FINAL REPORT

Removing Nitrate from Stormwater with Biochar Amendment to Roadway Soils

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16. Abstract

A combination of field and laboratory studies evaluated the impact of amending a wood-derived biochar to a roadway soil on stormwater runoff and water quality. At the field site, biochar amendment continued to demonstrate significant reductions in peak stormwater flow and cumulative runoff volume three years after construction. More limited water quality data indicate the biochar amendment reduced NO3 and TN concentrations in subsurface water that percolates through biochar-amended soil. The primary benefit of biochar amendment on reducing stormwater pollutant loading, though, was the reduction in stormwater runoff volume.

A companion column study was conducted using soil samples from the Delaware field site. A series of artificial storm events demonstrated that biochar positively affected volumetric moisture content, water infiltration, and total phosphorus reduction. However, both treatments leached total nitrogen and nitrate, with the biochar-amended columns leaching more than the native roadway soils. A separate column study incorporated biochar at the same application rate as the field site into four other field soils and also tested the application of compost to separate soil columns. This study also found improved hydrologic function from both amended soils, but in this case, both biochar- and compost-amended soils transported less nitrogen than native soils. Effluent from both unamended and biochar-amended soils showed substantial phosphorus and phosphate reduction, while reductions from compost-amended soils were lower. Differences between field and column data suggest that the mechanisms by which biochar affects nitrogen removal are complex and may be difficult to predict without a more fundamental understanding of biochar's effect on microbial processes.

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1. PROBLEM

The adverse effects of nitrogen loading and sedimentation on the health of the Chesapeake and Delaware Bays are two major issues currently facing state and local regulators within these watersheds. Increasing populations in the watersheds can lead to higher levels of urbanization and land development with ever increasing impervious cover giving rise to increased stormwater runoff and excessive soil erosion and flooding. Practical and economical treatment of stormwater runoff is of vital importance to the cleanup of the bays and for state municipalities as they try to meet the nutrient loading requirements of the Bay's TMDL reduction program. Unfortunately, achieving required nutrient loading reductions with current technologies are enormous. For example, costs are projected to exceed $720 million by 2020 to achieve nutrient removal standards with traditional technologies for Maryland State Highway Administration. Roadway greenways could represent a marvelous opportunity for the infiltration and treatment of urban stormwater runoff through the enhancement of existing roadside filter strips and swales without the high costs of purchasing additional highway right-of-way or constructing new stormwater treatment facilities.

We propose an entirely new approach that has the potential to dramatically increase nutrient removal efficiency, particularly nitrate, while simultaneously reduce stormwater volume and avoid adding new infrastructure – the addition of biochar to highway greenways or roadway soils. Rather than capture stormwater for treatment in new treatments systems, existing highway greenways are "enhanced" thus providing stormwater treatment without the cost of new infrastructure or purchasing additional right-of-way. Thus, currently owned assets are maximized.

2. METHODOLOGY

In this study, a commercial pinewood biochar, Soil Reef Biochar which is pyrolyzed at 550℃, was amended into a constructed roadside filter strip located along Route 896 in Middletown, DE. Two roadside filter strips, one amended with and one without biochar, were carefully instrumented to measure infiltrating water quality, soil moisture content, and stormwater runoff quantity and quality entering and exiting the filter strips. The construction of this field site was completed with support from the National Fish and Wildlife Foundation (NFWF), which also supported monitoring of the site for approximately 1.5 years. This MATS-UTC project supported an additional full year of monitoring, including water quality measurements of infiltrating water that were not part of the NFWF project.

In addition to the field study, a two-dimensional multiphase flow and transport model was developed for the roadway site. By using this model to fit a typical storm event, the importance of various processes by which biochar-amendment alters stormwater hydrology could be understood. The modeling effort was necessary to determine the most critical soil properties were by which biochar caused significant reductions of stormwater runoff.

Finally, recognizing the challenge of understanding the processes by which biochar amendment alters nutrient dynamics at the field scale, laboratory column experiments were conducted using cores extracted from the biochar-amended and unamended filter strips at the field site. Nutrient removal from these cores were studied in the laboratory using synthetic storm events.

2.1. INFLUENCE OF BIOCHAR ON STORMWATER INFILTRATION AND POLLUTANTS - FIELD

2.1.1. Field Site Design and Construction

The site selected was located along Route 896 in New Castle County, Delaware, just south of the Summit Bridge at Bethel Church Road. A system of trench drains and catch basins were installed to collect stormwater runoff from the roadway and two filter strips measuring 6.1 × 1.8 × 0.3 m (width x length × depth) abutting the roadway as shown in Figure 1. The filter strips were constructed in November 2015. Drainage areas to each filter strip and to the roadway trench were generally equal in area and provided comparable runoff characteristic to each section. A 4% mix, by mass, of biochar was amended to a depth of 30 cm within the biochar filter strip by tilling. A control filter strip was identically prepared but without biochar amendment. Once prepared, both strips were stabilized and seeded.

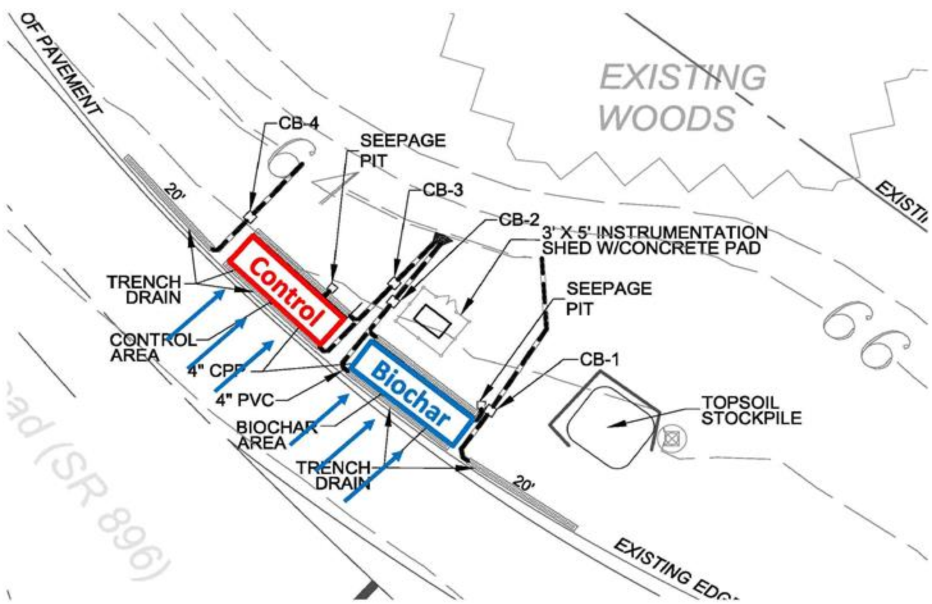

Figure 1. Summit Bridge Field Site Layout

2.1.2. Field Instrumentation

The site was instrumented with devices to measure and collect stormwater runoff from the roadway (influent) and after passing across each filter strip (effluent). Subsurface perforated pipes were also installed to collect water samples underground after passing through the filter strips. A cross sectional view through one filter strip (both are identical in design) illustrating the subsurface perforated pipe on the downgradient edge of a filter strip is shown in Figure 2. Automated water samplers were also installed to collect composite water samples for surface water influent, what flowed onto the filter strips, and surface water effluent, what ran off of each filter strip, over the course of a rain event. Meteorological data were collected by an on-site Isco 674 Rain Gauge rain gauge.

