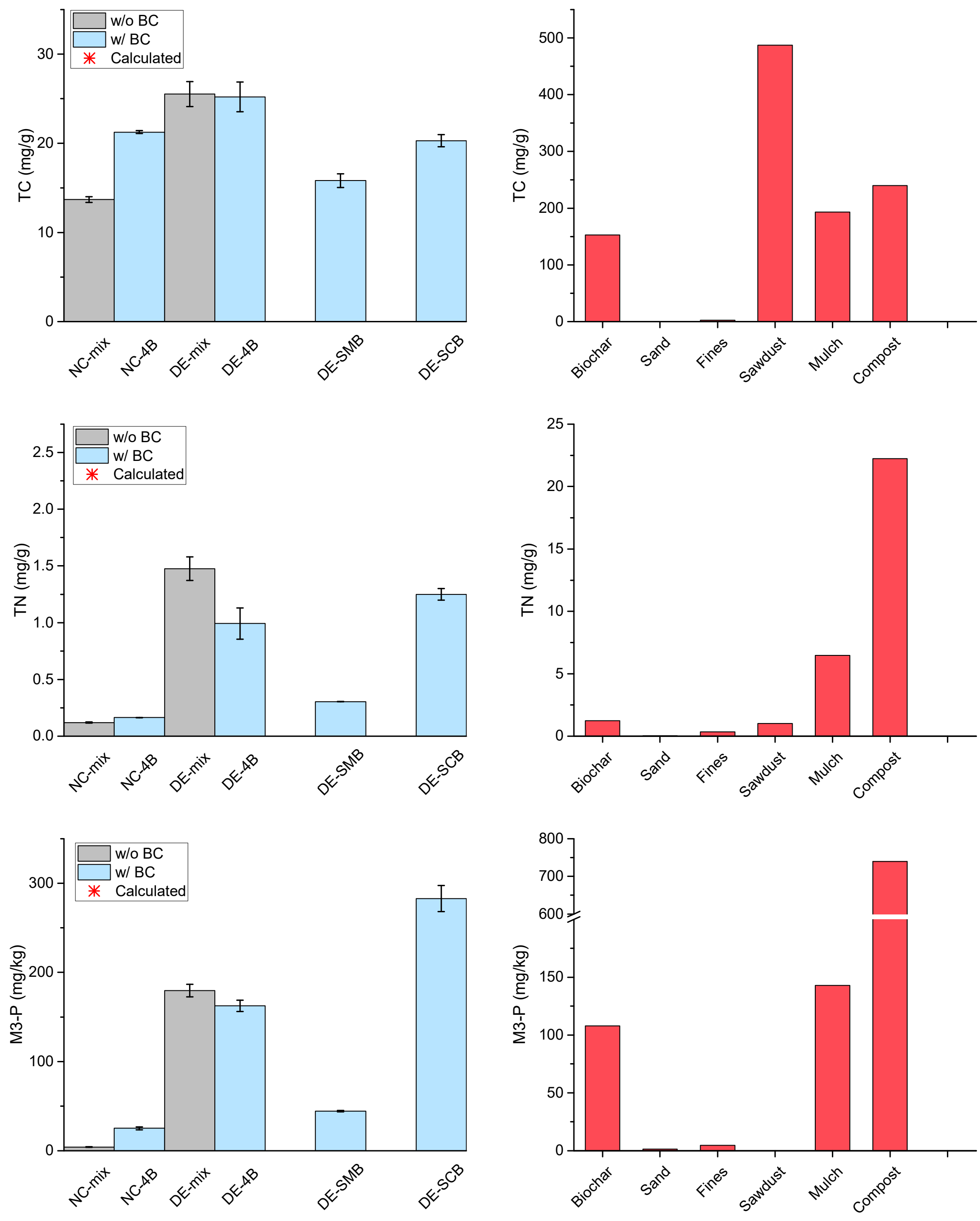

Figure 1. Total carbon (TC), total nitrogen (TN), and Mehlich 3 extractable phosphorus (M3-P) contents of six bioretention media (left column) and seven individual components.

b. Column Experiments

i. Column Setup

Column experiments were conducted to evaluate the performance of the six media described above: North Carolina bioretention medium with and without biochar, Delaware bioretention medium with and without biochar, and some components (either sand and mulch or sand and compost) of the Delaware bioretention medium with biochar. Twelve columns were constructed for the experiments. Each column was assembled with a clear schedule 40 PVC pipe (5.0 cm i.d., 5.8 cm o.d., 76 cm length), a clear PVC cap (5.8 cm i.d.) as the bottom end, a polypropylene perforated sheet (5.8 cm diameter, 0.5 cm thickness with staggered rows of 0.5 cm diameter holes on 0.8 cm centers) in the bottom cap to support the media, and a 2.5 cm diameter PVC rod glued to the cap. A 1.0 cm diameter barbed fitting was drilled through the bottom PVC rod and cap that was connected to 1.0 cm i.d. PVC tubing, which served to provide inflow for the leaching experiments and to collect outflow from the stormwater experiments. At 10 cm from the top of each column, a 1.3 cm i.d. barbed fitting was drilled into the sidewall of the column that was connected to a 1.3 cm i.d. PVC tubing. This outlet fitting allowed for overflow from the column during stormwater experiments: if the infiltration capacity of the bioretention media was too small, water would pool above the media surface and exit the system through this tubing in the side wall. This feature allowed for the column experiments to mimic natural surface runoff that ocurrs when the infiltration capacity of bioretention media is exceeded.

Each filter medium was packed into columns, two columns for each medium, with columns packed to 60 cm depth at the designed bulk densities listed in Table 1. Before packing, a layer of 150 μm nylon sheet was placed on the bottom polypropylene perforated sheet to hold small particles, while after packing another 150 μm nylon sheet and polypropylene perforated sheet were placed on the top of each packing successively. The nylon sheet on the top surface prevented floating and erosion of bioretention media during the leaching experiments.

ii. Leaching Experiments

During the leaching experiments, 12 columns, two for each filter medium, were set up as shown in Figure 2(a) and Figure 3. First the columns were saturated by pumping 5mM $CaSO_4$ solution (adjusted pH to ~7) upward at ~116.8 mL/h until the water in the columns reached to the 1.3 cm i.d. overflow fitting. The time for water in each column reaching overflow fitting was recorded. The column mass differences before and after saturation were also recorded. After saturation, six rounds of leaching experiments were conducted following the time schedule showed in Figure 4. In each round, 5mM $CaSO_4$ solution was continually pumped upward at ~116.8 mL/h for 10 hours. One composite effluent sample (~1168 mL) was collected from the overflow tubing of each column for each leaching experiment. The pH and electric conductivity (EC) were measured for the influent and effluent solutions, and samples were filtered with 0.22 μm nylon membrane filters before storage at 4℃. These samples were analyzed for total organic carbon (TOC) and total dissolved nitrogen (TDN) with a carbon/nitrogen (CN) analyzer, while total dissolved phosphorus (TDP) was determined by inductively coupled plasma mass spectrometry (ICP).

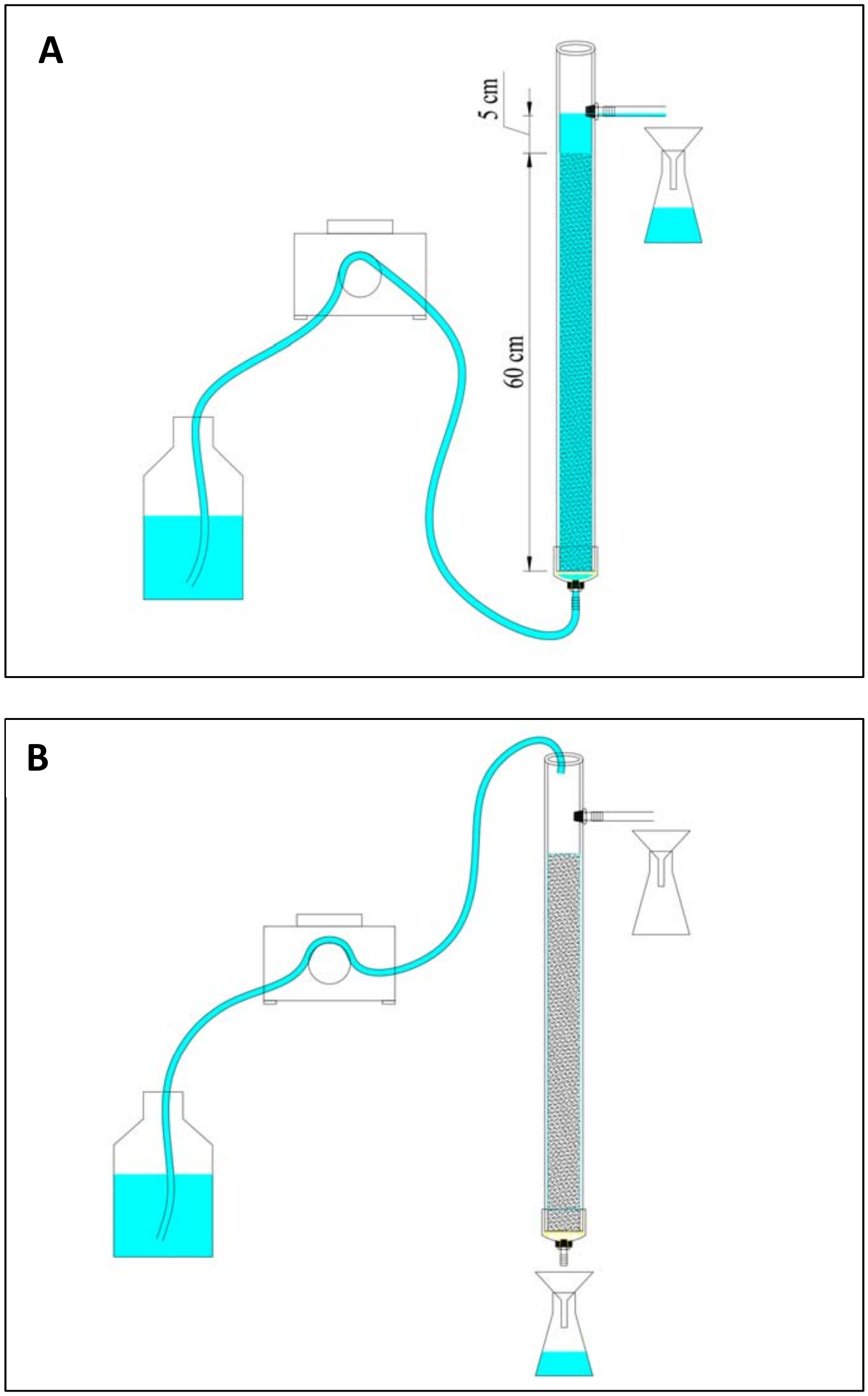

Figure 2. The column setup of the leaching (a) and nutrient removal (b) experiments.

