

Sustainable Design Guidelines to Support the Washington State Ferries Terminal Design Manual: Assessment of Copper and Zinc Adsorption to Lignocellulosic Filtration Media Using Laboratory and Field Scale Column Tests for the Purpose of Urban Stormwater Remediation

WA-RD 816.3

**David Yonge
Vince McIntyre
Joseph Smith
Ian Norgaard
Michael Wolcott**

October 2016



**Washington State
Department of Transportation**
Office of Research & Library Services

WSDOT Research Report

Agreement T4120, Task 23
WA-RD 816.3

**SUSTAINABLE DESIGN GUIDELINES TO SUPPORT THE WASHINGTON
STATE FERRIES TERMINAL DESIGN MANUAL:**

**ASSESSMENT OF COPPER AND ZINC ADSORPTION TO
LIGNOCELLULOSIC FILTRATION MEDIA USING LABORATORY AND FIELD
SCALE COLUMN TESTS FOR THE PURPOSE OF URBAN STORMWATER
REMEDATION**

Final Report

Submitted By:

**David Yonge
Vince McIntyre
Joseph Smith
Ian Norgaard
Michael P. Wolcott**

**Washington State University
Pullman, WA 99164**

**Prepared for
The State of Washington
Department of Transportation
Roger Millar, Secretary**

October 2016

TECHNICAL REPORT DOCUMENTATION PAGE

1. Report No. WA-RD 816.3	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Sustainable Design Guidelines to Support the Washington State Ferries Terminal Design Manual: Assessment of Copper and Zinc Adsorption to Lignocellulosic Filtration Media Using Laboratory and Field Scale Column Tests for the Purpose of Urban Stormwater Remediation		5. Report Date October 2016	
		6. Performing Organization Code Enter any/all unique numbers assigned to the performing organization, if applicable.	
7. Author(s) David Yonge, Vince McIntyre, Joseph Smith, Ian Norgaard, Michael Wolcott		8. Performing Organization Report No. Enter any/all unique alphanumeric report numbers assigned by the performing organization, if applicable.	
9. Performing Organization Name and Address Washington State University Department of Civil and Environmental Engineering Pullman, WA 99164-2910		10. Work Unit No.	
		11. Contract or Grant No. Agreement T4120, Task 23	
12. Sponsoring Agency Name and Address Research Office Washington State Department of Transportation Transportation Building, MS 47372 Olympia, WA 98504-7372 Project Manager: Lu Saechao 360.705.7260		13. Type of Report and Period Covered Research Report	
		14. Sponsoring Agency Code	
15. Supplementary Notes This study was conducted in cooperation with the U.S. Department of Transportation, Federal Highway Administration.			
16. Abstract This report represents the third and final phase of a three-part effort aimed at providing Sustainable Design Guidelines for Washington State Ferry terminals, specifically addressing the efficacy for removal of copper and zinc using a biobased filter media both in laboratory and field conditions. This work supplements previous reports that detail design concepts in implementation of stormwater strategies to be deployed on waterfront structures. The Bainbridge Island ferry terminal staging area was selected as the field test site. A pilot scale adsorption column and submersible weir system was designed and constructed to fit within an existing stormwater vault. Laboratory and field scale continuous flow column studies were performed on raw and torrefied Douglas-fir Crumbles® (<i>Psuedotsuga menziesii</i>), charcoal (also referred to as biochar), and pea gravel to evaluate their effectiveness for adsorbing soluble forms of copper and zinc. Laboratory column tests indicated that the most efficient adsorption for both copper and zinc was non-torrefied wood, followed in order by pea gravel, torrefied wood, and charcoal. Increasing influent column flow by a factor of four resulted in no statistically significant difference in effluent metal concentration. A deicer flush performed on torrefied wood and charcoal columns following adsorption tests resulted in over an order of magnitude increase in column effluent copper and zinc concentration, indicating that bypassing the filtration system during deicer runoff events should be considered.			
17. Key Words Sustainability, Ferry Terminals, Stormwater, Washington state, Runoff, Filtration, Copper, Zinc		18. Distribution Statement No restrictions. This document is available through the National Technical Information Service, Springfield, VA 22161.	
19. Security Classif. (of this report) None	20. Security Classif. (of this page) None	21. No. of Pages 88 pages	22. Price

Disclaimer

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Washington State Department of Transportation or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

Executive Summary

This report represents the third and final phase of a three part effort aimed at providing Sustainable Design Guidelines for Washington State Ferry terminals. Specifically, this report addresses efficacy for removal of copper and zinc using a biobased filter media both in laboratory and field conditions. This work supplements previous reports that detail design concepts in implementation of stormwater strategies to be deployed on waterfront structures.

Practical engineering solutions to address growing municipal stormwater issues are needed to maintain a healthy relationship between humans and the environment. In the Pacific Northwest, elevated soluble zinc and copper concentrations originating from urban stormwater runoff provide a significant threat to native salmon and steelhead populations. In response to urbanization, existing stormwater infrastructure needs to be upgraded to treat non-point source pollution, including soluble metals, prior to entering the receiving water. Media filtration BMPs provide the flexibility and small treatment footprint needed for retrofit applications that are space limited, such as ferry terminal staging areas. An effective yet low-cost filtration media needs to be identified to remove soluble metals of concern from urban runoff. Lignocellulosic materials have shown promise as an available and effective filtration media. Its use has been evaluated in its raw form, thermally treated (torrefied), and carbonized.

Laboratory and field scale continuous flow column studies were performed on raw and torrefied Douglas-fir Crumbles® (*Psuedotsuga menziesii*), charcoal (also referred to as biochar), and pea gravel to evaluate their effectiveness for adsorbing soluble forms of copper and zinc. Laboratory column tests indicated that the most efficient adsorption for both copper and zinc was non-torrefied wood, followed in order by pea gravel, torrefied wood, and charcoal. Increasing influent column flow by a factor of four resulted in no statistically significant difference in effluent metal concentration. A deicer flush performed on torrefied wood and charcoal columns following adsorption tests resulted in over an order of magnitude increase in column effluent copper and zinc concentration, indicating that bypassing the filtration system during deicer runoff events should be considered.

The Bainbridge Island ferry terminal staging area was selected as the field test site. A pilot scale adsorption column and submersible weir system was design and constructed to fit within an existing stormwater vault. During each storm event, the column's design allowed stormwater to enter laterally through the top of the column, pass vertically downward through the media, and exit to the submersible weir that was used to determine flow. The performance of charcoal was tested initially by collecting data from three runoff events. Based on the laboratory performance of raw wood crumbles, the charcoal was replaced and data for nine storm events were obtained over the remainder of the field investigation. Column influent and effluent samples were collected during selected stormwater runoff events using automated samplers. The samples were analyzed for soluble and total copper and zinc, total and volatile suspended solids and pH. Column flow and rainfall data was also collected during the field investigation.

The data indicated that, overall, the raw wood crumbles yield greater percent soluble metal removal and lower metal concentrations compared to the charcoal. The average effluent soluble copper concentration for raw wood column was 4.8 µg/L, matching the acute concentration discharge limit to marine waters, while the biochar column effluent average was 10 µg/L. Both column media exhibited soluble zinc concentrations less than the acute and chronic discharge limit of 90 and 81 µg/L, respectively. Care must be taken in inferring firm conclusions from field results, however. Flow, metal and suspended solids concentrations can be highly variable during field studies. For example, long antecedent dry periods occurred during charcoal testing, resulting in overall higher metal and suspended solids concentrations compared to testing when the column contained raw wood crumbles. The field data does support the findings of the laboratory column testing, however; raw wood crumbles yielded greater percent removal and lower effluent soluble copper and zinc concentrations compared to charcoal.