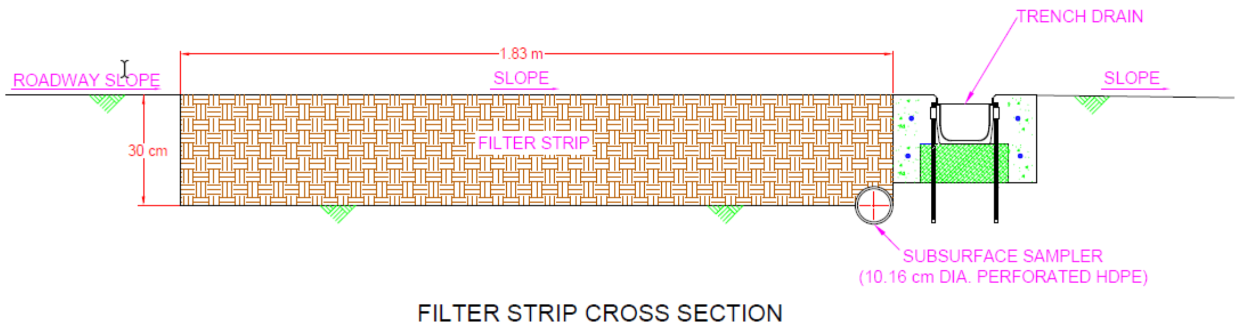

Figure 2. Cross section through biochar-amended and unamended filter strips.

Three ISCO 6712C water samplers were installed to collect water samples and to act as data loggers for measuring flow rates and cumulative runoff volume from each filter strip. In order to accomplish this task, ultrasonic sensors were installed at the outlet ends of each of the collection trenches. These sensors monitored the changing water levels in the trenches and the measurements were recorded in the data loggers within the ISCO water samplers. Water level readings were then converted to flow estimates using calibration equations derived from time and volume measurements collected during actual rain events. The system operated on the premise that the higher the water level, the higher the flow rate.

Eight Decagon GS-1 Water Content Sensors were installed in the biochar-amended and unamended (control) filter strips, four in each region, and were connected to Em50 data loggers. These sensors monitored and recorded the volumetric water content of the filter strips over time. These sensors were positioned to monitor volumetric water contents at two depth ranges -- 1-15 cm and 15-30 cm. The sensors were also separated spatially, front and rear in the filter strips: two sensors monitored the soil just off the roadway and two sensors monitored the soils toward the rear of the filter strips.

Soil temperature and water potential data were collected and analyzed using Decagon MPS-6 underground electronic sensors connected to the on-site data loggers. One soil water potential/temperature sensor was installed toward the rear of each filter strip. Daily variations in soil temperature and water potential were monitored and recorded from both the biochar and control filter strips throughout the project.

2.1.3. Water Quality Measurements

Water quality data were obtained for nine storm events in 2018. Samples were collected from five locations at the test site during the storm events. The different sampling locations and types of samples are listed in Table 1. Subsurface samples (S2-1, S2-2, S3-1, S3-2) were collected from 4 in diameter, horizontal perforated pipes located at 30 cm depth on the downgradient edge of the biochar-amended and unamended test sections. These pipes, one for each test section, extended the width of the test regions. Water extracted from the pipes is representative of water that exits the soil zone and percolates deeper into groundwater. The groundwater discharges to a nearby creek that empties into the Chesapeake Bay.

Table 1. List of sampling locations for water quality samples at Route 896 and Bethel Church Road, DE field site.

Location Designator	Description
C1	Composite surface water sample of stormwater as it exits the roadway
C2	Composite surface water sample of stormwater as it exits the biochar-amended roadway section
C3	Composite surface water sample of stormwater as it exits the unamended roadway section with no biochar
S2-1	Instantaneous subsurface sample at near start of storm event collected at 30 cm depth at downgradient edge of biochar-amended region
S2-2	Instantaneous subsurface sample at near end of storm event collected at 30 cm depth at downgradient edge of biochar-amended region
S3-1	Instantaneous subsurface sample at near start of storm event collected at 30 cm depth at downgradient edge of unamended region
S3-2	Instantaneous subsurface sample at near end of storm event collected at 30 cm depth at downgradient edge of unamended region

Water samples were filtered to measure total suspended solids, and the filtrate was analyzed for a range of constituents listed in Table 2 with the experimental method. All water quality analyses were conducted by the University of Delaware Soil Testing Laboratory.

Table 2. Water quality parameters measured and laboratory method

Parameter	Instrument and Method
pH	Accumet pH meter model AB15 and a SymPHony pH electrode (Fisher Scientific, Pittsburgh, PA).
EC	VWR Model 1052 conductivity meter with a platinum dip cell (VWR Scientific, Philadephia, PA).
$NH4^+$, $NO3^-$, and $NO2^-$	Colorimetrically using a Bran and Luebbe AutoAnalyzer 3 (Bran&Luebbe, Buffalo Grove, IL).
P, K, Ca, Mg, Mn, Zn, Cu, Fe, B, S, and Al	Inductively coupled plasma optical emission spectroscopy using a Thermo ICAP 7600 Duo View ICP Spectrometer (Thermo Elemental, Madison, WI).
TC, TIC, TOC, TN_b	Direct combustion, except for total organic carbon which was calculated by difference using an Elementar Vario-Cube TOC Analyzer (Elementar Americas, Mt. Holly, NJ)

2.1.4. Modeling of a Selected Storm Event

Numerical simulations of one example storm event were conducted for two reasons. First, the model was used to ascertain if the observed impact of biochar on stormwater runoff was consistent with independent measurements of biochar's influence on soil hydraulic properties. Second, the model was used to explore which soil properties were most important for controlling stormwater runoff reduction.

Model simulations were performed using iTOUGH2 (Finsterle, 2004). The iTOUGH2 code is an extension of TOUGH2, a general-purpose numerical simulation program for multiphase fluid flow in porous media, which was developed in the Earth Sciences Division of Lawrence Berkeley National Laboratory (Pruess et al., 1999). To model both surface and subsurface flow in the filter strips, iTOUGH2 was modified and these modifications are described in Akhavan et al. (2013). This modified iTOUGH2 code has been previously tested and verified (Akhavan et al., 2013).

The parameters for water retention and hydraulic conductivity needed in iTOUGH2 were obtained from disc infiltrometer measurements made at the site for the NFWF-funded project. These measurements are reported elsewhere (Imhoff and Nakhli, 2017).