Figure 3. Photographs of column setups for evaluating six bioretention media.

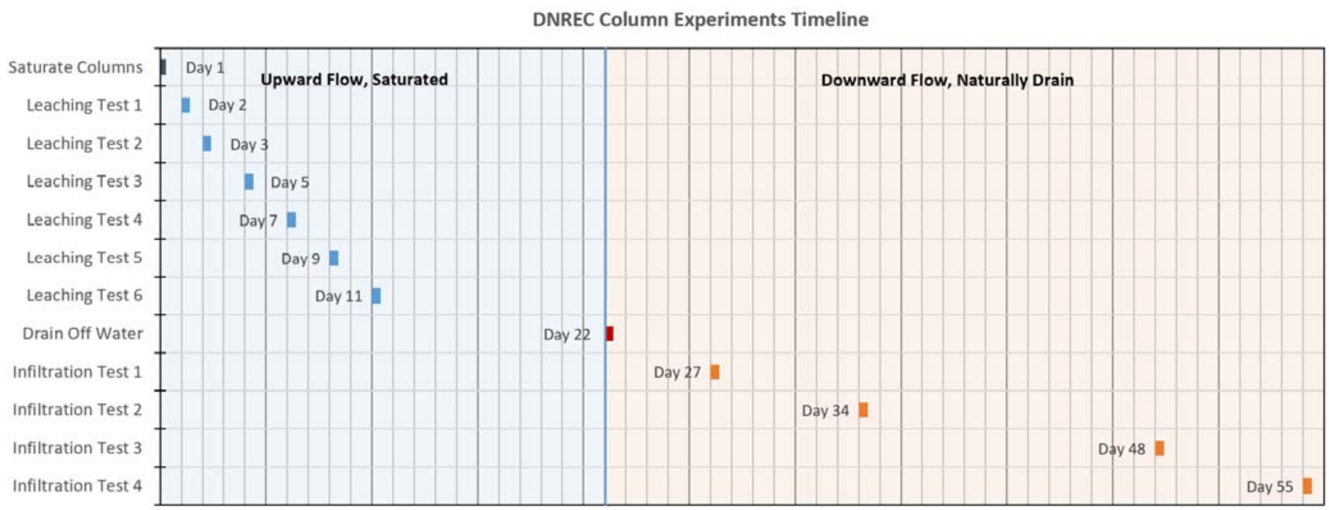

Figure 4. The timeline of the leaching (light blue highlight) and infiltration (light orange highlight) experiments.

iii. Stormwater Infiltration Experiments

Before the stormwater infiltration experiments, water in the saturated columns from the leaching test was drained by disconnecting the bottom tubing on Day 22 and re-setting up each column as shown in Figure 2(b) for subsequent infiltration tests. Four rounds of stormwater infiltration tests were conducted on the days listed in Figure 4 to evaluate the effect of each mixture on nutrient removal from synthetic stormwater and stormwater infiltration rate. The influent solution contained 5mM $CaSO_4$, 2 mg/L NO_3-N ($NaNO_3$), and 0.6 mg/L PO_4-P (Na_2HPO_4) with pH adjusted to ~7. This solution was pumped into the top of each column at ~116.8 mL/h for 10 hours for each infiltration test. Most of this water percolated through each bioretention medium, while depending on the medium and the infiltration test some water ponded on the surface and was then discharged as surface water runoff, which exited the top fitting above the surface of the bioretention column. The ponded water depth was recorded every 30 minutes, and the surface water runoff was also weighed every 30 minutes. One composite effluent sample was collected from the bottom of each column for each infiltration test. The pH and EC were measured for each influent and effluent sample, and theses samples were filtered with 0.22 μm nylon membrane filters before storage at 4℃. TDN and TDP were analyzed with the methods mentioned above, while NO_3-N and NH_4-N were measured colorimetrically using a Bran&Luebbe AutoAnalyzer 3 (Bran&Luebbe, Buffalo Grove, IL). PO_4-P was also analyzed.

c. Planted Pot Experiments

Planted pot experiments were designed to evaluate the potential benefit of biochar amendment on survivability and plant growth in Delaware bioretention medium, Biosoil-14, and the North Carolina bioretention medium. It was hypothesized that biochar would increase the plant available water content and thus enable plants to survive during periods of drought.

The Delaware medium was amended with 4% biochar, and the North Carolina medium was amended with 2 and 4 % biochar by mass. The compositions of the media tested in the pot experiments are given in Table 1. While six bioretention media were tested in the column experiments, five were evaluated in the planted pot experiments. The media common to both studies were NC-mix, NC-4B, DE-mix, and DE-4B.

Table 2. Percent composition by mass of the five bioretention used in planted pot experiments.

Abbrev.	Mixture (dry mass fraction)
NC-mix	88% sand, 8% fines, 4%sawdust (NCDWQ bioretention filter media)
NC-2B	86% sand, 8% fines, 4% sawdust, 2% biochar (NC w/ 2% biochar)
NC-4B	84% sand, 8% fines, 4% sawdust, 4% biochar (NC w/ 4% biochar)
DE-mix	89% sand, 6% mulch, 5% compost (DNREC Biosoil-14)
DE-4B	85% sand, 6% mulch, 5% compost, 4% biochar (DNREC Biosoil-14 w/4% biochar)

Media were packed into 20 1-gallon plastic pots: five different test media with four replicates for each medium. All pots were packed with at least 15 cm of soil depth. Initially, leaching experiments were conducted to decrease the quantity of soluble salts in the media, which was believed to inhibit plant growth in previous tests. Pots were leached for three days with dechlorinated tap water with 120 mg/L $CaCl_2$ to mimic nutrient-free stormwater water at a hydraulic loading rate of 240 mL/hour for 10 hours each day. Electrical conductivity and pH of the effluent were measured during each leaching test.

After the leaching tests, switchgrass (Latin name: *Panicum Virgatum*), a common grass grown in bioretention media, was planted in each pot on March 5, 2019. A plug of switchgrass was placed in each pot and the pots were placed in a plant growth chamber in the University of Delaware's greenhouse where humidity and temperature were controlled. A photograph of the pots with media and plants are shown in Figure 5.

Figure 5. All medium treatments planted with switchgrass.

In the growth chamber, the daytime temperature was set at 75 ºF while 73 ºF was set as the nighttime temperature. Relative humidity was kept constant at 50% for day and night. Light was cycled on and off in the chamber to mimic the day/night cycle over each 24-hour period. Plants were watered once a week over four months (March-July 2019) with a synthetic stormwater solution: 2.6 L water was added to each pot to mimic a 10-hour storm event. The artificial stormwater used in these experiments is listed in Table 3.

Table 3. Composition of synthetic stormwater used in planted pot experiments.

Parameter	Value (mg/L, except pH)	Source
pH	7.0	HCl or NaOH
Total Dissolved Solids	120	$CaCl_2$
Phosphorous	3 (as P)	Na_2HPO_4
Nitrate	2 (as N)	$NaNO_3$
Ammonium	2 (as N)	NH_4Cl

The volumetric water content (VWC) of each pot was measured twice a week with a time-domain reflectometry (TDR) sensor and by weighing the pots before and after watering. To monitor the plant growth in the pots, the maximum height of each plant, known as the shoot height, and the number of tillers were measured weekly. The chlorophyll content of plant leaves was also measured at selected times. To quantify nutrient removal rates for the planted pots, nitrogen and phosphorus concentrations in the cumulative effluent for selected synthetic storm events were measured. Nutrient leaching tests were conducted on July 19 and July 26, 2019. These dates corresponded to watering dates for the plants. On each date, 2.6 L of the artificial stormwater was added to each pot using the same hydraulic loading rate of 240 mL for 10 hours as used in the watering experiments. The water that dripped from the bottom of each pot was well mixed and then sampled. Samples were filtered and stored at 4 C^0 until analysis.

Finally, water stress experiments were initiated. Here, weekly plant watering was ceased for six weeks to mimic drought conditions that might occur during dry periods in the summer. Volumetric water content, plant height, chlorophyll content, and number of tillers were measured at selected times to evaluate if biochar amendment would enhance the survivability of plants under dry conditions. A timeline summarizing the dates associated with all steps in the planted pot experiments is provided in Table 4.

Table 4. Timeline of the planted pot study.

Activity	Date
Packing the pots	12/5/18
Leaching the pots	12/15/2018-12/18/2018
Transplanting the plants	3/5/19
Weekly watering	3/5/19-7/29/2019
Measurements of Vertical height of plants	3/5/19-7/26/2019
Measurement of the number of tillers	3/5/19-7/26/2019
Measurement of Volumetric Water Content	3/5/19-7/26/2019
Chlorophyll level measurement - 1	7/10/19
Chlorophyll level measurement - 2	7/17/19
Chlorophyll level measurement - 3	7/24/19
Nutrient Removal Test - 1	7/19/19
Nutrient Removal Test - 2	7/26/19
Water stress period	7/30/2019-ongoing

3. Experimental Results

a. Column Experiments

The results from the leaching tests are shown in Figure 6. Significant quantities of organic carbon and nutrients were leached in the first leaching event on Day 1, but these quantities decreased with leaching event. Biochar amendment to the North Carolina and Delaware bioretention media, NC-4B and DE-4B, respectively, resulted in a significant decrease in leached TOC. Leached TDN was also less for DE-4B than for the Delaware medium without biochar, DE-mix, while biochar amendment did not significantly affect TDP concentrations in the leached water. Leaching tests with and without the mulch and compost in the Delaware medium, DE-SMB and DE-SCB, indicate that most of the carbon, nitrogen, and phosphorus leaching from the Delaware medium came from compost.