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1. Introduction and Background

Both stormwater quantity and quality can have negative environmental impacts. Decreased stormwater quality and increased quantity has been directly correlated to population growth, urbanization, and land development that results in an increased percentage of impervious surfaces.¹ Significant nationwide stream, lake, and estuary impairment is directly attributed to this low-quality, high-quantity urban runoff.^{1,2} Impairment due to stormwater quantity manifests in the form of changes to established seasonal flow patterns, disruption and degradation of habitat, abnormal stream energy fluctuations, and resulting changes to species populations and communities.^{1,3} Water quality impairment is attributed to pollutants that have been identified as having harmful impacts on aquatic ecosystems and human health.¹ Stormwater runoff was identified as being the primary source of elevated heavy metal concentrations and are the fifth most reported cause of waterbody pollution in the United States.^{1,4,5}

Dissolved metals naturally exist in surface waters due to mineral dissolution, with normal background concentrations varying with location depending on the physical and chemical characteristics of the surrounding soil.⁴ In the Pacific Northwest, zinc (Zn) and copper (Cu) are two heavy metals of particular concern. While they present relatively low toxicity to humans, their allowable surface water limits into fresh and saltwater bodies are relatively low (Table 1).⁶ Significant adverse health effects manifest in fish and other aquatic invertebrates when exposed to relatively low levels of soluble zinc and copper.^{3,7} Anadromous salmonids, of which five species are currently classified as “threatened” in Washington State, are particularly sensitive.^{7–11} Salmonids exposed to acute and/or chronic soluble zinc and copper concentrations during various life stages exhibit negative impacts that include reduced reproductive ability, navigation confusion during migration, altered feeding habits, gill damage, decreased oxygen consumption, changes to blood and serum chemical composition, and increased mortality rate.^{7–9,12,13}

Table 1. Soluble zinc and copper USEPA regulatory discharge limits.

Metal	Discharge to Freshwaters (µg/L)		Discharge to Marine Waters (µg/L)	
	Acute (1 hr. ave)	Chronic (4 day ave)	Acute (1 hr. ave)	Chronic (4 day ave)
Zinc	120 ^a	120 ^a	90	81
Copper	13 ^a	9 ^a	4.8	3.1

Sources: National Recommended Water Quality Criteria: 2002. EPA-822-R-02-047. USEPA, 2002.

Water Quality Standards for Surface Waters: Toxic substances. WAC 173-201A-240. Washington State, 2008.

a. The tabulated values correspond to a hardness of 100 mg/L as CaCO₃.

Primary anthropogenic sources of zinc and copper in watersheds are attributed to vehicle fluid leaks, vehicle component wear (brake pad dust, tire wear, engine wear, ect.), deposition from

atmospheric pollution, copper and zinc containing pesticides and fertilizers, galvanized metal surfaces, and moss controlling agents.^{9,12,14–16} Zinc and copper concentrations in urban stormwater vary widely depending on the region, source, and pathway.¹⁶ However, typical values range nationally from 20 – 5,000 µg/L total zinc and 5 – 200 µg/L total copper.¹⁶ In highly galvanized industrial locations, it's not uncommon to see dissolved zinc concentrations up to 15,000 µg/L in runoff.¹⁷

Zinc and Copper exist in aquatic environments as divalent free metal ions and as formed complexes with inorganic ligands or natural organic matter (NOM).^{7,13,18} Toxicity to marine organisms is attributed to the free metal ion form.¹⁸ Primary removal from the water column occurs via sedimentation and metabolic uptake by organisms.⁷

The 2012 Stormwater Management Manual for Western Washington (SMMWW) details best management practices (BMPs) that are established in the State of Washington for treating stormwater quality and quantity.¹⁹ Sedimentation ponds or “wetpools” can be highly effective at removing metals adsorbed onto particulates and grass-lined swales provide filtration and biological uptake of soluble metals through vegetation, however, these BMPs require a significant footprint that many urban retrofit sites cannot accommodate.¹⁹ One option that addresses limited space requirements is filtration.¹⁹

Filtration BMPs used to treat contaminated runoff are attractive due to their versatility, ease of operation, and controllability.¹⁹ The filter media can be engineered to treat unique stormwater compositions and space requirements are generally less than for other BMPs.¹⁹ The mechanisms for metal contaminant removal from stormwater using a filtration BMP is through the removal of metal bound particulates and adsorption of soluble metal species.²⁰

Common stormwater treatment filtration medias include sand, crushed rock, dolomite, gypsum, and perlite.¹⁹ Granular activated carbon (GAC), a staple for drinking water and wastewater treatment, has also been investigated alongside novel medias such as agricultural wastes, compost, recycled natural fibers, and various biomass derived chars.^{24–27} Research has shown GAC to effectively adsorb heavy metals, however, production costs and issues with regeneration have kept it from being widely accepted as a feasible option to treat municipal stormwater.²⁸ This research project evaluated three novel filter media for the removal of zinc and copper – raw wood crumbles, torrefied wood crumbles and fast pyrolyzed charcoal (biochar).

Charcoal derived from fast pyrolysis is largely a byproduct of the global biofuels initiative.²⁹ Since the mid-1970's oil shortage in the United States, researchers have been investigating pathways to convert lignocellulosic biomass into liquid fuels.²⁹ One such pathway is pyrolysis.²⁹ During pyrolysis, biomass is heated in an anoxic environment allowing volatile gases to escape without combustion.²⁵ The collected volatilized gasses and excreted tars are then purified and treated to form biofuels, bio-oils, and biochemicals.²⁸ Charcoal is the carbonized spent biomass residual.²⁵ Charcoal has been termed “biochar” when produced for and used in soil amendment

applications or other environmental management processes and will be referred to as such continuing forward in this report.³⁰

The parent feedstock for biochar (i.e. softwood, hardwood, bark, corn stover, animal manure, rice husks, straw, ect.) can determine its eventual adsorption application and removal efficacy.²⁵ Additionally, adsorption effectiveness is dependent on pyrolysis temperature, atmosphere, and residence time^{25,28,31}. Researchers have been attempting to optimize adsorption performance by adjusting these governing parameters, increasing surface area through activation, and chemically modifying the surface functional groups.²⁸ Research has shown that standard, modified, and activated biochar is effective to varying degrees at removing soluble metals and a range of organic compounds.^{28,32,33}

Torrefied wood was also investigated in this report as a novel adsorption media. Torrefaction is a mild pyrolysis process intended to preserve the biomass heating value while volatilizing off low caloric value gases like CO₂, water, and some organic acids.^{34,35} The resulting wood exhibits darkened color, weakened structural integrity, enhanced hydrophobicity, increased energy density, heightened resistance to biodegradation, and significantly reduced weight.²⁸ Torrefaction is currently used to decrease transportation costs, increase fuel quality, improve storability, and as a preprocessing treatment.³⁴

Since torrefaction maintains the biomass pore structure integrity, it has been stated that it lacks the easily accessible sites of adsorption that biochar and activated carbons contain and would not perform as effectively.²⁸ Because of this, torrefied wood is not typically considered for adsorption applications.²⁸ However, in a recent review of cellulosic biosorption, Hubbe, 2013, indicated that torrefied wood should not be immediately discounted as a sorbent based solely on limited surface area.³⁶ He highlighted the diverse surface chemistry developed by torrefaction and theorized that torrefied wood retained structural integrity may be advantageous and worthy of investigation.³⁶

The overall objective of this project was to evaluate the effectiveness of raw wood crumbles, torrefied wood crumbles and biochar to remove copper and zinc from stormwater runoff. Both laboratory and field experiments were performed using laboratory scale continuous flow columns and a pilot scale column that was placed at the Bainbridge Island ferry terminal.