Each filter strip, biochar-amended or unamended, was modeled separately using a two-dimensional domain perpendicular to the roadway. Each filter strip was sloped 2^{o} to match field conditions. The model domain was 3.0 x 3.0 m (length x height). Overland flow was described using the Saint-Venant/Strickler-Manning equations, while two-phase flow of air and water were described in the subsurface using a multiphase form of Darcy's law (Akhavan, et al., 2013). Storm event #44 was selected for modeling because antecedent soil conditions were relatively dry which allowed for significant time-dependent changes in water contents for model fitting. Hydraulic boundary conditions included measured rainfall and runoff from the roadway onto the filter strips. For the bottom boundary, the water table was assumed to be at 2 m depth at the start of the simulations. No flow conditions were specified along the vertical boundaries within the soil. Measured volumetric water contents from TDR sensors were used as initial conditions for the biochar-amended filter strip, while hydrostatic conditions were assumed as initial conditions for the unamended filter strip.

A schematic of the model domain that shows the highway runoff, rainfall input, model boundary conditions, and the 30-cm deep filter strips is shown in Figure 3.

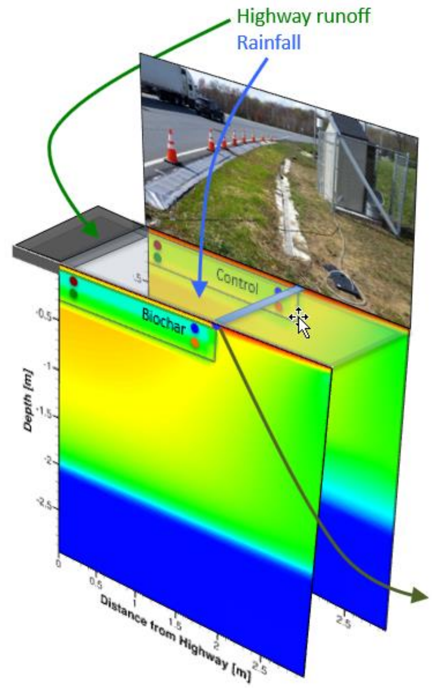

Figure 3. Schematic of model domain showing highway runoff from roadway, rainfall input, position of the water table, and the initial volumetric water content in the biochar-amended and unamended (control) filter strips (wetter soil is bluer).

A plot of the influent roadway runoff and the rainfall for storm #44 are shown in Figure 4.

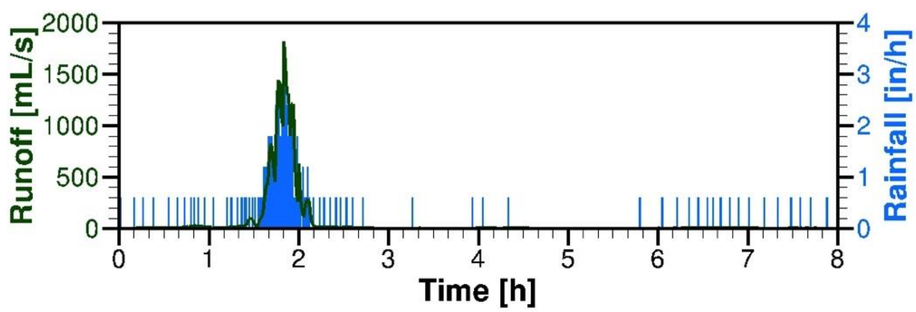

Figure 4. Instantaneous runoff from the roadway (green) and instantaneous rainfall (blue) measured at the site for storm #44.

2.2. INFLUENCE OF BIOCHAR AMENDMENT ON STORMWATER INFILTRATION AND POLLUTANTS - LAB

2.2.1. Experimental Design

Soil Core Collection Soil cores were collected from the field site in November 2017. Three soil cores were collected from each filter strip using an AMS core sampler. Soil cores were taken in 3-inch vertical segments to prevent the samples from compacting.

Column Design The soil segments were dry-packed into 1.05 in. inner diameter clear PVC columns to their field dry bulk densities. The biochar-amended soils were packed to a dry bulk density of 1.08 g cm^{-3} while the roadway soil was packed to a dry bulk density of

1.36 g cm^{-3}. Following the recommended agricultural application rate (Calcium Sulfate Source Gypsoil, 2018), 62.2 mg of solid $CaSO_4$ was lightly mixed into the top of each soil column in order to maintain the soil structure throughout the experiment.

Artificial Storm Events A synthetic stormwater with a concentration of 2 mg L^{-1} (as N) $NaNO_3$ and 3 mg L^{-1} (as P) Na_2HPO_4 was used. The synthetic stormwater was applied to each column at a rate of 7 mL every 5 minutes for an hour. This is designed to mimic a 2-year, 60-min storm for New Castle County, DE, where the field site is located. The design of the artificial storm events used in this study is specific to the field site described above. The columns were allowed to drain for up to 24 h and the effluent was collected for analysis. This process was done one time with DI water in order to saturate the columns and then 3 times with the synthetic stormwater mixture. The cumulative effluent from each of the final 3 storm events was analyzed for water quality. Due to poor drainage and low output volumes, two soil columns were excluded from further analysis, leaving effluent samples from four of the columns: two amended with biochar and two unamended.

Leaching Test To evaluate nutrient leaching, field-aged biochar, fresh biochar, roadway soil, and a mixture of 4% biochar by mass and roadway soils were rinsed with DI water. Both the fresh and field-aged biochar were SoilReef biochar. The field-aged biochar was sieved from the media of a bioretention site in Charlottesville, Virginia, where it had been for 3.5 years. For each experiment, 3 g of each material was added to 40 mL of DI water in 50 mL centrifuge tubes and shaken at 200 rpm for 3 h, followed by centrifuging at 4500 rpm for 15 min, and then removing the supernatant. All leaching tests were performed in duplicate. The supernatant from each sample was analyzed using spectrophotometric lab methods for ammonium, nitrate, total nitrogen, phosphate, and total phosphorus using a Hach DR 3900 spectrometer and a Hach DRB 200 to digest samples. Total phosphorus was measured using Hach TNT 843 kits with a range of 0.05-1.50 mg L^{-1} PO_4-P (Hach Company, 2016a). Nitrate was measured using either Hach TNT 835 kits with a range of 0.2-13.5 mg L^{-1} NO_3-N (Hach Company, 2018a) or Hach TNT 836 kits with a range of 5-35 mg L^{-1} NO_3-N (Hach Company, 2018b). The nitrate kit tests follow the dimethylphenol method. Ammonium was measured using Hach TNT 830 kits with a range of 0.015-2.00 mg L^{-1} NH_3-N that follows the salicylate method (Hach Company, 2016b). Total nitrogen was measured using Test N' Tube reagent total nitrogen set with a range of 0.0-25.0 mg L^{-1} N and follows the persulfate digestion method (Hach Company, 2014).

2.2.2. Hydrologic and Water Quality Measurements

Sample Analysis Effluent from each column was analyzed for nitrate, total phosphorus (TP), and total nitrogen (TN). Samples were refrigerated until chemical and nutrient analyses were completed within 48 hours of sample collection. Nitrate was analyzed by ion chromatography with a Dionex ICS-5000+ with Dionex IonPac AG18, 2 × 50 mm and Dionex IonPac AS18, 2 × 250 mm analytical columns. Total nitrogen was determined by using a Shimadzu 5000A TC/TN analyzer. Effluent samples were analyzed for total phosphorus using spectrophotometric lab methods for total phosphorus using a Hach DR 3900 spectrometer and a Hach DRB 200 to digest samples. We used Hach TNT 843 kits with a range of 0.05-1.50 mg L^{-1} PO_4-P to measure the concentration of total phosphorus. Additionally, the height and weight of each column was recorded before and after all storm events to monitor volumetric moisture content and compaction.