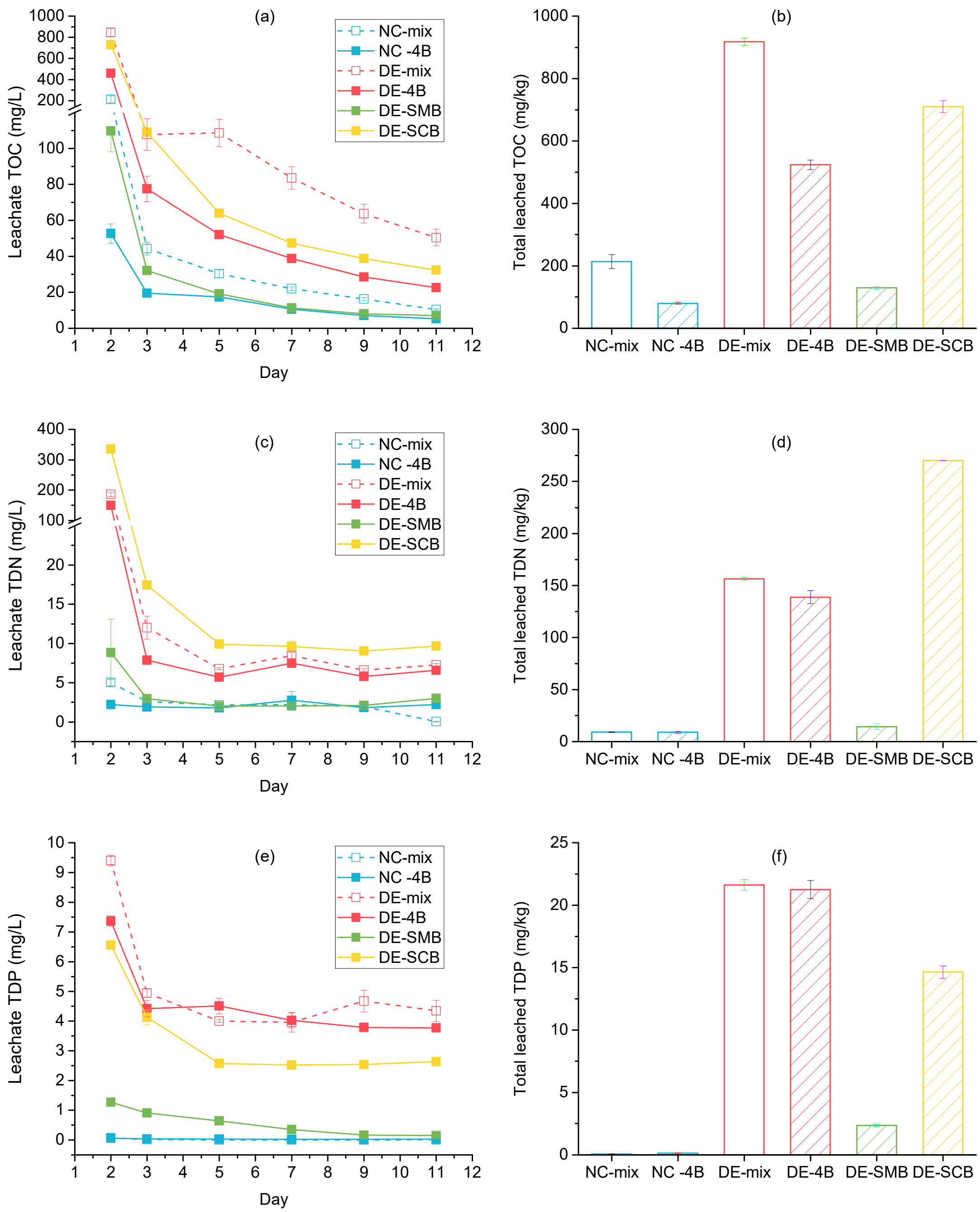

Figure 6. Leaching tests data for bioretention media before stormwater infiltration experiments: (a-b) total organic carbon (TOC), (c-d) total dissolved nitrogen (TDN), and (e-f) total dissolved phosphorus (TDP). For each constituent, the left plot illustrates the concentration in leached water and the right plot the total mass leached.

Four synthetic storm events were conducted following the leaching tests, with approximately one week of "rest" between each stormwater event as indicated in Figure 4. The concentrations of nitrogen in the influent and in the cumulative effluent for each test are shown in Figure 7.

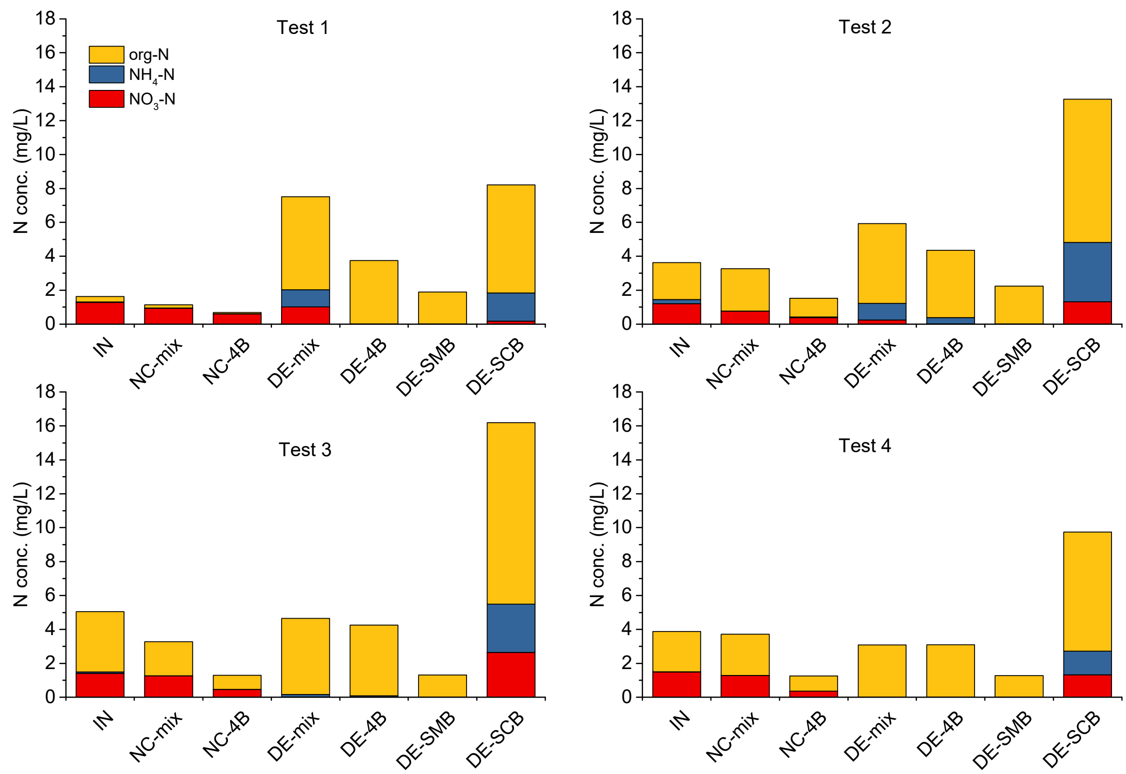

Figure 7. Different forms of nitrogen in the influent and effluents from six bioretention media for four infiltration tests.

While the influent nitrogen was predominantly nitrate for Test 1, as would be expected from the composition of the synthetic stormwater, a significant quantity of organic nitrogen was detected in Tests 2-4, approximately equal to the nitrogen as nitrate concentration. This was an unexpected result. Further investigation suggested that the source of this organic nitrogen was a very fine biochar dust that was generated in the laboratory in which these experiments were conducted by a daily sieving operation. This fine dust was deposited into the influent container, which was used to deliver synthetic stormwater to all 12 columns simultaneously. The concentration of organic nitrogen was approximately 50% of the total nitrogen for Tests 2-4, and the total nitrogen concentration was ~ 4 mg/L for these tests rather than 2 mg/L, which was expected based upon the composition of the synthetic stormwater.

Results for the North Carolina and Delaware bioretention media indicate that when biochar is added at 4% by mass, the removal of nitrogen increased significantly. The North Carolina bioretention medium without biochar (NC-mix) resulted in minimal removal of nitrate and organic nitrogen, as illustrated for Tests 1-4 in Figure 7. On the other hand, for all tests with biochar amendment (NC-4B) significant reductions in both organic nitrogen and nitrate in the effluent were observed. The improvement in nitrogen removal with biochar amendment was less significant for the Delaware bioretention medium, though, with only modest reductions observed for Tests 3 and 4, for example. For the Delaware bioretention medium, the compost served as a significant source of nitrogen that continued to contribute to effluent nitrogen and mitigated the beneficial effects of biochar.

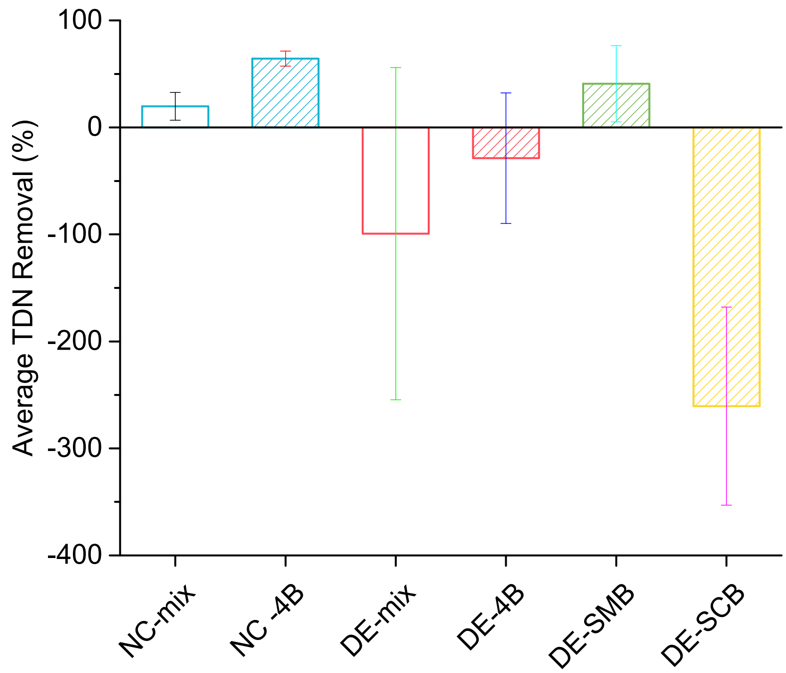

Figure 8. Average percent removal of total dissolved nitrogen over all four tests for each medium. Negative removal indicates bioretention medium leaches more nitrogen than is removed. Error bars represent ± one standard error of the mean.