2. Experimental Methods

Bench scale and field scale tests were performed to evaluate the effectiveness of biochar, torrefied wood, and raw wood for the removal of selected stormwater contaminants. The contaminants studied included total and soluble copper and zinc and suspended solids based on their prevalence in runoff and potential negative environmental impact. The filter media evaluated included biochar, torrefied wood crumbles and raw wood crumbles. Media equilibrium sorption capacity was determined by developing single and multisolute adsorption isotherms. Laboratory column tests were employed to evaluate performance under continuous flow conditions. A pilot scale filter column was designed and installed at the Bainbridge Island,

WA ferry terminal and field data was collected over a 12 month period (April 2015 – April 2016.). The media was also subjected to tests to define their physical and chemical characteristics.

2.1 Media Evaluated

Three materials were evaluated for zinc and copper adsorption: (i) biochar, (ii) torrefied wood crumbles and (iii) raw wood crumbles. Laboratory adsorption column tests were also performed on pea gravel that was used to hold the media in place and evenly distribute flow during column testing. Photographs of the media are shown in Figure 1.

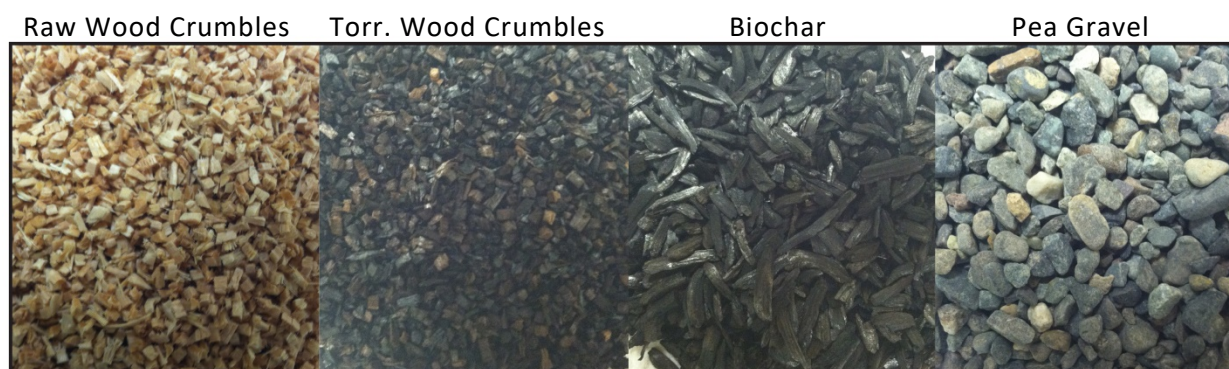


Figure 1. Photographs of the media.

The biochar used in this project was sourced from Biochar Products, a startup company located in Halfway, Oregon that produces biochar and bio-oil via fast pyrolysis.³⁷ The char was produced using beetle-killed, lodge pole pine that was fast pyrolyzed using a mobile, pilot scale Abri Tech reactor.³⁸ Prior to entering into the reactor, the feedstock was dried and pulverized using a gas-fired chain flail dryer. The reactor itself used an externally heated hot shell auger with an inert high density 2 mm steel heat carrier. The mean operating temperature for the main auger and the carrier reservoir was 400 °C and the average total residence time in the system was six minutes. No carrier gas was used during processing. Once received, the biochar was roughly sieved (US series, number 6 and 8 mesh) through a large capacity, dual screen shaker table to remove bulk fines. It was then dried at 103 °C for 24 hours and sieved again using a RAINHART Co. 637 Mary Ann® laboratory sifter to further remove fines and achieve a more uniform media. The size fraction passing through the 6 mesh sieve (3.35 mm) and retained on the 8 mesh sieve (2.36 mm) was utilized in the laboratory and field column experiments.

Two millimeter, Douglas-fir Crumbles™ were sourced from Forest Concepts, LLC, located in Auburn, Washington. The media was produced from an industrial grade, Doug-fir veneer that was passed through a paper-shredder-like rotary shearing machine (cutters set at 1.6 mm) resulting in uniform wood cube particles.³⁹ It was then screened to a nominal 2mm size and dried to approximately 8% moisture content prior to shipping.

The Doug-fir crumbles were torrefied at Washington State University (WSU) using a bench scale continuous auger pyrolysis reactor. The feed auger passed through a Lindberg/Blue M Tube Furnace set at 270 °C with an approximate residence time of 30 minutes. Torrefaction occurred in the presence of air which was supplied from a compressed air tank at a flow of 4.5 liters per minute. The torrefied wood was then sieved to remove fines using a RAINHART Co. 637 Mary Ann® laboratory sifter. The fraction used in testing was retained on a US Series 10 mesh (2.00 mm) sieve. Raw wood crumbles were also sieved in the same manner prior to utilization.

Pea gravel was used as a top layer in the continuous flow columns to help disperse the influent flow and stabilize the media by opposing buoyant forces under saturated conditions. It was sourced from Atlas Sand & Rock in Pullman, Washington. Prior to use, the pea gravel was washed in tap water to remove dust, dirt and sand and then allowed to dry overnight at room temperature.

2.2 Media Characterization

Select physical characteristics of all four media investigated are listed in Table 2. The measurements taken and calculations used to develop Table 2 are included in the Appendix.

Table 2. Physical characteristics of the media.

Media	Biochar	Raw Wood	Torrefied Wood	Pea Gravel
Mean Particle Size (mm)	2.55	2.19	1.97	4.40
Moisture Content	8%	4%	4%	1%
Compacted Volumetric Mass Density (oven dried g/L)	98	150	172	1706

Scanning Electron Microscopy (SEM) was performed on the media to allow for visual analysis of surface structure. Imaging was afforded by an FEI Quanta 200 scanning electron microscope at The Franceschi Microscopy and Imagine Center, Washington State University. To improve conductivity, the torrefied wood and raw wood were gold sputtered prior to scanning. Biochar's conductivity allowed it to be imaged without sputtering.

Fourier Transform Infrared (FTIR) spectroscopy was used to define major surface functional groups on the media. Analysis was performed using a Thermo Nicolet Nexus 670 spectrometer at the Composite Materials and Engineering Center, Washington State University. Samples were prepared for analysis by grinding and collecting material that passed a 60 M (<0.250 mm) US Series sieve. A 3 mg sample was then mixed with 300 mg KBr and formed into a pellet for analysis.

Background copper and zinc concentrations were determined for the media using USEPA method 200.7 that determines total recoverable metals by acid extraction followed by quantification using inductively coupled plasma mass spectrometry (ICPMS).⁴⁰

2.3 Adsorption Equilibrium Tests

Single and multi-solute equilibrium adsorption isotherm data was generated for biochar and torrefied wood as the sorbents and zinc and copper as the sorbates. The data was generated at room temperature ($20 \pm 1^\circ\text{C}$) using a series of 250 mL amber glass packer bottles with Teflon-lined caps. All bottles contained a known mass of sorbent, solution volume, and initial concentration of sorbate(s). The bottles were placed on a tumbling table operating at approximately 15 inversions per minute for 24 hours prior to analyzing for soluble metal concentration.

Copper and zinc stock solutions (1000 mg/L) were prepared using reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 (Fischer Scientific) dissolved in 18 M Ω deionized (DI) water. The stock solutions were diluted with DI water containing 0.01 M NaNO_3 , yielding a typical ionic strength found in stormwater, to a volume of 200 mL at predetermined sorbate concentrations (Table 3).⁵⁸ A known mass of sorbent and a predetermined volume of 1 M NaOH or 1 M HNO_3 was added to each bottle so that the pH following equilibration would be between 6.0 and 6.5. Initial liquid-phase metal concentrations and sorbent mass for single and multi-solute systems are presented in Table 3.