Performance Calculations The load for each pollutant moving into and out of each soil column was calculated as follows:

$$Load_i = C_i V_i$$

where C_i is the concentration and V_i is the effluent volume of sample *i*. The performance for column was characterized by the percent reduction in load between the inlet and outlet of each column.

2.2.3. Other

Supplemental Work An additional column study was conducted using four different soil textures collected from sites in Virginia. Three soil mixtures for each texture were prepared in duplicate: unamended soil, soil amended with 4% Soil Reef biochar by mass as applied at the Delaware field site, and soil amended with 30% compost by volume as recommended by the Virginia Department of Environmental Quality (Virginia Dept. of Environmental Quality, 2011), in order to determine whether either media offers superior nutrient or sediment removal, and whether that tendency varies with original soil texture. For this study, some experimental set-up conditions were changed. The inner diameter and height of these columns were 2 inches and 16 inches, respectively. Columns were filled with 12 inches of field-damp soil mixture and treated with calcium sulfate at the same areal rate as the original study.

The same synthetic stormwater mixture was applied, with a 250 mL storm volume determined based on these columns' larger surface area and an average 1-y, 1-h storm in Virginia. Six storms were conducted. After the first three storms, columns were emptied, the soils air-dried for 24 hours, then repacked to simulate the effects of periodic deep tillage of roadside soils. After a 30-day latent period, the final 3 storms took place. Effluents were analyzed for nutrients as above, and flow rates, compaction, and gravimetric moisture retention measured to determine physical and hydrological conditions that might influence effluent nutrient concentrations.

3. FINDINGS

3.1. INFLUENCE OF BIOCHAR ON STORMWATER INFILTRATION AND POLLUTANTS - FIELD

3.1.1. Stormwater Runoff Results – Hydrology

In the previous NFWF-supported study, over a 1.5-y period biochar amendment resulted in a significant decrease in peak flow rate and cumulative runoff volume at the field site. Data collected for peak flow rate from that study are shown in Figure 5. Each red triangle represents the peak flow rate from roadway runoff for one storm event, while the black and dark blue symbols (plotted at the same probability of exceedance) correspond to peak flow rates for the same storm event for unamended (black) and biochar-amended (dark blue) filter strips. Data are plotted against probability of exceedance: storms with small rainfall have a high probability of exceedance and may not result in any measurable runoff from the roadway (bottom left corner). As the rainfall amounts increase for larger storms, the peak flow rates from the roadway get larger, as do peak flow rates from the unamended filter strip (tilled) and from the biochar-amended filter strip (tilled – biochar). For the very largest storm events, the peak flow rates from the biochar-amended and unamended filter strips converge, as the impact of biochar on reducing the peak flow rate is negligible (top right corner).

Data collected in 2018 from this MATS-UTC project are plotted separately from the 2016-2017 data. Because there are fewer data in 2018, roadway runoff data for each 2018 storm event (light blue triangles) were matched with a corresponding peak roadway runoff data from 2016-2017 (red triangles). The corresponding peak flow rate from the unamended filter strip (green squares) and biochar-amended filter strip (red circles) were then plotted. The green symbols lie almost directly on top of the black symbols for the 2016-2017 peak flow rates, indicating that the performance of the unamended filter strip in 2018 on reducing peak flow rate is unchanged from 2016-2017. The red circles for the biochar-amended filter strip in 2018 are scattered around the data collected for 2016-2017, the dark blue symbols. Overall, the data indicate that the performance of the biochar-amended filter strip in 2018, almost three years after construction of the site, was similar to that recorded in the first 1.5-y of operation. Thus, data indicate biochar amendment continued to result in significant reductions in stormwater flow after three years of operation.

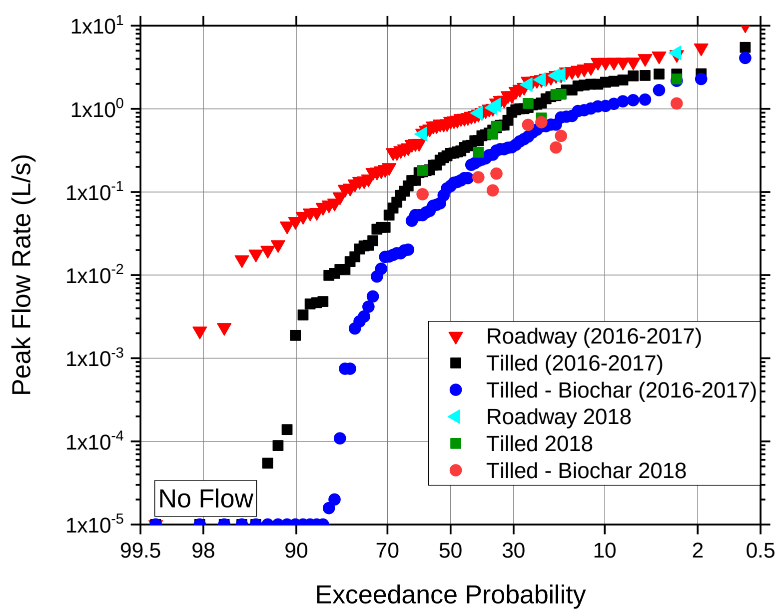

Figure 5. Peak flow rates for storm events at the roadway test site. Most data shown are from 2016-2017. Data in 2018 are plotted separately to determine if there was a noticeable effect of biochar aging.

3.1.2. Stormwater Runoff Results – Water Quality

Water quality data were obtained from nine storm events in 2018. Samples were collected from five locations listed in Table 1. C1, C2 and C3 are surface runoff samples from roadway, unamended filter strip, and biochar-amended filter strip, respectively. S2-1 and S2-2 are subsurface samples from biochar-amended filter strip at start and end of storm, respectively. S3-1 and S3-2 are subsurface samples from unamended filter strip at start and end of storm, respectively.

Box plots of P, NO_3-N, NH_4-N and TN_b are shown below in Figures 6-9, respectively. From these figures the following observations are made:

- For surface water samples from biochar-amended and unamended roadway soils (C2 and C3), there was no significant difference in concentration of any pollutant - P, NH_4-N, NO_3-N, or TN_b. Thus, biochar amendment did not affect the quality of stormwater that flowed along the surface of biochar-amended roadway soil.
- While there was no significant difference in P and NH_4-N concentrations in subsurface water collected beneath the biochar-amended (S2 samples) and the unamended (S3 samples) soils, concentrations of the N compounds, NO_3-N and $TN_{b,}$ were significantly different and always smaller in samples from beneath biochar-amended soil.
- A significant difference was noted in P concentrations in subsurface water collected beneath the both biochar-amended and unamended soils (S2 and S3 samples) when compared to the roadway influent (C1 samples) water samples.
- Of the N compounds, only TN_b from the unamended soil (S3 sample) displayed a significant difference in concentration when compared to the roadway influent (C1 samples) and was *higher* than the concentration measured in the roadway influent.