The average percent removal of total dissolved nitrogen (TDN) over all four tests is shown Figure 8. For both the North Carolina and Delaware bioretention media, biochar reduced the mean TDN concentrations. For the North Carolina medium, biochar amendment increased the mean TDN removal rate from 20 to 64%, a factor of three improvement. For the Delaware medium, biochar amendment improved the mean TDN removal rate from -99% to -29%. Adding biochar reduced nitrogen leaching from the Delaware medium. The source of nitrogen leaching is primarily from compost in the Delaware medium. Thus, when compost is replaced with biochar in the Delaware medium (DE-SMB), TDN removal rate is positive and 40%. It is also important to note that the error bars and thus the uncertainty in the treatment efficiency are large for the Delaware medium but small for the North Carolina medium. This occurred primarily because the mulch and compost in the Delaware medium were not stable and continued to leach nitrogen compounds over the four tests, with amounts leached changing with infiltration event.

The concentrations of phosphorus in the influent and in the cumulative effluent for each test are shown in Figure 9. While phosphorus was only added as phosphate in the synthetic stormwater, a small amount of organic phosphorus was measured in the influent for Tests 3 and 4, which we believe was associated with biochar dust. Most of the phosphorus in the influent for all tests was phosphate.

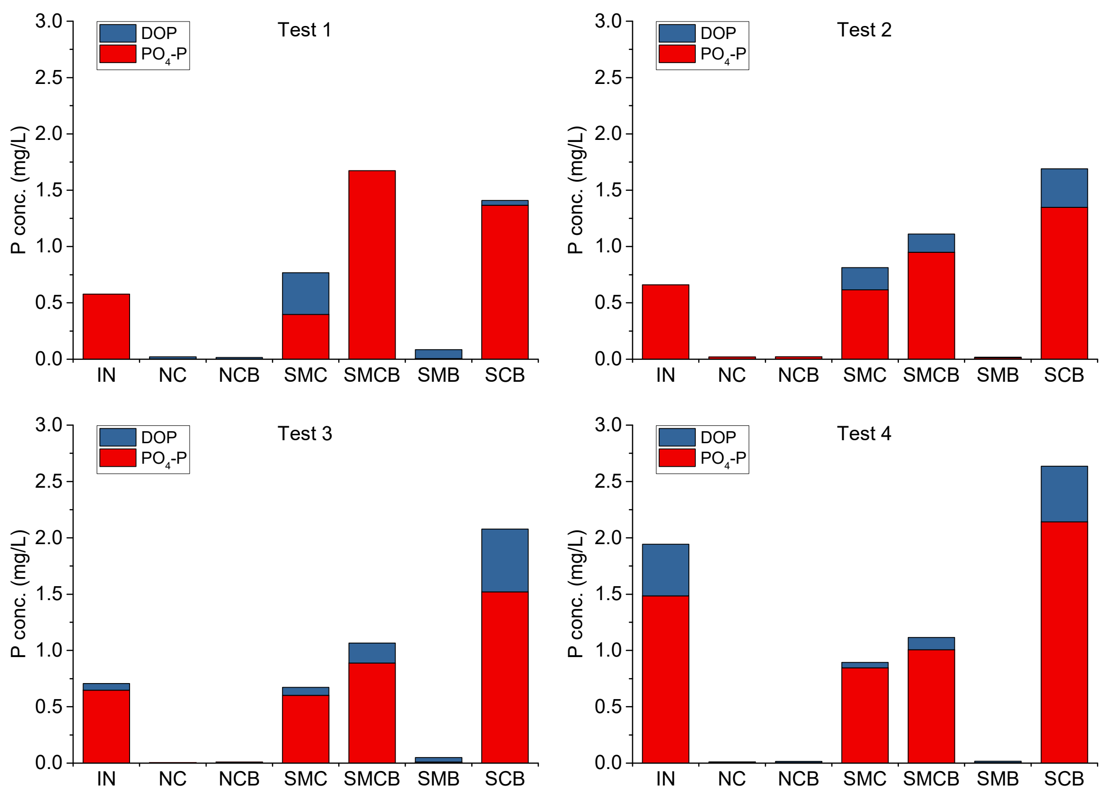

Figure 9. Different forms of phosphorus in the influent and effluents from six bioretention media for four infiltration tests.

The North Carolina bioretention medium was efficient in removing total dissolved phosphorus (TDP) as shown in Figure 9. The average removal rates for all four tests are shown in Figure 10. Either with or without biochar amendment, TDP removal was 98-100%. The removal rate for the Delaware medium was much less, with the average removal rate -61% and 1% for the medium with or without biochar, respectively. The error bars for these data are large and associated with the significant leaching of phosphorus from the compost in the Delaware bioretention medium (see Figure 6). With compost removed, the average removal rate for TDP was 94%. While the addition of biochar improved removal of TDN in both North Carolina and Delaware bioretention media, biochar either had no effect (North Carolina) or a detrimental effect (Delaware) on removal of TDP. Since phosphate was the dominate form of TDP in the influent (see Figure 9), is primarily remove by adsorption and precipitation in bioretention media, and since biochar was not believed to enhance this process significantly, the fact that biochar did not improve removal of TDP was not unexpected.

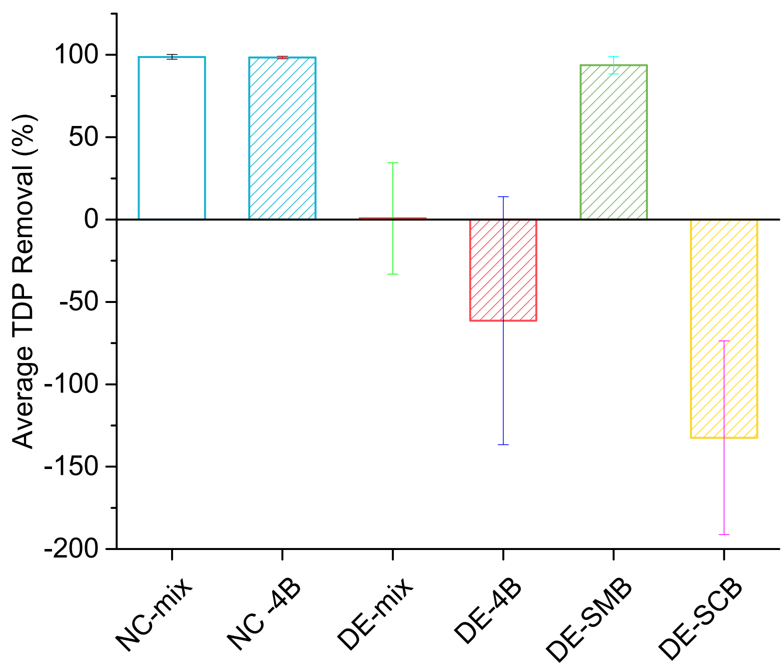

Figure 10. Average percent removal of total dissolved phosphorus over all four tests for each medium. Negative removal indicates bioretention medium leaches more phosphorus than is removed. Error bars represent ± one standard error of the mean.

Two other observations about the impact of biochar amendment on the bioretention media in these experiments should be noted. First, biochar amendment improved the stormwater retained in the bioretention media. Figure 11 illustrates this result for Test 4, were the volumetric water content retained in the media are shown after drainage ceased from all media in Test 4. Biochar amendment increased water retention for both the North Carolina and Delaware media, by approximately 20% for both media. Increasing water retention will result in better capture of stormwater for treatment and aid plant growth.

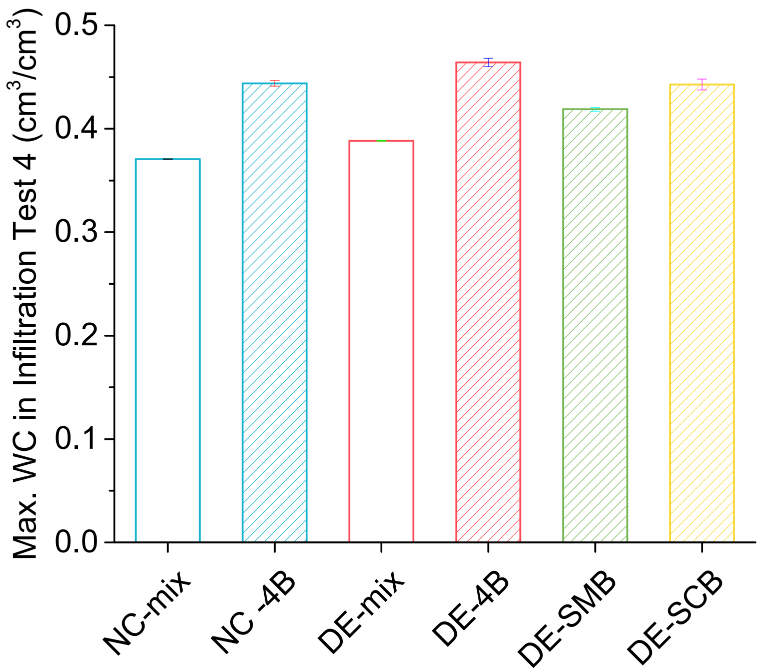

Figure 11. Volumetric water content retained in bioretention media after drainage of stormwater for Test 4. Error bars represent ± one standard error of the mean.

Biochar amendment also improved the bulk density of the media, as shown in Figure 12. The reduction in dry bulk density with biochar may enhance plant root growth.