For both single- and multi-solute systems, triplicate control bottles were tested using previously stated procedures but without sorbent. The results indicated negligible sorption to bottle walls and the cap liner. Additionally, all glassware was cleaned by soaking overnight in 20% (v/v) HNO_3 and rinsed with 18 M Ω DI water.

Table 3. Initial liquid phase metal concentrations and sorbent masses used for single-solute and multi-solute systems. Note: due to a shortage of sorbent, only two copper single-solute tests were performed on 1g and 3g biochar.

Metal System	Target Initial Liquid Phase Metal Concentration (mg/L)	Sorbent Mass (g)	Sorbent Mass Tested in Triplicate (g)
Single Solute, Cu	Cu – 7	1, 2, 3, 4, 5	1, 3, 5
Single Solute, Zn	Zn – 10	1, 2, 3, 4, 5, 7, 9	1, 3, 5
Multi-solute, Cu & Zn	Cu – 2.5 Zn – 4.5	1, 2, 3, 4, 5	1, 3, 5

Liquid phase metal concentrations were measured by ICPMS at the Washington State University GeoAnalytical Laboratory (Pullman, WA), using an Agilent 7700 ICP-MS. Prior to analysis all samples were filtered through a 0.45 µm mixed cellulose esters filter (GE Healthcare) and acidified to pH less than or equal to 2.

Following quantification of the liquid phase sorbate concentration, the solid phase sorbate concentration was calculated using equation 1.

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e is the equilibrium solid phase concentration (mg sorbate/g sorbent), C_e is the equilibrium liquid phase concentration (mg/L), C_o is the initial liquid phase concentration (mg/L), V is the sorbate volume (L), and m is the mass of sorbent (g).

The empirical Freundlich equation (equation 3) was used to describe the single solute isotherm data as it was shown to yield the best fit of the data compared to the Langmuir equation.

$$q_e = K_F C_e^{1/n} \quad (3)$$

The fitting constants, K_F and $1/n$, were determined using non-linear regression.

2.4 Bench Scale Column Tests

Laboratory scale column tests were performed on raw and torrefied wood crumbles, biochar, and pea gravel to evaluate performance under continuous flow conditions. Columns were constructed from clear, extruded acrylic. Each column was 30.5 cm long with a 10.2 cm outer diameter (OD) and a 9.5 cm inner diameter (ID). Two layers of Phifer® fiberglass screen with a 0.16 cm mesh was affixed to the bottom of the columns, to retain the media, using 10.2 cm dia. hose clamps.

Columns experiments were performed in triplicate for each media. Each column was packed incrementally with media using a vibrating table until a stabilized compacted height of 20.3 cm was reached. Packed column density values are reported in Table 2. Following compaction, 5.1 cm of pea gravel was carefully placed on top of the media. Since pea gravel was used as packing material, column tests were also performed using pea gravel alone to determine its contribution to metal adsorption.

Synthetic stormwater was made in 379 L batches and stored in high-density polyethylene (HDPE) containers. Deionized (DI) water (resistivity of $\geq 2\text{M}\Omega$) was used as the foundation for the batch synthetic stormwater. Individual metal stock solutions (1000 mg/L) of copper and zinc were made using reagent grade, granular cupric chloride dihydrate and zinc chloride (Fisher Scientific). DI water was spiked with a known volume of each stock solution to achieve target influent concentrations of 300 $\mu\text{g/L}$ zinc and 100 $\mu\text{g/L}$ copper. The pH of the synthetic stormwater was adjusted to 6.1 ± 0.2 using a 1 M NaOH stock solution made from reagent grade sodium hydroxide pellets (J.T. Baker). A HACH® Benchtop pH meter combined with an IntelliCAL™ Ultra Refillable pH probe, designed for low ionic strength samples, was used to measure pH. The synthetic stormwater solution was mixed for 1 minute with a PVC rod and allowed to equilibration for a minimum of 12 hours prior to use. Following the equilibrium period, pH was checked to assure that it was within the desired range.

A high flow, dual-head, variable speed Cole-Parmer peristaltic pump (model #7549-30) connected to a network of 1.6 cm ID vinyl tubing was used to convey the synthetic stormwater from the feed barrel to the top of the columns. Norprene® tubing (1.3 cm ID) was used inside the peristaltic pump head. At the top of the columns, the influent flow was distributed and applied across the surface area using HDPE distribution heads. Effluent samples were collected at the base of the columns using acid washed laboratory glassware. A schematic of the setup is displayed in Figure 2.

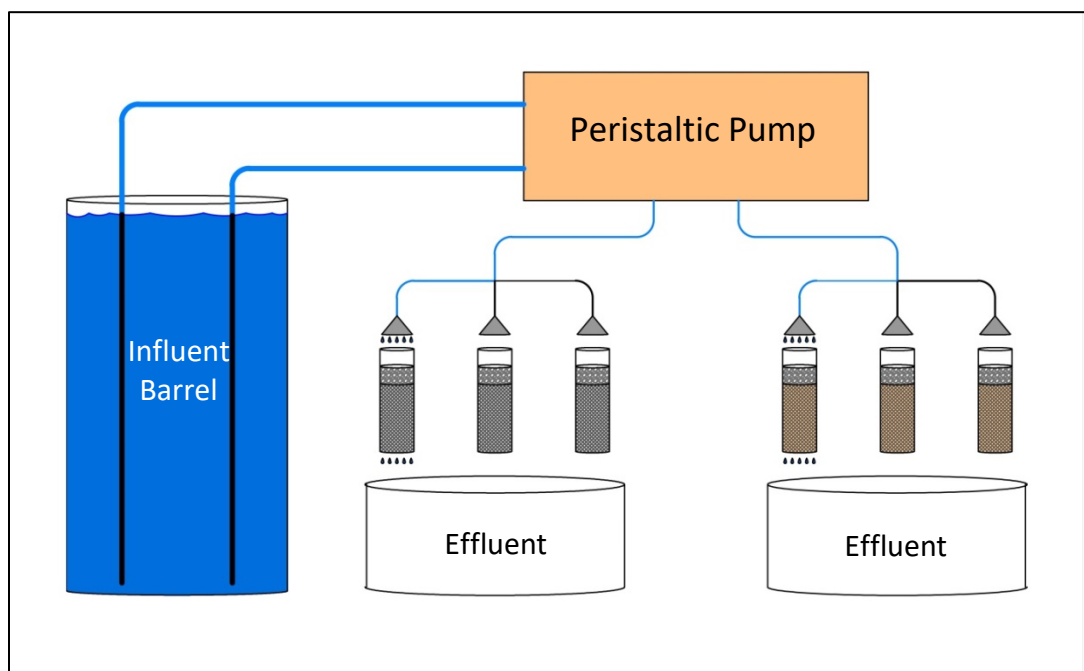


Figure 2. Laboratory scale continuous flow column system.

All materials in contact with stormwater were selected based on their documented inert properties. All stormwater conveyance materials were tested periodically for metals removal to

ensure accuracy of the data. No significant metal sorption was detected in the conveyance system.

Each column test event consisted of two sets (e.g. biochar and torrefied wood or raw wood and pea gravel) of triplicate columns being exposed to the same feed solution at the same flow rate. The dual-head pump allowed for two out of the six columns to be tested simultaneously (Figure 2). On/off valves were used to change influent flow between columns during operation.