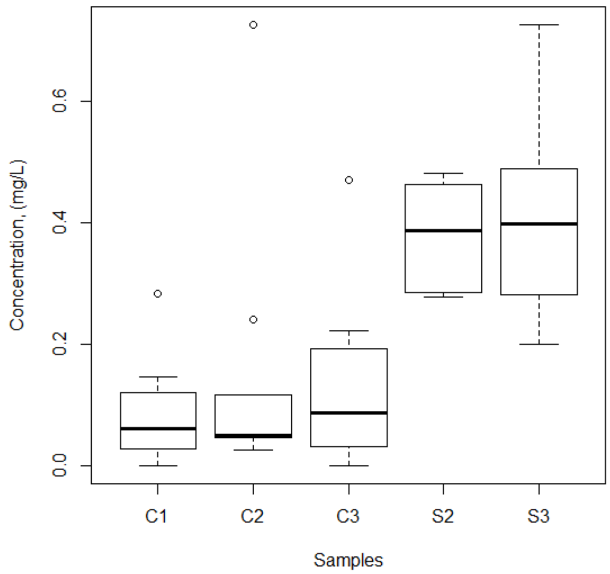

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Figure 6. Dissolved P of water samples collected from storm events in 2018. See Table 3 for definitions of nomenclature for samples.

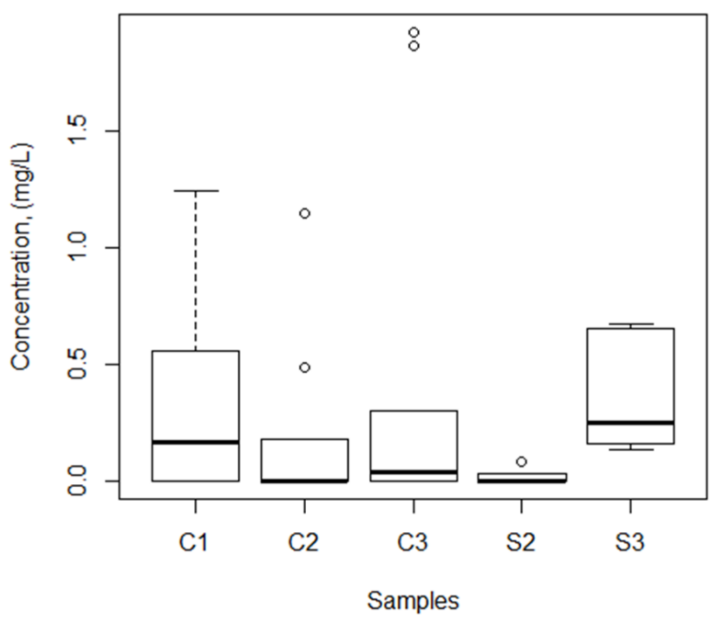

Figure 7. Dissolved NO3-N of water samples collected from storm events in 2018. See Table 3 for definitions of nomenclature.

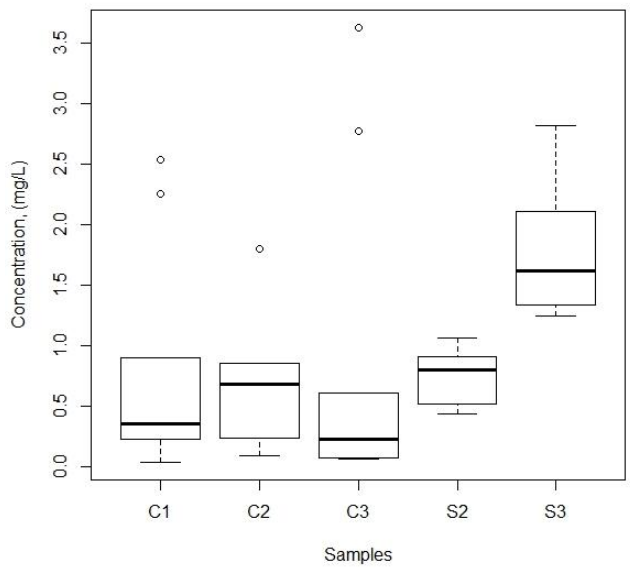

Figure 8. Dissolved TNb of water samples collected from storm events in 2018. See Table 3 for definitions of nomenclature.

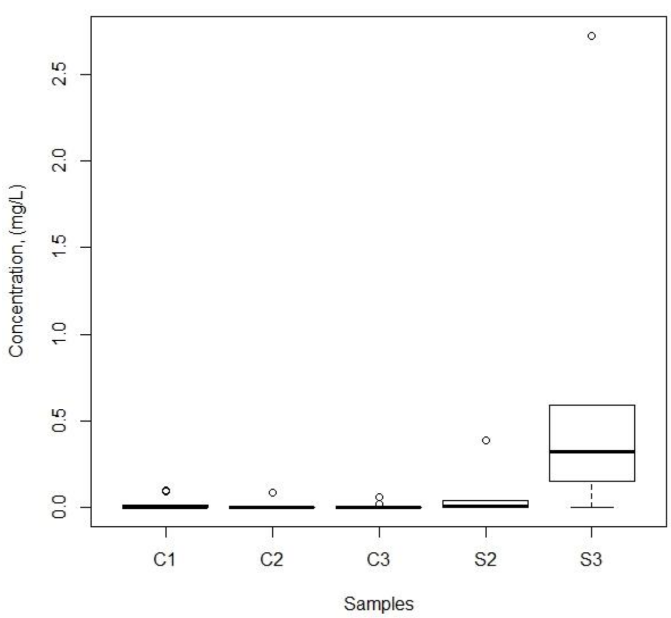

Figure 9. Dissolved NH4 of water samples collected from storm events in 2018. See Table 3 for definitions of nomenclature.

Paired t-tests were used to determine if there were statistically significant differences in pollutant concentrations in surface water samples (C2 and C3) and subsurface water samples (S2 and S3) for biochar-amended and unamended test sections. The results of these tests are summarized in Table 3. There were no statistical differences in pollutant concentrations in surface water samples from the two test sections. However, the data indicate that while water percolating through biochar-amended and unamended regions had similar P concentrations, concentrations of N compounds were statistically *smaller* from the biochar-amended soil.

Table 3. Results of paired t-tests for stormwater pollutant concentrations shown in Figures 6-9. When mean concentrations are significantly different, the pollutant concentrations from biochar-amended regions were always smaller than corresponding concentrations from unamended samples.