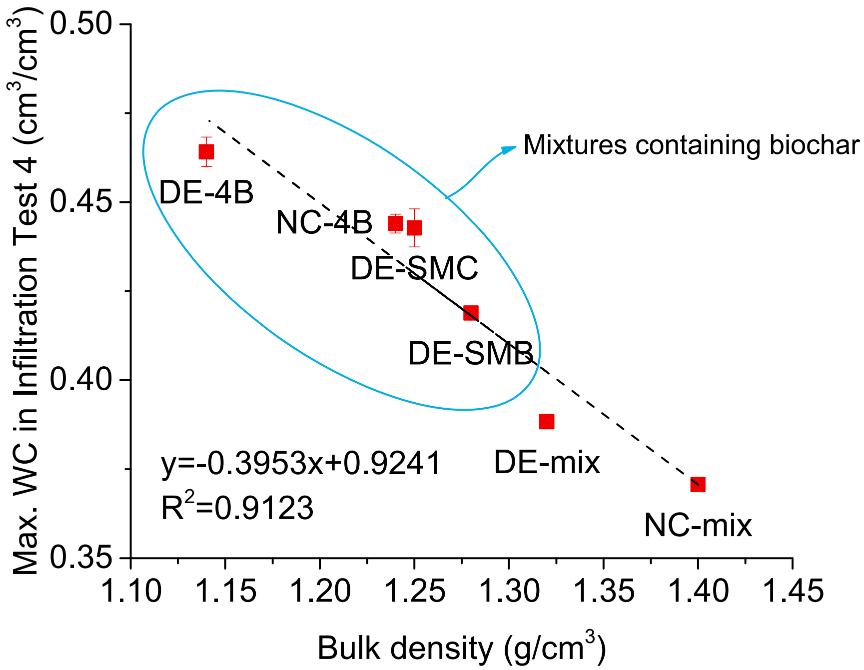

Figure 12. Volumetric water content retained in bioretention media after drainage of stormwater for Test 4 plotted against dry bulk density of each medium. Error bars represent ± one standard error of the mean.

b. Planted Pot Experiments

i. Nutrient Removal

Two nutrient removal tests during synthetic stormwater experiments were conducted on July 19 and 26/ 2019. Samples were obtained from the effluent after plant watering. NO_3-N, PO_4-P, TDN, and TDP removal rates are shown below in Figures 13-16. Error bars on the graphs show the standard error of the mean of four replicates for each media type

From the Figures 13-16, these observations are made:

- The removal of NO_3-N was highest in media amended with 4% biochar. Percent removal was as much as 70% in the North Carolina medium amended with 4% biochar, but as small as 40% in the unamended North Carolina medium. Similar results occurred for the Delaware bioretention medium. The NO_3 removal rate was approximately 58% in the amended medium but 35% in the unamended medium. The higher removal rates in North Carolina versus Delaware media may be because of the increase in residence time. The Delaware media had higher infiltration rates (almost doubled that of North Carolina media), which resulted in smaller residence times that directly affects removal by denitrification.

- Removal of PO_4-P was higher in North Carolina media compared to Delaware media. Since P is the fundamental nutrient for plant growth, PO_4-P might be taken up by switchgrass as a source of P. There was no significant difference in PO_4-P removal rate in biochar amended and unamended media for each treatment.
- A significant difference in TDN removal was observed in amended and unamended media for each bioretention type. Removal rates for TDN were higher in 2% and 4% amended media than the unamended North Carolina medium, with TDN removal rate higher with 4% than 2% biochar content. However, the Delaware media (amended and unamended) had a negative removal rate indicating nitrogen leached from the media. The biochar amended Delaware medium leached less TDN than the unamended medium.
- The removal of TDP in North Carolina media decreased slightly with increasing biochar content. Although there was no statistically significant difference in TDP removal for biochar-amended or unamended media, TDP removal was higher in the unamended than the 2% and 4% amended North Carolina medium. In contrast to the North Carolina media, TDP leaching was observed in the Delaware medium just as was observed for TDN. TDP leaching was higher in the biochar-amended Delaware medium than the unamended medium.

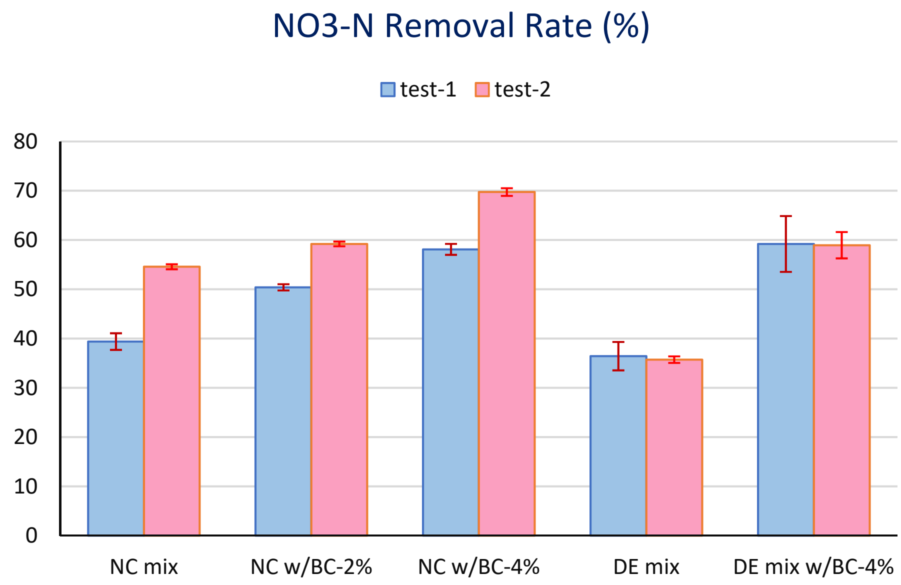

Figure 13. Nitrate removal rate for all bioretention media. Error bars represent the standard error of the mean of four replicates.

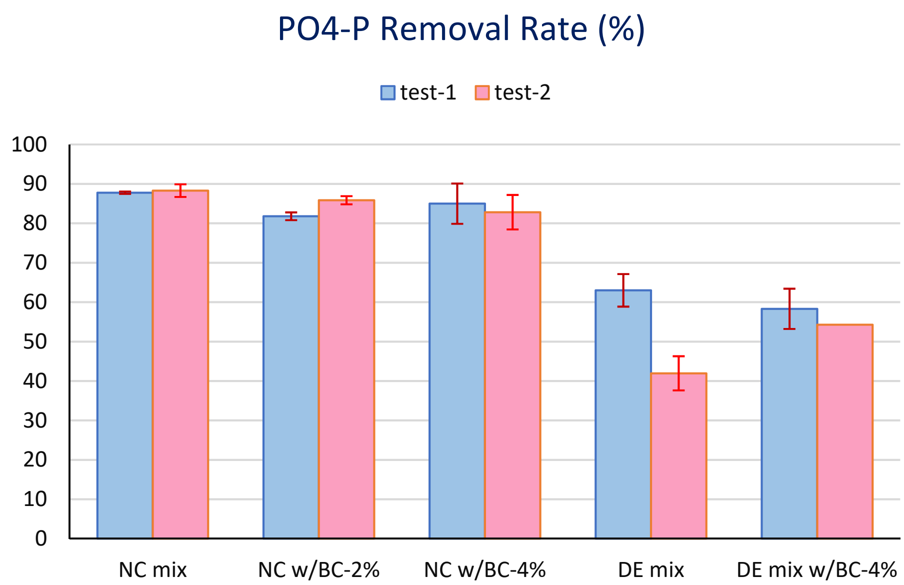

Figure 14. Phosphate removal rate for all bioretention media. Error bars represent the standard error of the mean of four replicates.

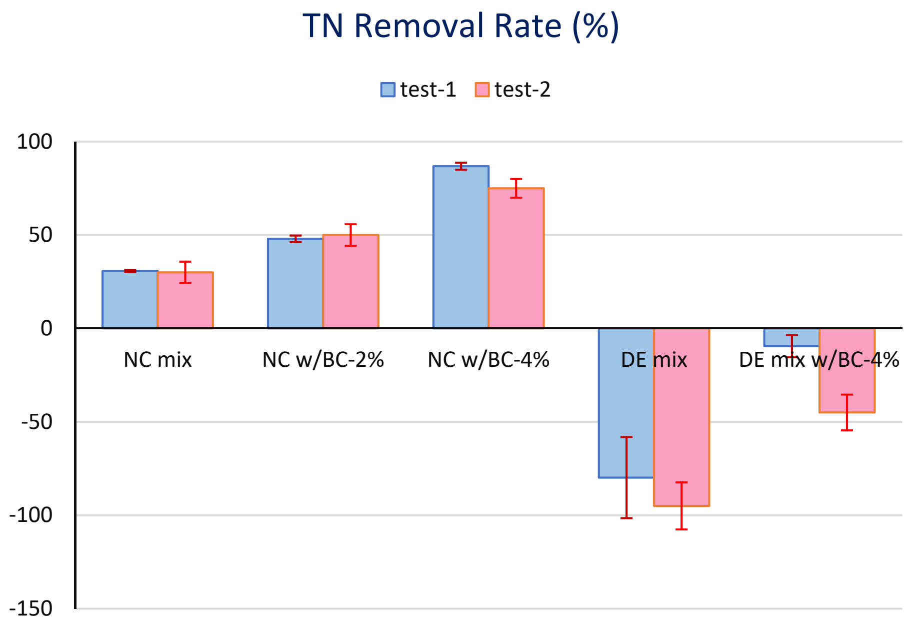

Figure 15. Total dissolved nitrogen (TDN) removal rates for all bioretention media. Error bars represent the standard error of the mean of four replicates.