Metals removal testing was divided into two, 40 storm event phases differentiated by event duration. During Phase I, each event lasted 20 minutes per column. Phase II events lasted 80 minutes per column. Both phases were conducted at an influent flow rate of 0.76 lpm.

During Phase I testing, both discrete and composite effluent samples were collected. Composite samples were developed for each event by collecting 20 mL samples in laboratory glassware at $t = 1, 5, 10, 15,$ and 20 minutes. These samples were then combined to produce a composite. In addition, 80 mL discrete samples were collected and tested every 5th event at $t = 1, 10,$ and 20 minutes. A portion of all samples were filtered, the same day of collection, using Whatman™ 0.45 μm mixed cellulose ester membrane filters and placed in SARSTEDT 15mL sterile screw-cap vials and preserved by adding nitric acid to $\text{pH} < 2$.⁴⁰ Another aliquot was similarly preserved without filtration for later comparison against filtered values to check for metal retention by the filters and/or sorption to effluent particulate matter. The remaining sample in the glassware was used to measure pH. An influent sample was extracted from the feed water barrel during each event and prepared for analysis in the same manner. Method blanks were also prepared to check for contamination due to improper cleaning and/or sample handling. These blanks were prepared using 18 M Ω DI water and exposing it to the same procedures as the samples. All samples were delivered and tested for zinc and copper concentrations by ICPMS (WSU Peter Hooper GeoAnalytical Lab) within two weeks of sampling.

The same columns used in Phase I were subjected to Phase II testing where event duration was extended from 20 to 80 minutes while flow was maintained at 0.76 lpm. Effluent samples were collected for analysis at $t = 1, 20, 40, 60,$ and 80 minutes. Additionally, six influent samples were taken from the feed water barrel at equally distributed intervals throughout each series of events. After 10 events, effluent sample collection intervals were reduced to $t = 1, 40,$ and 80 minutes and influent samples reduced to 3 per event series feed water batch. Processing, preservation, and analysis of the samples followed the methods described previously.

The USEPA recommends using mixed cellulose esters (MCE) filter membranes for evaluation of dissolved metals based on their relatively inert performance.⁴¹ However, MCE filters are not completely inert and even a slight metal removal interference can have a significant impact when measuring low (ppb) concentrations. The 30 influent samples tested showed an average loss through filtration of $18 \pm 4 \mu\text{g/L}$ zinc and $29 \pm 4 \mu\text{g/L}$ copper. This equates to approximately 6% zinc removal and 30% copper removal from the filtered influent samples. Since the influent contained no particulate matter it can be assumed that the decrease in concentration is a result of sorption to the filters. Ninety effluent samples were tested and

showed an average loss through filtration of 5 ± 2 µg/L zinc and 12 ± 3 µg/L copper. Effluent concentrations are continuously changing, however, initial copper effluent values were less than 5 µg/L which makes a 12.3 µg/L interference unacceptable. This is why the Phase I & II data reported in the results and discussion section are of unfiltered samples. Filtered values are included in the appendix.

Additional tests performed during Phase I & II consisted of measuring effluent total suspended solids and comparing interval sample concentrations to composites. Total suspended solids in the effluent was measured per USEPA method 1684, section 11.⁴²

After Phase II was complete, high flow tests and a deicer flush that simulated parking lot deicer application, were performed on the same torrefied wood and biochar columns. During the short-term increased flow testing, the Phase I & II flow rate (0.76 lpm) was doubled (1.5 lpm) and quadrupled (3.0 lpm). During these higher flow events, flow duration was maintained at 80 minutes. Influent and effluent sample collection, preparation, and quantification was performed as previously discussed. America West Environmental donated Calcium Chloride with BOOST™ (CCB) for salt flush testing. CCB is listed by WSDOT as a commonly utilized liquid anti-icing agent that is applied during light to moderate snow events.⁴³ CCB is a low-toxicity salt solution combined with proprietary additives that enhance performance and inhibit corrosion.⁴⁴ WSDOT recommends an application rate of approximately 30 gallons CCB per lane mile.⁴³ The concentration of calcium chloride in CCB is 32 percent and it has a density of 1.345 g/mL.⁴³ While fully miscible in water, CCB's enhanced viscosity binds the product to the target surface allowing for slower dilution and longer periods between application.^{45,46} Design storm (6 mo., 24 hr.) tabulated values for Bainbridge Island were taken from the Stormwater Management Manual for Western Washington (SWMMWW) and parking lot stormwater volume was calculated using the SCS runoff method, (equations 1 – 3).⁴⁷

$$S = \frac{1000}{CN} - 10 \quad (1)$$

Where: S = weighted curve number (in.)
CN = curve number (98.00 for asphalt)

$$P_e = \frac{(P - 0.2S)^2}{(P + 0.8S)} \quad (2)$$

Where: P_e = runoff (in.)
P = rainfall (1.87 in. for Bremerton, WA. SWMMWW)

$$V = P_e * A \quad (3)$$

Where: V = runoff volume (in^3)
 A = catchment area (in^2)

The simulated influent salt flush concentration was calculated assuming the applied CCB, from one application, was contained in one-half of a design storm runoff volume – calculated to be 126,861 Liters. The estimated applied volume of CCB to the Bainbridge Island catchment (detailed information in section 2.3) was 117 L. This resulted in an influent CCB concentration of 1.24 g CCB/L correlating to an influent calcium concentration of 144 mg Ca^{2+} /L. In the laboratory, the salt flush event duration was 80 minutes at a flow rate of 0.76 lpm. No metals were added to the influent during this event. The pH did not require adjustment as it was within the desired target influent range. Discrete effluent samples were taken at $t = 1, 20, 40, 60,$ and 80 minutes. Two influent samples were taken per column set at equally distributed intervals. After the salt flush, a standard stormwater test event was performed on the columns to evaluate the media response after being exposed to the anti-icing agent.

Following completion of all column tests performed on biochar and torrefied wood, the media metal concentration was determined by acid extraction.⁴⁰ A representative sample from each column (six columns total) was taken from the top, middle, and bottom of the media along with a portion of the pea gravel. The samples were oven dried at 60 °C and then ground into a powder using a mortar and pestle – pea gravel samples were excluded from the grinding procedure.⁴⁰ One gram of each sample was mixed with diluted (1+1) hydrochloric (10 mL) and nitric acids (4 mL) and refluxed at 95 °C for 30 minutes. The samples were cooled, diluted to 100 mL using 18 MΩ water, and allowed to rest for 24 hours. The supernatant was drawn off the top and analyzed for zinc and copper concentrations using ICPMS. Total metals desorbed from the media was then determined from the ICPMS results, using equation 4, and compared to the values calculated using the difference between influent and effluent concentrations, the associated volume of stormwater treated, and the mass of media in the column.

$$\frac{mg\ metal}{g\ media} = \frac{C*V*D}{W} \quad (4)$$

Where: C = metal concentration in the extract (mg/L)
 V = Volume of the extract (0.1 L)
 D = Dilution Factor (undiluted =1)
 W = Weight of the sample (1.0 g)

2.5 Field Scale Column Testing

The Bainbridge Island ferry terminal was selected as the field test site. The catchment used in this project was a paved, 1.5 acre, vehicle staging area set aside for traffic waiting to board the ferry to catchment boundary is shown below in Figure 3.