Constituent	**t-Test for Surface Water (C2 and C3)**	**t-Test for Subsurface Water (S2 and S3)**	**t-Test for Subsurface Water (C1 and S2)**	**t-Test for Subsurface Water (C1 and S3)**
P	No difference in means at 95% confidence level (p = 0.589)	No difference in means at 95% confidence level (p = 0.698)	Means differ at 95% confidence level (p = 0.001) S2 > C1	Means differ at 95% confidence level (p = 0.004) S3 > C1
NO_3-N	No difference in means at 95% confidence level (p = 0.201)	Means differ at 95% confidence level (p = 0.018) S3 > S2	No difference in means at 95% confidence level (p = 0.060)	No difference in means at 95% confidence level (p = 0.927)
TN_b	No difference in means at 95% confidence level (p = 0.530)	Means differ at 95% confidence level (p = 0.017) S3 > S2	No difference in means at 95% confidence level (p = 0.909)	Means differ at 95% confidence level (p = 0.005) S3 > C1
NH_4	No difference in means at 95% confidence level (p = 0.957)	No difference in means at 95% confidence level (p = 0.146)	No difference in means at 95% confidence level (p = 0.304)	No difference in means at 95% confidence level (p = 0.159)
C1 =	Roadway Influent			
C2 =	Surface Tilled w/ Biochar			
C3 =	Surface Tilled			
S2 =	Subsurface Tilled w/ Biochar			
S3 =	Subsurface Tilled			

3.1.3. Modeling Results for a Selected Storm

One objective of the modeling exercise was to ascertain if the influence of biochar amendment on stormwater runoff reduction was consistent with biochar's influence on soil hydraulic properties. Parameters describing the pressure-saturation-permeability relationship were varied in the model to obtain the best match with field data for storm #44, while maintaining parameters within the parameter space determined from disk infiltrometer data. If the modeled stormwater runoff reduction data were in reasonable agreement with field measurements, then the observed impact of biochar amendment on stormwater runoff reduction would be consistent with biochar's effect on soil properties.

Results of the model fits are shown in Figures 10 and 11 for the unamended and biochar-amended filter strips, respectively. In the model fitting exercise, greater weight was given to matching the stormwater runoff measurements, the bottom plots in both Figures 10 and 11. The volumetric water contents were point measurements and deemed less representative of 6-m wide filter strips. The model was able to match the stormwater runoff data reasonably well, for both instantaneous flow rates and cumulative runoff volumes. Fits to the cumulative runoff volume were better than the peak flow rates. It is important to note that the model assumed homogeneous soil properties within each filter strip and a uniform surface roughness. Visually, the filter strips were not homogeneous, with patchy growth of grass evident in both strips.

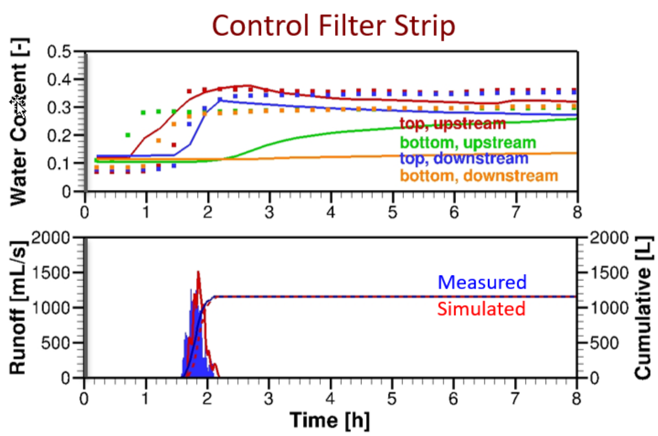

Figure 10. Model results for the unamended filter strip without biochar. Measured (data) and model-predicted (lines) volumetric water content, top plot. Measured (blue) and model-predicted (red) instantaneous and cumulate runoff, bottom plot.

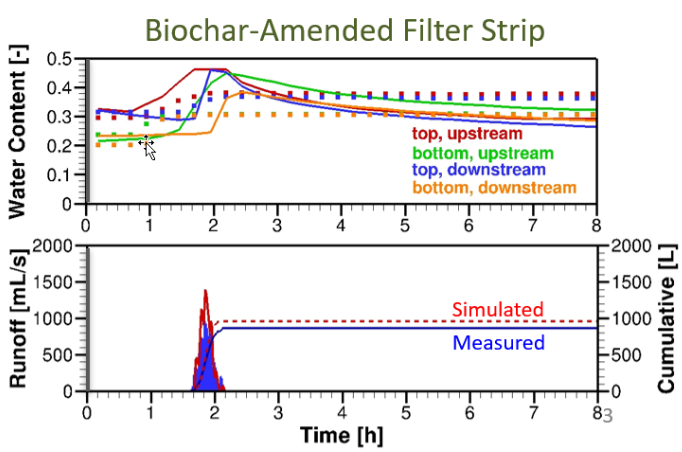

Figure 11. Model results for the biochar-amended filter strip. Measured (data) and model-predicted (lines) volumetric water content, top plot. Measured (blue) and model-predicted (red) instantaneous and cumulate runoff, bottom plot.

The best-fit model parameters for soil hydraulic properties are given in Table 4 along with measured data from disk infiltrometer measurements at the site. The model fits shown in Figures 10 and 11 were achieved using parameters within the range of the measurements. This result indicates that the impact of biochar on reducing stormwater runoff is consistent with independent measurements of bicohar's impact on soil properties. The model was able to fit the measured data if biochar increased the permeability of the soil by approximately 100%.

Table 4. Mean model soil parameters (measured, blue) and ranges of measured parameters (black) from disk infiltrometer measurements of each filter strip medium and the background sandy loam soil. Best-fit model estimates were used to fit data in Figures 10 and 11.

	Measured	Range	Estimate
Biochar-Amended Filter			
Permeability k [Darcy]	2.16	1.88 - 3.34	*3.34*
van Genuchten n [-]	1.26	1.26 - 1.62	*1.62*
van Genuchten α [1/cm]	0.31	0.18 - 0.31	0.23
Porosity ϕ [%]	45.9	41.2 - 51.1	46.9
Control Filter			
Permeability k [Darcy]	1.97	0.69 - 4.30	1.49
van Genuchten n [-]	1.33	1.27 - 1.50	1.27
van Genuchten α [1/cm]	0.20	0.12 - 0.30	0.26
Porosity ϕ [%]	39.0	35.3 - 42.3	38.9
Sandy Loam			
Permeability k [Darcy]	0.99	0.18 - 3.69	*3.69*
van Genuchten n [-]	1.52	1.23 - 1.98	1.24
van Genuchten α [1/cm]	0.17	0.09 - 0.30	0.14
Porosity ϕ [%]	36.8	32.4 - 38.6	*38.6*

A sensitivity analysis was conducted using the model to determine which of the soil hydraulic properties were most important for reducing stormwater runoff in biochar-amended media. These results are shown in Figure 12 and indicate that the soil permeability and the van Genuchten parameter 'n' in the pressure-saturation-permeability relationship are most important for affecting cumulative runoff in the biochar-amended filter strip.

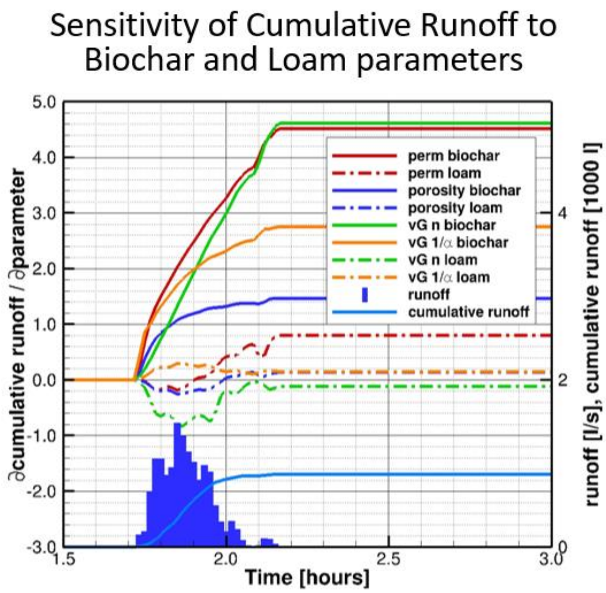

Figure 12. Sensitivity of cumulative runoff from biochar-amended filters strip to soil hydraulic parameters for storm #44. Cumulative runoff is most sensitive to the soil permeability and the van Genuchten parameter 'n' in the pressure-saturation-permeability relationship.