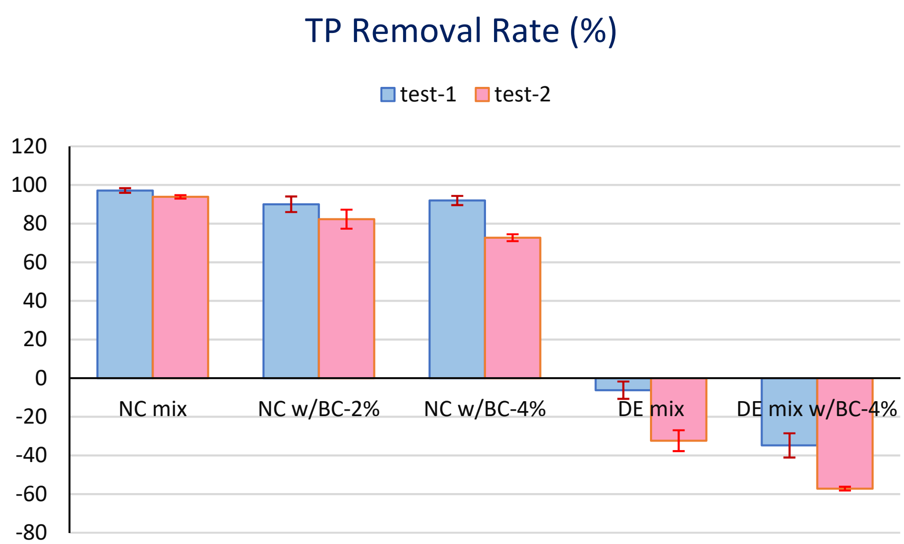

Figure 16. Total dissolved phosphorus (TDP) removal rates for all bioretention media. Error bars represent the standard error of the mean of four replicates.

A single factor Analysis of Variance (ANOVA) was applied to analyze the data using R (version 3.6.1). Tukey's Honestly Significant Difference (HSD) test was applied for the analysis of interactions between treatments. Statistical significance of the data set was determined at a 95% confidence interval ($p < 0.05$), and results are summarized in Tables 5 and 6 for Tests 1 and 2, respectively. The statistical tests confirm the observations noted above: biochar amendment resulted in significantly improved removal of NO_3-N and TDN in North Carolina and Delaware media, but resulted in significantly decreased removal of TDP for the North Carolina (Test 2 only) and Delaware media. While the improvement in removal of TDN with biochar amendment was expected, we did not anticipate the reduction in TDP removal. This observation is consistent with the results from the column experiments but is unexplained.

Table 5. Tukey's HSD test for nutrient removal rate in media types for Test 1.

Constituent	HSD test for media type NC-NCw/BC-2%	HSD test for media type NC- NCw/BC-4%	HSD test for media type NB2%-NB4%	HSD test for media type DEmix-DEw/BC-4%
NO3-N	No difference in means at 95% confidence level (p=0.100)	***Means differ at 95% confidence level (p=0.001) NCB>NC***	No difference in means at 95% confidence level (p=0.236)	***Means differ at 95% confidence level (p=0.003) DEB>DEmix***
PO4-P	No difference in means at 95% confidence level (p=0.890)	No difference in means at 95% confidence level (p=0.616)	No difference in means at 95% confidence level (p=0.982)	No difference in means at 95% confidence level (p=0.966)
TDN	No difference in means at 95% confidence level (p=0.740)	***Means differ at 95% confidence level (p=0.010) NCB>NC***	No difference in means at 95% confidence level (p=0.099)	***Means differ at 95% confidence level (p=0.001) DEB>DEmix***
TDP	No difference in means at 95% confidence level (p=0.730)	No difference in means at 95% confidence level (p=0.892)	No difference in means at 95% confidence level (p=0.997)	***Means differ at 95% confidence level (p=0.001) DEmix>DEB***

Table 6. Tukey's HSD test for nutrient removal rate in media types for Test 2.

Constituent	**HSD test for media type NC-NCw/BC-2%**	**HSD test for media type NC- NCw/BC-4%**	**HSD test for media type NB2%-NB4%**	**HSD test for media type DEmix-DEw/BC-4%**
NO3-N	No difference in means at 95% confidence level (p=0.105)	***Means differ at 95% confidence level (p=5.7E-6) NBB>NC***	***Means differ at 95% confidence level (p=0.0005) NBB>NB***	***Means differ at 95% confidence level (p=1E-07) DEB>DEmix***
PO4-P	No difference in means at 95% confidence level (p=0.871)	No difference in means at 95% confidence level (p=0.571)	No difference in means at 95% confidence level (p=0.979)	No difference in means at 95% confidence level (p=0.054)
TDN	No difference in means at 95% confidence level (p=457)	***Means differ at 95% confidence level (p=0.011) NCB>NC***	No difference in means at 95% confidence level (p=0.255)	***Means differ at 95% confidence level (p=0.005) DEB>DEmix***
TDP	No difference in means at 95% confidence level (p=0.169)	***Means differ at 95% confidence level (p=0.004) NC>NCB***	No difference in means at 95% confidence level (p=0.315)	***Means differ at 95% confidence level (p=0.0001) DEmix>DEB***

ii. Plant Growth

The maximum plant height was measured for each plant through time, and the mean heights for each bioretention medium, four replicates each, are plotted through 20 weeks in Figure 17. For the North Carolina media, with and without biochar, plants grew rapidly in the first seven weeks and then maximum plant height plateaued. Decreases in maximum plant height were observed for the North Carolina media without biochar from week 7 through week 20. On the other hand, maximum plant heights for the Delaware media, with and without biochar, continued to increase through week 20. The more favorable growth in Delaware media was expected, since these media contained compost that both retained more water and leached more nutrients than the North Carolina media.

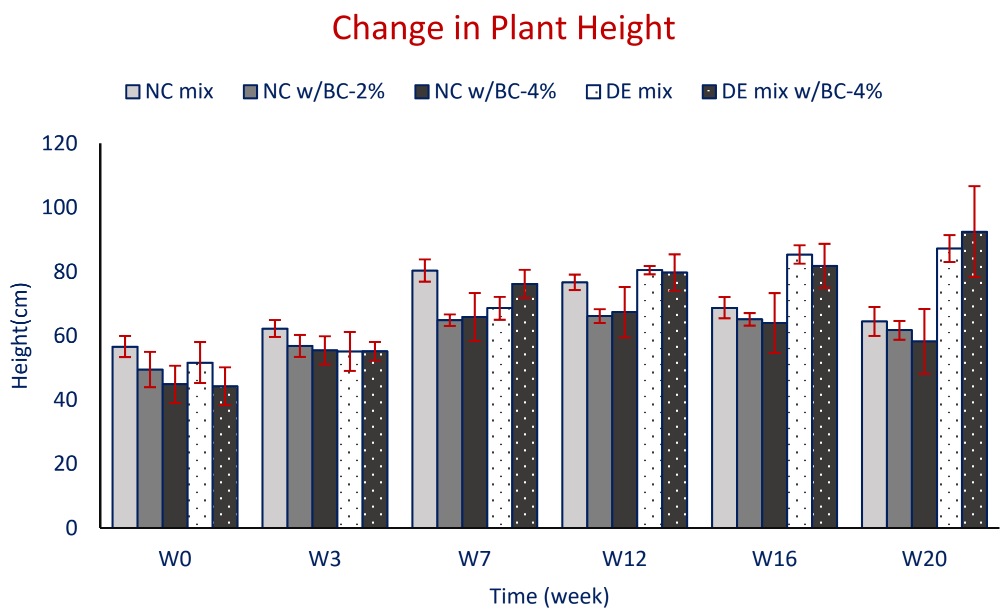

Figure 17. Maximum plant height under normal watering conditions averaged over the four replicates of each bioretention medium. Error bars represent the standard error of the mean of four replicates.

The relative increase in plant height between the start of the experiments, week 0, and week 20 was calculated from

$$relative\ increase = \frac{BC20 - BC0}{C20 - C0} \quad (1)$$

where *C0* is the initial parameter measurement of unamended media without biochar (NC-mix and DE-mix), *C20* is the parameter measurement of unamended media in week 20, *BC0* is the initial parameter measurement of biochar-amended media (NC-2B, NC-4B, and DE-4B), and *BC20* is the parameter measurement of amended media in week 20. These results are presented in Figure 18. For both the North Carolina and Delaware media, addition of biochar at either 2 or 4% by mass increased maximum plant height by approximately 150% over media without biochar.

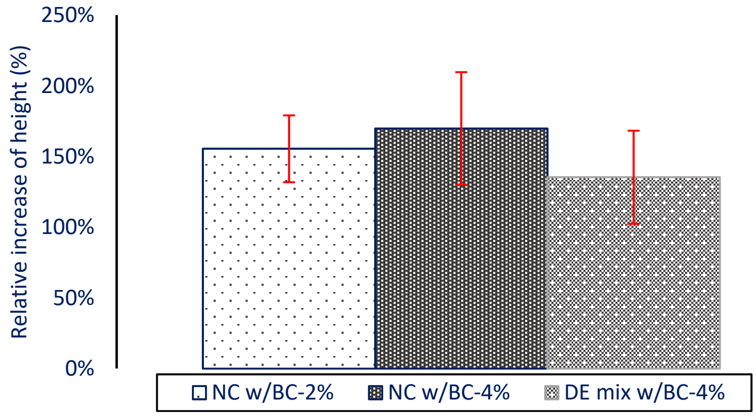

Figure 18. The relative increase of maximum plant height in biochar-amended media relative to unamended media without biochar. Error bars represent the standard error of the mean of four replicates.

Another measure of plant growth is the number of tillers for each plant, where a tiller is a stem produced by grass plants after the initial parent shoot grows. The growth rate of tillers, tillering, is significantly influenced by soil water. If soil moisture is low, few tillers form. The mean number of tillers observed for each plant in each bioretention medium is plotted in Figure 19. The mean number of tillers per plant generally remained the same or decreased with time for the North Carolina media, with biochar amendment mitigating this decrease. For plants in the Delaware media, though, the number of tillers increased in weeks 16 and 20.

Equation (1) was used to calculate the relative increase in tillers for each biochar treatment, and these results are shown in Figure 20. Biochar amendment showed a modest improvement in the number of tillers measured in the North Carolina medium: 60% and 20% for 2 and 4% biochar amendment, respectively. On the other hand, biochar amendment in the Delaware medium improved the relative change in number of tillers by a factor of 7. The reason for the more significant effect of biochar on tillering in the Delaware medium is unknown.