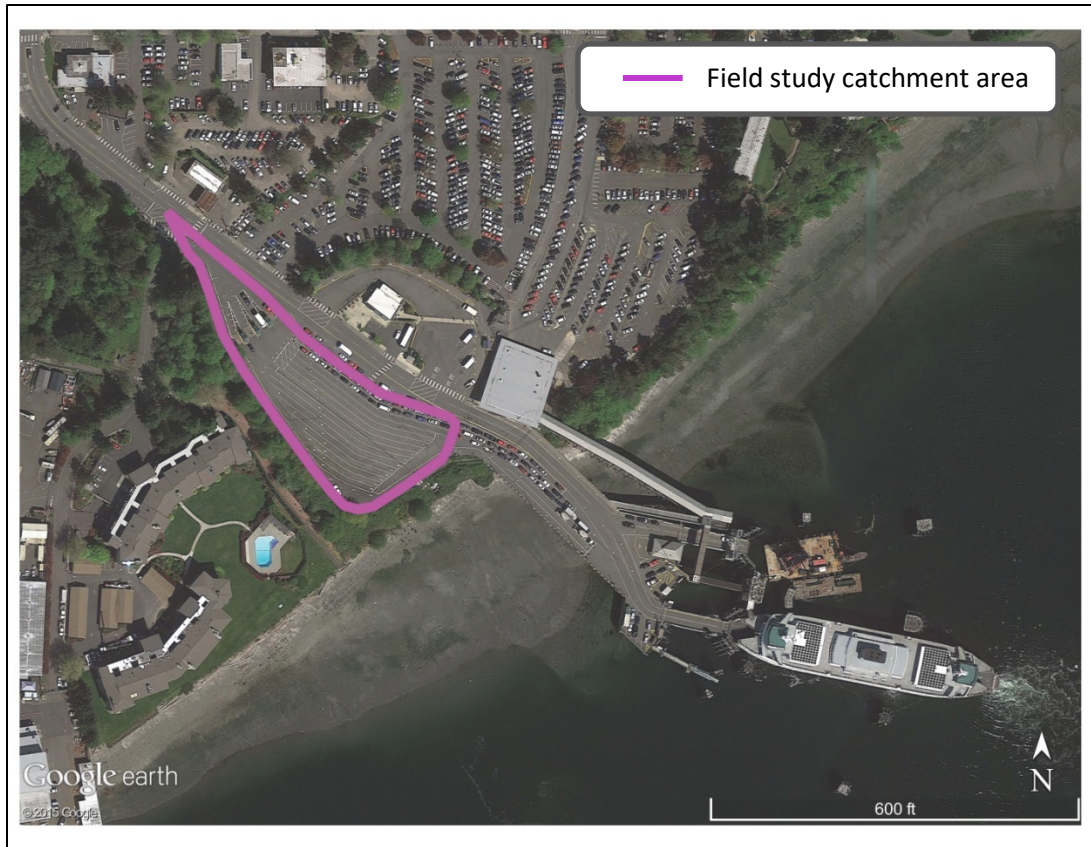


Figure 3. Bainbridge Island, WA ferry terminal with field study catchment area indicated.

A subsurface stormwater network collects the staging area runoff and conveys it to a subsurface, dual chambered, concrete vault that is located on the southern edge of the property (Figure 4). Stormwater enters into the first chamber, passes over a dividing barrier, and fills the second chamber. The dimensions of the entire vault are 1.8 m (6 ft) wide, 3.0 m (10 ft) long, and 1.2 m (4 ft) deep. The two chambers are divided along the length of the vault with the dimensions of the first chamber being 1.8 x 0.6 x 1.2 meters and the second being 1.8 x 2.4 x 1.2 meters.

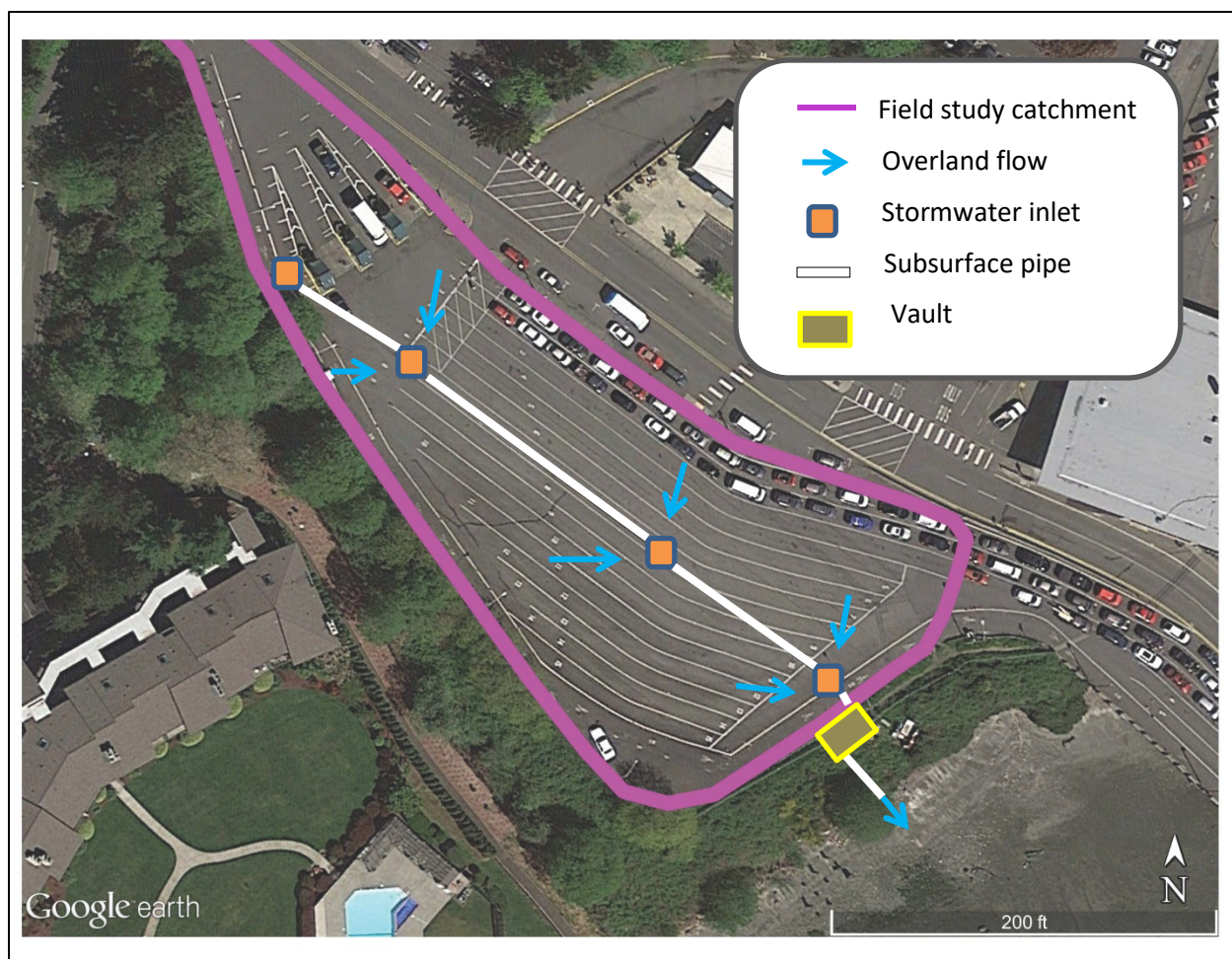


Figure 4. Field study stormwater catchment. *Symbols are not to scale and are exaggerated in size. Map is provided for qualitative purposes only.

Six existing filters were removed from the second chamber to make room for the installation of our prototype filter and effluent weir box that was used for flow monitoring. Column influent and effluent samples were collected using two Teledyne ISCO® 6712 full-size portable samplers. Samples were not iced during or immediately after collection due to the travel distance between WSU and Bainbridge Island. Rainfall data was collected using a Sigma® tip bucket rain gauge with data recorded on one of the samplers. Both samplers were programmed to collect up to 24 discrete samples during a storm event on a preselected time interval of 2 minutes. Sample collection was initiated based on water height inside the column effluent weir box.