3.2. INFLUENCE OF BIOCHAR AMENDMENT ON STORMWATER INFILTRATION AND POLLUTANTS – LAB

3.2.1. Hydrologic Measurements

The biochar-amended columns compacted 0.7±0.5%, while the native roadway soils compacted 1.4±0.6% during the experiment. The average volumetric moisture contents of the biochar and native roadway soil columns were 0.41±0.006 and 0.36±0.004, respectively. Additionally, the biochar-amended columns drained in 4±0.5 hours, while the native roadway soils drained in 6.7±0.7 hours. Thus, the repacked columns from the Delaware field site indicate that biochar amendment reduces compaction, increases water retention, and increases infiltration/drainage rate. These observations were also made from field data collected at the Delaware site.

3.2.2. Water Quality Measurements

For the laboratory column experiments, the average percent change in nitrate and total nitrogen (TN) mass entering and exiting columns is shown in Figure 13. Significantly more nitrogen species are exiting the biochar amended columns, although the variability in data is significant between storms and the two column replicates.

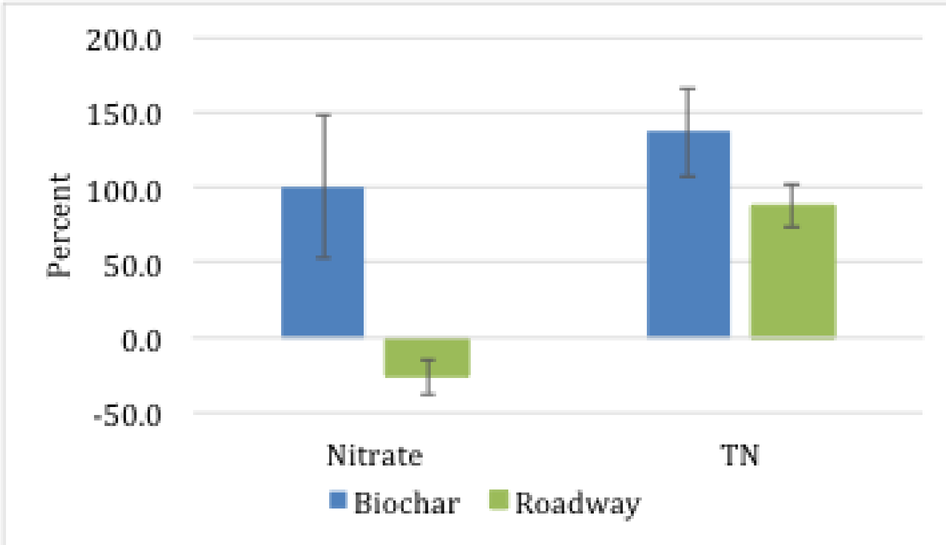

Figure 13. Average percent change in nutrient mass entering and exiting columns across all storm events and soil treatments. Standard errors of the estimated averages are shown.

The biochar-amended columns reduced total phosphorus mass by 97.5 ± 0.22% and the native roadway soils reduced total phosphorus mass by 97.6 ± 0.75 %.

Nutrient Mobilization The percentages of available nutrients, both from the influent stormwater and from the column matrix itself, that were mobilized during a storm event for each treatment are shown in Figure 14.

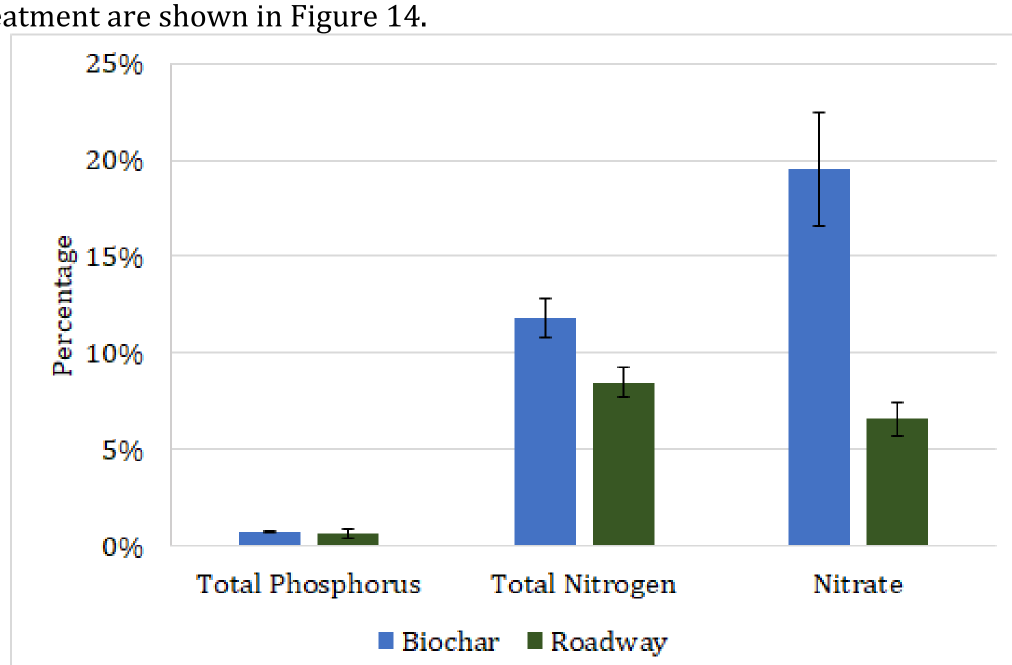

Figure 14. Percent mobilized per treatment across storm events

Batch Leaching test - Ammonium leaching was negligible for each material. A comparison of the mass of available of nutrients for field-aged and new biochar is shown in Figure 15.