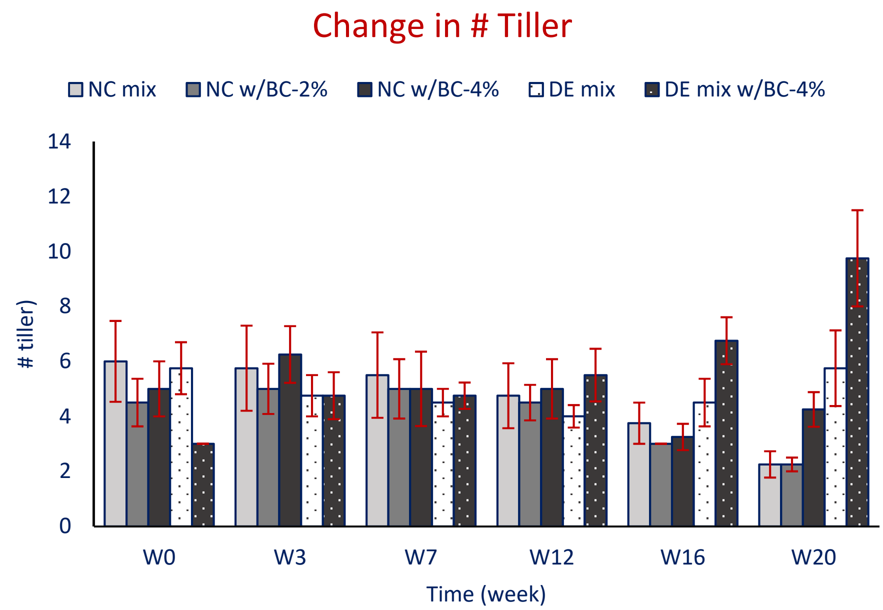

Figure 19. Mean number of tillers for each plant associated with each bioretention media for the 20-week growing period. Error bars represent the standard error of the mean of four replicates.

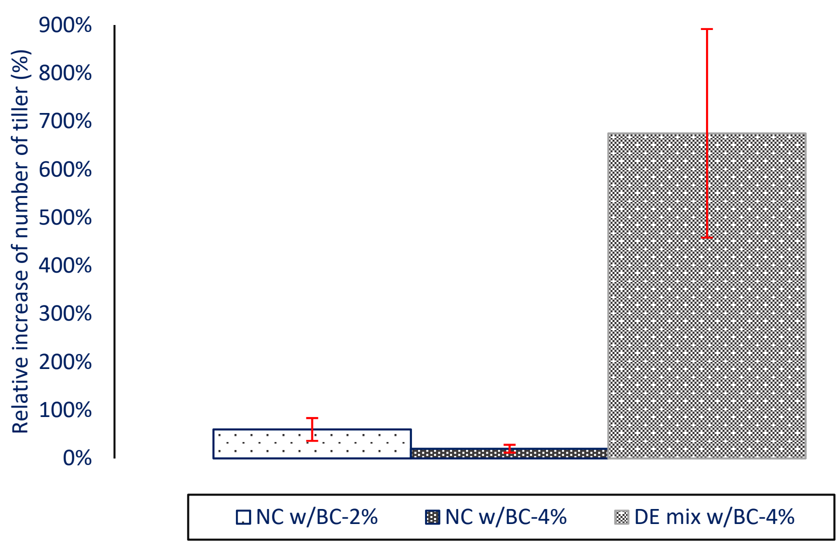

Figure 20. Relative change in the number of tillers associated with biochar amendment for the 20-week growth period. Error bars represent the standard error of the mean of four replicates.

iii. Chlorophyll Level

The leaf chlorophyll concentration of the plants (Leaf SPAD) was determined by using a SPAD meter (SPAD502 MINOLTA. Inc., IL, US) on July 10 (W18), July 17 (W19) and July 24 (W 20). Leaf SPAD values are shown in Figure 21. Values are the mean of the four replicates in each treatment medium.

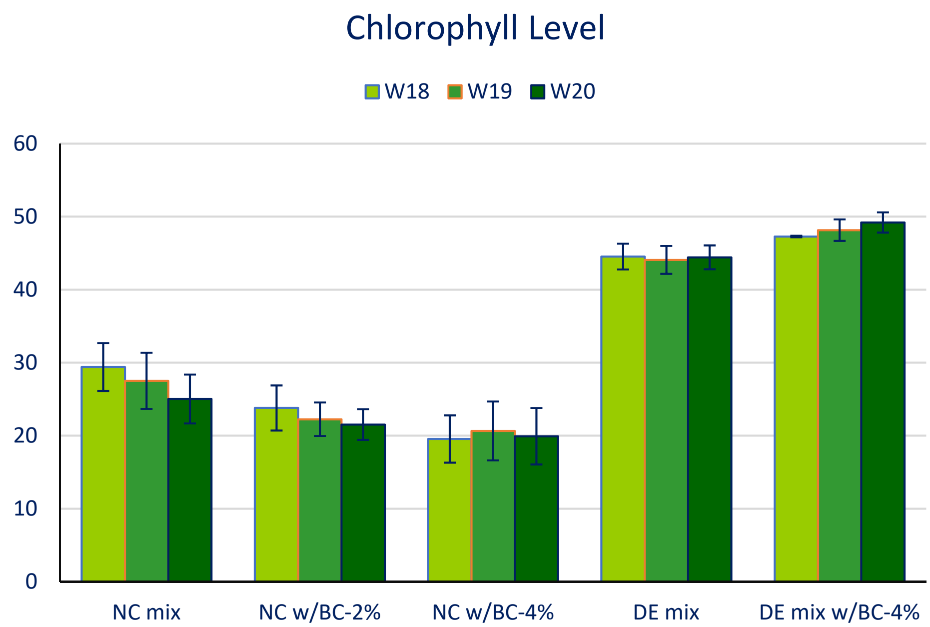

Figure 21. Mean Leaf SPAD for plants bioretention media in weeks 14,15 and 16. Error bars represent the standard error of the mean of four replicates.

A single factor ANOVA was used to analyze the data using R (version 3.6.1). Tukey's HSD test was applied for the analysis of interactions between treatments. Statistical significance of the data set was determined at a 95% confidence interval, and these results are shown in Table 7. Chlorophyll concentrations decreased slightly with increasing biochar content for the North Carolina medium, possible because biochar enhanced TDN removal from stormwater which might cause a slight nitrogen deficiency in plants (Figure 15). By week 18, the leaves of plants in biochar-amended media had turned yellow. However, the data were quite variable and for this reason the Leaf SPAD concentrations were not statistically significant for treatments with or without biochar in the North Carolina medium at 95% confidence level (Table 7).

In contrast to North Carolina medium where biochar amendment caused slight reductions in mean Leaf SPAD (Figure 21), biochar amendment to the Delaware medium resulted in chlorophyll concentrations that were slightly higher than in unamended media (Figure 21). However, because of significant variability in the measurements, the differences observed in Figure 21 between biochar-amended and unamended Delaware media were not statistically significant (Table 7).

The more dominant effect on chlorophyll concentration was the effect of the compost and mulch in the Delaware medium. Leaf SPAD was significantly larger in all packings of the Delaware medium than the North Carolina medium, as shown in Figure 21.

Table 7. Tukey's HSD test for differences in Leaf SPAD between bioretention media.

Constituent	HSD test for media type NC-NCw/BC-2%	HSD test for media type NC- NCw/BC-4%	HSD test for media type NB2%-NB4%	HSD test for media type DEmix-DEw/BC-4%
W18	No difference in means at 95% confidence level (p=0.652)	No difference in means at 95% confidence level (p=0.107)	No difference in means at 95% confidence level (p=0.698)	No difference in means at 95% confidence level (p=0.956)
W19	No difference in means at 95% confidence level (p=0.707)	No difference in means at 95% confidence level (p=0.0.480)	No difference in means at 95% confidence level (p=0.995)	No difference in means at 95% confidence level (p=0.855)
W20	No difference in means at 95% confidence level (p=0.879)	No difference in means at 95% confidence level (p=0.660)	No difference in means at 95% confidence level (p=0.992)	No difference in means at 95% confidence level (p=0.71)

iv. Volumetric Water Content – Non-Water Stress Periods

The volumetric water content (VWC) of each planted pot was measured with a TDR sensor as well as manually by weighing the pots before and after watering. Manual water content data and TDR output indicate that biochar increased the volumetric water content in North Carolina and Delaware bioretention media, as shown in Figures 22 and 23 for one example measurement period. Similar results were observed for all other measurement weeks. In all cases, biochar amendment resulted in significantly larger VWC than unamended media. These differences suggest biochar amendment may enhance plant survivability during periods of drought stress.

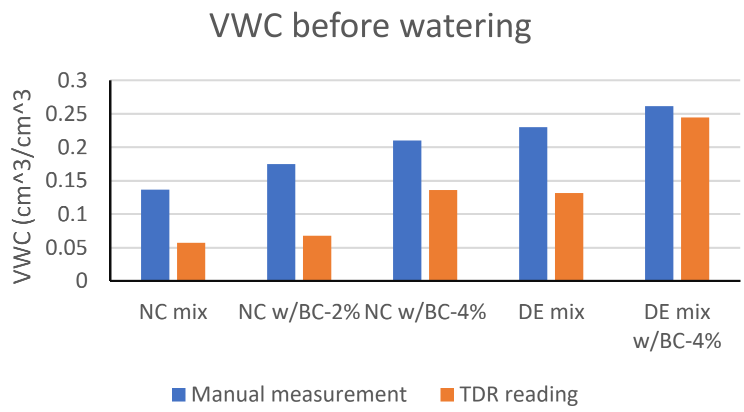

Figure 22. Mean volumetric water content for each bioretention medium before the time for one week of watering (26 July-2019).