The weir box was designed to operate submerged and had interchangeable v-notch weir plates ranging from 10° to 90° that can be installed based upon the expected flow range. For this project, the weir box was equipped with the 20° v-notch weir plate that could measure flows up to 258 lpm. A schematic diagram of the weir box is shown in Figure 5.

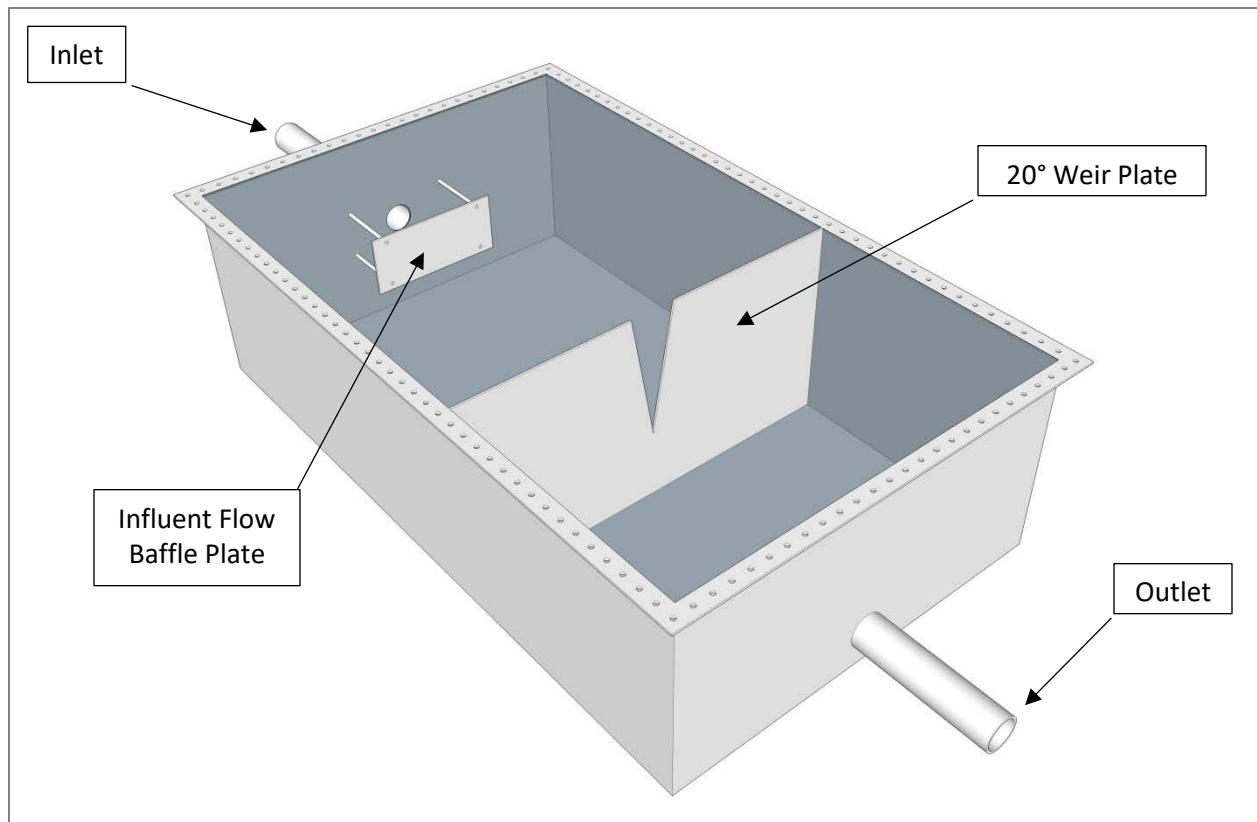


Figure 5. Schematic of the submersible weir box with a sharp-crested, 20° v-notch weir plate inserted and lid removed.

A pressure transducer anchored inside the weir box, on the influent side of the weir plate, was used to measure water height in front of the weir plate. Prior to field installation, the weir was calibrated at WSU's hydraulics laboratory. The resulting empirical equation relating water height to flow is shown along with the Kindsvater-Carter design equation used for v-notch weirs (Eqn. 5) that applies to v-notch weirs other than 90° in Figure 6.⁴⁸ Dimensions of the weir box, partial contraction calculations, and calibration data for all interchangeable weir plates are included in the appendix.

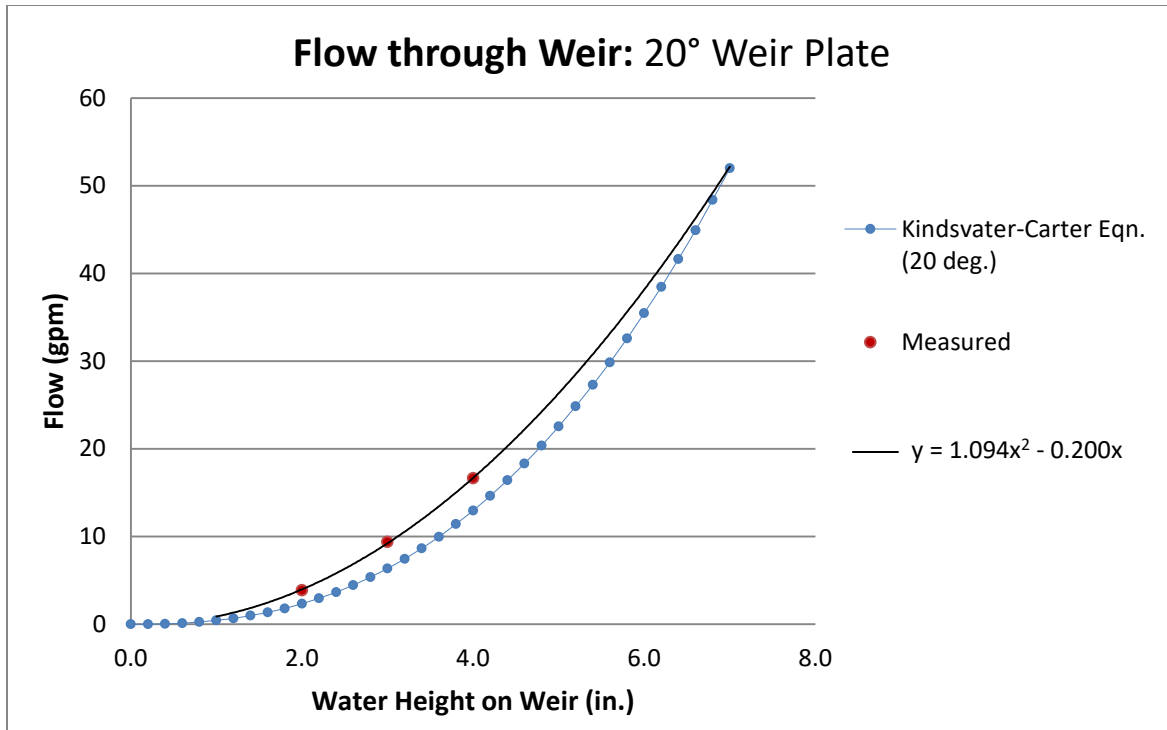


Figure 6. Laboratory calibration data and Kindsvater-Carter predictions for a 20° partially contracted v-notch weir.

$$Q = 4.28 C_e \tan\left(\frac{\theta}{2}\right) \left(\frac{H+k}{12}\right)^{\frac{5}{2}} \quad (5)$$

Where: Q = flow (cfs)
 C_e = effective discharge coefficient, tabulated value (s^{-1})
 θ = angle of the v-notch (degree)
 H = head over the weir (in.)
 k = head correction factor, tabulated value (in.)