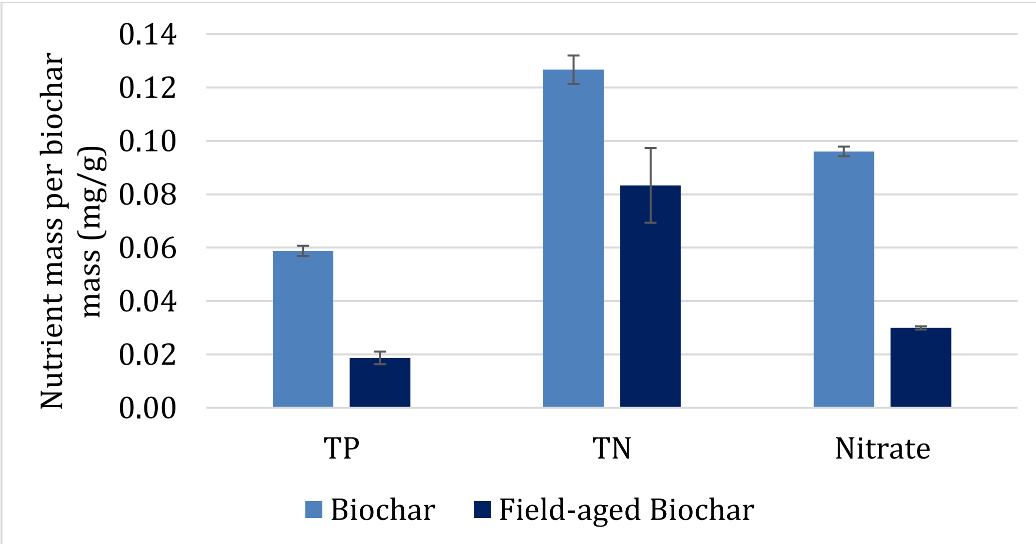

Figure 15. Comparison of available nutrients from fresh and field-aged biochar

3.2.3. Other

In the supplemental study, biochar-amended Virginia soils demonstrated the greatest moisture retention and compaction resistance of the three mixtures. After the final storm of a six-storm series, moisture retained by the soil matrix beyond its field-damp condition averaged 33.1±11.2 g for unamended soils, 52.3±4.0 g for compost-amended soils, and 78.1±3.6 g for biochar-amended soils. Unamended soils had compacted 16.8±0.7%, compost-amended soils had compacted 14.6±0.7%, and biochar-amended soils had compacted 13.1±1.3%, as compared to their original heights. Drainage rates were fastest in compost-amended soils, and faster in both types of amended soil than in unamended soils. Unamended columns produced their first 100mL of effluent in an average of 83.3±6.0 minutes, while biochar-amended columns produced that volume in 81.5±3.7 minutes and compost-amended columns did so in 70.9± 3.4 minutes.

Total nitrogen and nitrate masses were significantly higher in nearly every effluent sample than in the influent stormwater, indicating substantial leaching of one or more nitrogen species from some or all soil mixture components. Unamended soils leached the most nitrate and compost-amended soils leached the least, with effluent nitrate masses averaging 548.0±37.6% higher than influent mass in the unamended columns, 438.3±34.3% higher in the biochar-amended columns, and 198.3±16.6% percent higher in the compost-amended columns. All samples demonstrated a net reduction of both total phosphorus and phosphate mass between the influent and effluent. Unamended and biochar-amended soils reduced phosphate masses from influent stormwater by an average of 82.8±0.5% and 78.8±0.7%, respectively. Net reductions from compost-amended soils were less substantial, averaging 48.9±2.8%.

4. CONCLUSIONS

Field Testing and Modeling

The field study demonstrated that the biochar-amended filter strip continued to perform well up to three years after construction. Stormwater peak flow rate and cumulative runoff continued to be significantly smaller than those from an adjacent unamended filter strip, with results nearly identical to those from the first 1.5-y of observations.

Several important conclusions can be drawn from water quality data. First, while the cumulative volume and rate of flow of stormwater runoff from the biochar-amended filter strip were less than from the unamended region, the water quality of runoff was similar. There were no statistical differences in any water quality parameters. Thus, the primary process by which biochar-amendment reduces stormwater pollutant loading is reducing the volume of stormwater runoff, not the concentrations of pollutants in the runoff.

Second, samples from subsurface water exiting the filter strips and entering groundwater indicate that the native roadway soil contributes TN_b to infiltrating stormwater: concentrations from the unamended filter strip were significantly greater than in roadway runoff. Although the filter strip soil contributes nitrogen, measured concentrations of $NO3^-$and TN_b were statistically smaller in subsurface water from biochar-amended versus unamended soils. Thus, biochar amendment reduced concentrations of nitrogen compounds compared to unamended soil.

Modeling of stormwater flow at the field site indicated that the reason biochar amendment resulted in reduced stormwater runoff is increased soil permeability and changes to the shape of the water retention curve (van Genuchten model parameter, 'n'). Thus, the performance of biochar-amendment on stormwater runoff reduction at other sites in other types of soils might be predicted if information on the influence of biochar on these soil properties is known.

Laboratory Testing

The column studies showed that the volumetric water content of the biochar-amended soils was greater than the volumetric water content of the roadway soils. This suggests biochar is capable of improving water retention in roadway soils, which is consistent with data from the field site.

Both biochar-amended soils and the Delaware roadway soils compacted similar amounts. The addition of biochar moderately decreased susceptibility to compaction in Virginia soils.

The biochar-amended soils drained in less time than the Delaware and Virginia roadway soils. This implies that the addition of biochar can improve drainage rates, thus indicating a higher infiltration rate for biochar-amended soils, which again is consistent with filter strip data from the field site.

Compost also demonstrated these same hydrologic benefits in Virginia roadway soils, performing more effectively than biochar in terms of drainage rates but less effectively in terms of moisture retention and compaction resistance.

For biochar-amended soils and both the Delaware and Virginia roadway soils, there was a significant decrease in the total phosphorus loads across storm events. This suggests that both biochar and native roadway soils are capable of reducing total phosphorus. Compost-amended soils did not reduce phosphorus to the same extent in Virginia soil columns.

Biochar-amended soils and native soils leached total nitrogen across storm events in both experiments. This could be attributed to leaching of nitrogen that is stored in the soil or a burst of microbial activity that can occur due to wetting dry soils. However, in the native Delaware soils, nitrate was primarily mobilized from biochar-amended columns but not from the roadway soils. This suggests that biochar is not effective at reducing nitrate in this setting. For the Virginia soils, masses of both nitrate and total nitrogen were higher in the effluents of all soils than in the influent stormwater, indicating significant nitrogen leaching from the soils and both amendments. The results for nitrate removal from the column tests with biochar differ from results reported from the filter strips tested in the field.

The leaching test demonstrated that mobilization of nutrients from the soils and amendments can occur in both treatment types with less nutrient mobilization in the native Delaware roadway soils. This suggests that biochar did not positively affect the retention of total nitrogen and nitrate during the column studies. However, there was a significant difference in the mass of nutrient leached from field-aged and fresh biochar with the field-aged biochar leaching much less nutrient mass. This suggests that as biochar ages there is less potential for mobilization of nutrients.

5. RECOMMENDATIONS

The field study demonstrates that biochar amendment continued to result in a reduction of stormwater runoff after three years of operation, with no noticeable reduction in hydraulic performance. The water quality data from the field indicate that biochar amendment results in smaller nitrogen concentrations in infiltrating water compared to unamended soil. This result differs from the more controlled laboratory experiments using the same soil/biochar mixture. These differences are unexplained and indicate a need for further study into the fate of nitrogen in biochar-amended soil.

Both field and laboratory data indicate that biochar amendment of the Delaware roadway soil improves water retention and stormwater infiltration/drainage. This indicates that there are some potential benefits to using biochar as a BMP enhancement. Therefore, it would be of interest to further explore how the amount of biochar or type of biochar impacts water quality and hydrologic performance. Results also illustrate the need for field studies where moisture retention between storms and vegetation may play important roles in microbial communities and nutrient removals, and thus may identify additional important mechanisms that biochar could support with respect to stormwater management.

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