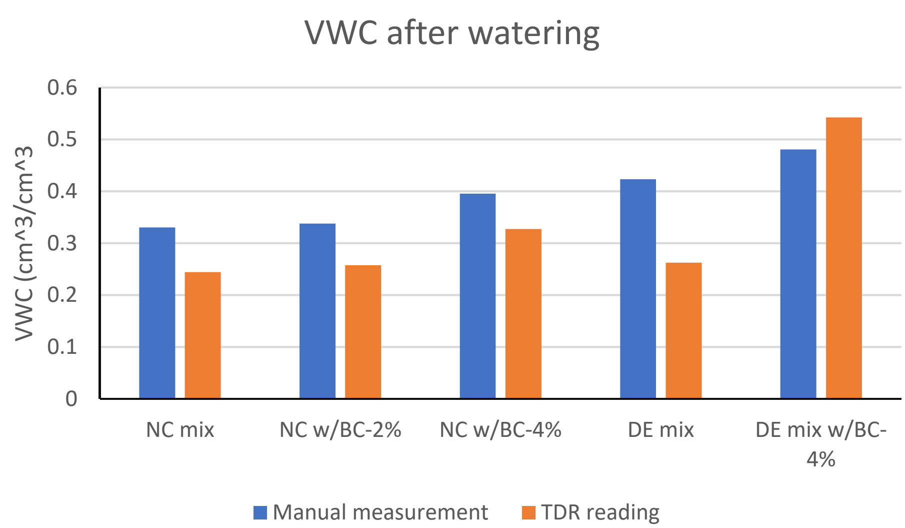

Figure 23. Mean volumetric water content for each bioretention medium after the time for one week of watering (26 July-2019).

v. Volumetric Water Content – Water Stress Period

The water stress period was initiated for six weeks to evaluate the effect of biochar amendment on the survivability of plants under drought-like conditions, mimicking dry periods that may occur in the summer. No water was added to the planted pots during this six-week period, and soil volumetric water content and chlorophyll levels in the plants were measured. Results of the measurements for volumetric water content and the chlorophyll level are shown in Figures 24 and 25, respectively. Measurements were taken on August 18, 2019, approximately two weeks into the water stress period.

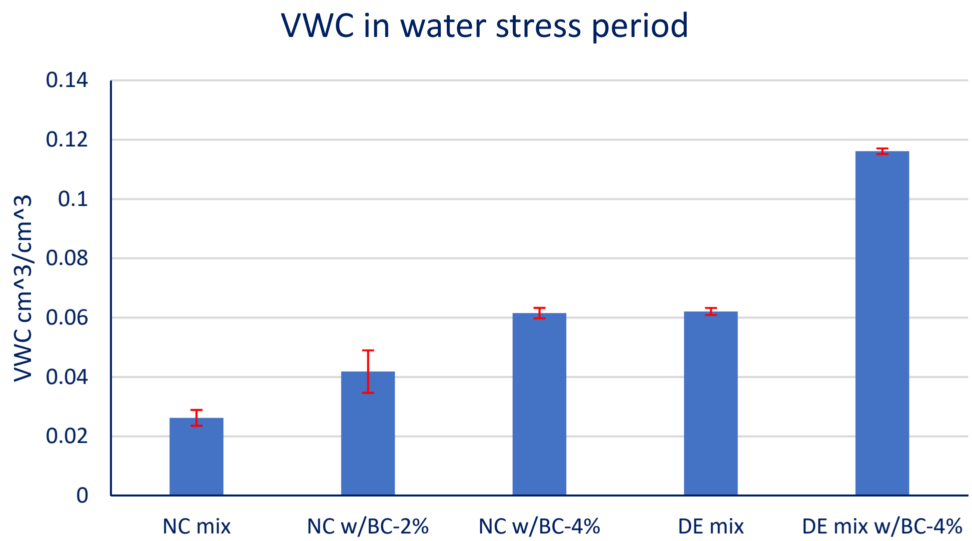

Figure 24. Mean volumetric water content of each medium after approximately two weeks under drought conditions. Error bars represent the standard error of the mean of four replicates.

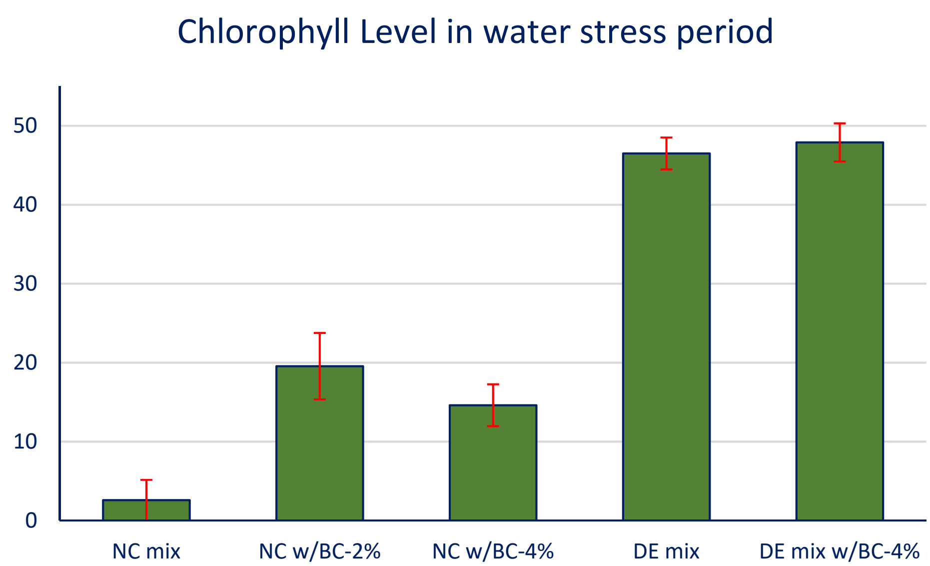

Figure 25. Mean Leaf SPAD of plants for each medium after approximately two weeks under drought conditions. Error bars represent the standard error of the mean of four replicates.

From Figures 24 and 25, the following observations are made:

- Biochar amendment enhanced the water availability for both North Carolina and Delaware bioretention media, with this improvement increasing with biochar content.
- Plants in the unamended North Carolina medium became wilted during the water stress period, which is reflected by the very low Leaf SPAD (Figure 25). However, plants in 2 and 4% biochar-amended North Carolina media were in better condition with higher Leaf SPAD, even though plant leaves were mostly yellow. In contrast, plants were still green in both the biochar-amended and unamended Delaware media, but Leaf SPAD was slightly higher in the biochar-amended medium.
- While there was a negligible difference in VWC for the North Carolina medium amended with 4% biochar and the Delaware medium (Figure 24), the Delaware medium without biochar had a significantly higher Leaf SPAD (Figure 25). The improved plant conditions in the Delaware medium likely resulted from the additional nutrients provided by the compost and mulch, which were absent in the North Carolina medium with 4% biochar. This effect is illustrated in Figure 26: planted pots in Delaware media on the left are much greener than planted pots in North Carolina media on the right.

Figure 26. Plant growth during water stress period (August 18, 2019): Delaware media with and without biochar (left image), and North Carolina media with and without biochar (right image).

4. Conclusions and Recommendations

The objective of this study was to evaluate if the improvement in nitrogen removal observed from biochar amendment to the North Carolina bioretention medium in the previous field study would be replicated in DNREC Biosoil-14, referred to as the Delaware bioretention medium in this investigation. Biochar amendment to both bioretention media improved the removal of total dissolved nitrogen (TDN). In column experiments, the average removal rate of TDN in the North Carolina medium with and without biochar at 4% by mass was 64 and 20%, respectively. Similar results were obtained for the Delaware medium, where TDN removal with and without 4% biochar was -99 and -30%, respectively. Biochar amendment reduced the leaching of nitrogen from the compost/mulch in the Delaware medium. These results were replicated in the planted pot experiments, where for two stormwater infiltration events 4% biochar amendment increased mean TDN removal rate from 30 to 80% and from -88 to -27% for the North Carolina and Delaware bioretention media, respectively.

Biochar amendment was not expected to affect removal of total dissolved phosphorus (TDP) significantly. In column experiments, biochar amendment to the North Carolina medium did not change TDP removal rates: with or without biochar a removal rate of 98-100% was achieved. Results were slightly different for the planted pot experiments, where 4% biochar amendment slightly decreased the mean TDP removal rate for two stormwater infiltration events from 94% to 83%. For the Delaware medium, though, biochar amendment resulted in increased leaching of TDP. In the column experiments, the mean TDP removal rate decreased from 0.7 to -61% with 4% biochar amendment. Similarly, in planted pot experiments the mean TDP removal rate decreased from -19 to -46%. The mechanism by which biochar causes increased leaching of phosphorus from the compost/mulch in the Delaware bioretention medium is unknown.

The influence of biochar amendment on plant growth under normal and water stress conditions was also examined. In the North Carolina and Delaware bioretention media under weekly watering, biochar amendment increased stored water that favors plant growth. Relative to conditions immediately after planting switchgrass, biochar amendment to both media resulted in taller plants with more tillers. While biochar amendment caused small decreases in chlorophyll concentrations in plant leaves in the North Carolina medium, in the Delaware medium biochar amendment increased chlorophyll concentrations. Because nutrient limitations were probably more significant in the North Carolina medium since it did not contain compost found in the

Delaware medium, biochar amendment may have caused a reduction in nutrient availability (sorbing organic nitrogen, for example) that affected chlorophyll content.

While data for the water stress period are still being collected, biochar amendment resulted in increased chlorophyll content of plant leaves in the North Carolina medium after approximately two weeks without watering. Here, the additional water retained because of biochar amendment in this medium enhanced plant vitality. While under weekly watering conditions biochar amendment resulted in slight reductions in the chlorophyll content of plant leaves in the North Carolina medium, under water stress conditions biochar amendment increased chlorophyll content. On the other hand, after approximately two weeks without watering biochar amendment resulted in no significant differences in chlorophyll content in the Delaware medium. This situation may change in subsequent weeks without watering, when the soil water deficit increases. Future data will be collected to assess this possibility for the Delaware bioretention medium.

In summary, in both column and planted pot experiments biochar amendment to the North Carolina bioretention medium resulted in improved removal of total dissolved nitrogen, minor changes to removal of total dissolved phosphorus, and improved water retention and plant growth, particularly during periods of water stress. Biochar amendment to DNREC Biosoil-14 resulted in reduced leaching of total dissolved nitrogen, increased leaching of total dissolved phosphorus, and improved plant growth. While the negative impact of biochar amendment on phosphorus leaching for DNREC Biosoil-14 was unexpected, this might be avoided if biochar was added to a sublayer in the bioretention system. Here, biochar might be placed in a sand layer below a layer of Biosoil-14 where plants are grown. In this configuration, biochar would provide the beneficial increase in nitrogen removal observed with the North Carolina medium while avoiding any increase in phosphorus leaching. Future studies might explore this design if the increase in phosphorus leaching from Biosoil-14 is deemed unacceptable.

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