The down-flow, field-scale adsorption column was constructed using 35.6 cm extruded acrylic (Figure 7). Stainless steel was used for all fasteners, connecting rods, and adjustable. The column was filled with 46 cm of biochar or raw wood crumbles, sandwiched between 5 cm of pea gravel. A stainless steel wire mesh screen was used to cover the PVC outlet of the column in order to prevent pea gravel or media from exiting. A flow distribution plate was built into the column lid to distribute flow across the media.

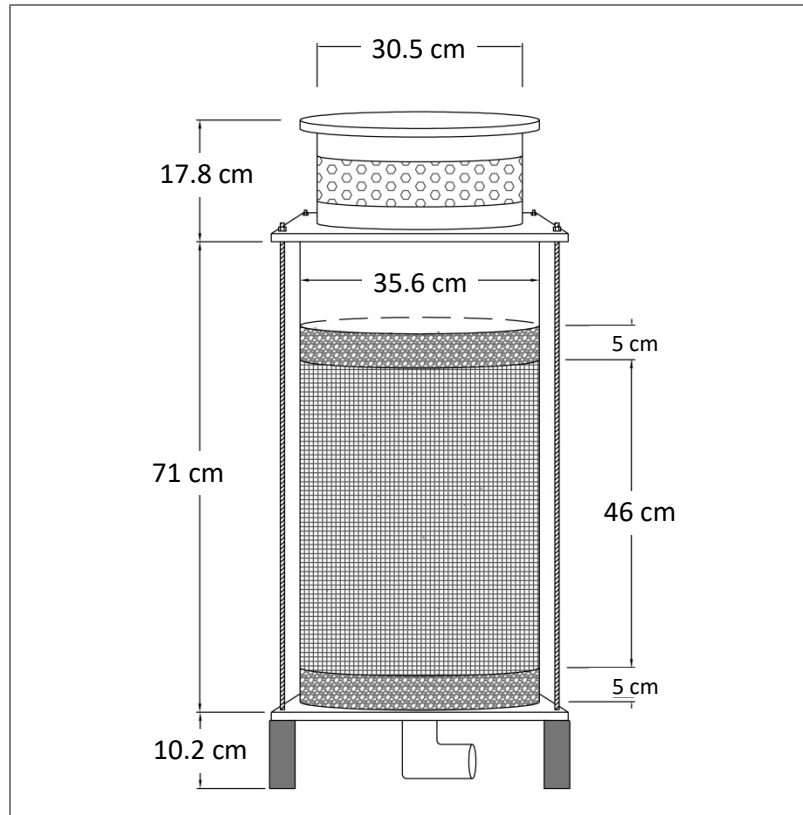


Figure 7. Schematic of the field-scale column.

During each storm event, the column's design allowed stormwater to enter laterally through the top of the column, pass vertically downward through the media, and exit via a 5.1 cm PVC pipe at the base of the column (Figure 7 and Figure 8). Effluent flow passed from the column into the weir box through 5.1 cm PVC conduit. Water passed over the v-notch weir and through the sidewall of the vault where it rejoined the storm flow. Influent and effluent column sampling was triggered by rising water level, measured by a pressure transducer that was affixed just upstream of the weir plate on the bottom of the weir box. Column inlet sampling was afforded by placing the inlet sample line near the inlet (top) of the column when the submersible pump was not used. When the pump was used, the inlet sample line was placed next to the inlet of the pump. The effluent sample line was attached to a sealed port installed in the conduit passing between the column and the weir box. A schematic of the field site stormwater sampling equipment configuration is shown in Figure 8.

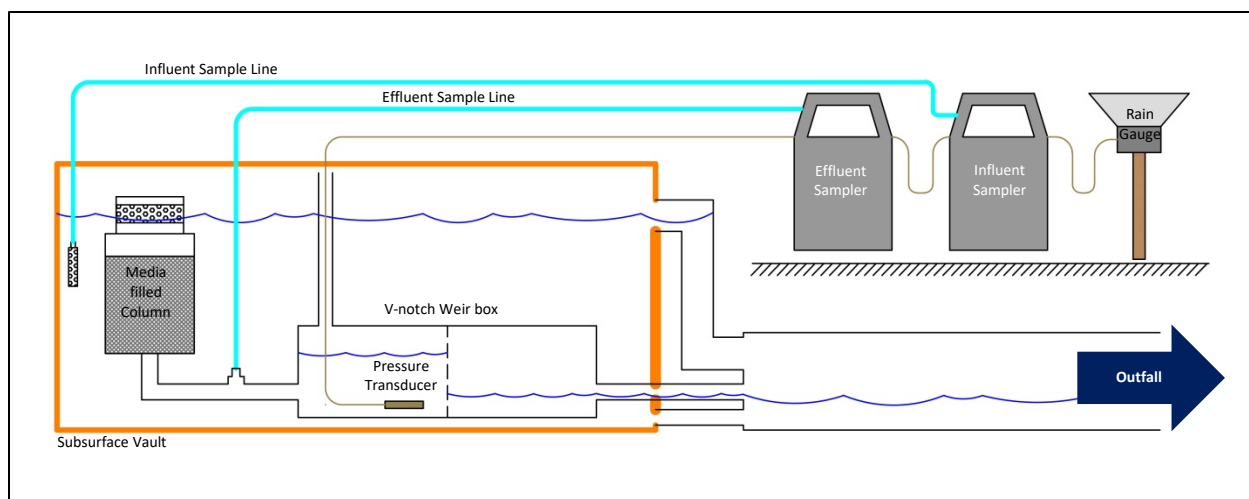


Figure 8. Schematic of the stormwater sampling configuration during a rain event (pump not shown).

Limited rainfall through the summer months prompted the installment of a submersible pump to capture minor rain events as well as significant storms. The pump was placed approximately 20 cm from the bottom of the vault and the discharge hose was connected to the top of the column.

Following each storm event, sample bottles were retrieved within seven days of collection, put on ice, and transported to our laboratory at Washington State University. Samples were stored for up to two weeks at 4 °C prior to preparation for analysis. For the first three storm events, discrete sample bottles 1-12 and 13-24 were composited and the composite samples were prepared for analysis. For storm events 4 – 12, discrete sample bottles 1-8, 9-16, and 17-24 were composited and prepared for analysis. Each composite sample was analyzed for total and soluble copper and zinc using EPA method 200.7.⁴⁰ Total suspended solids (TSS) and volatile suspended solids (VSS) were determined per EPA method 1684.⁴²

A sludge sample was taken from inside the vault after the August 29th storm event and tested for zinc and copper concentrations. Procedural steps for sludge sample preparation and analysis were determined from EPA 200.7 and EPA 1684 respectively.^{40,42} A particle size analysis was conducted on the sludge sample using a Malvern Mastersizer 3000.

3. Results and Discussion

3.1 Media Surface Structure

Scanning Electron Microscope (SEM) imaging results for raw wood, torrefied wood, and biochar are shown in Figure 9. The images, presented at 500-x and 5000-x magnification, show the materials' cross-sectional surfaces. Although observed differences between raw wood, torrefied wood, and biochar can be seen, care must be taken in drawing any firm conclusions since factors such as wood species and sample preparation could impact image results. The images presented at 5000-x magnification show that the capillary walls of raw and torrefied wood are similar and show spiral thickening ridges, while biochar has smooth walls that have begun to form cross-pores between capillaries. The introduction of cross-pores and the known formation of micropores (pores less than 2 nm; not visible) result in an increase in surface area that is potentially available for adsorption.

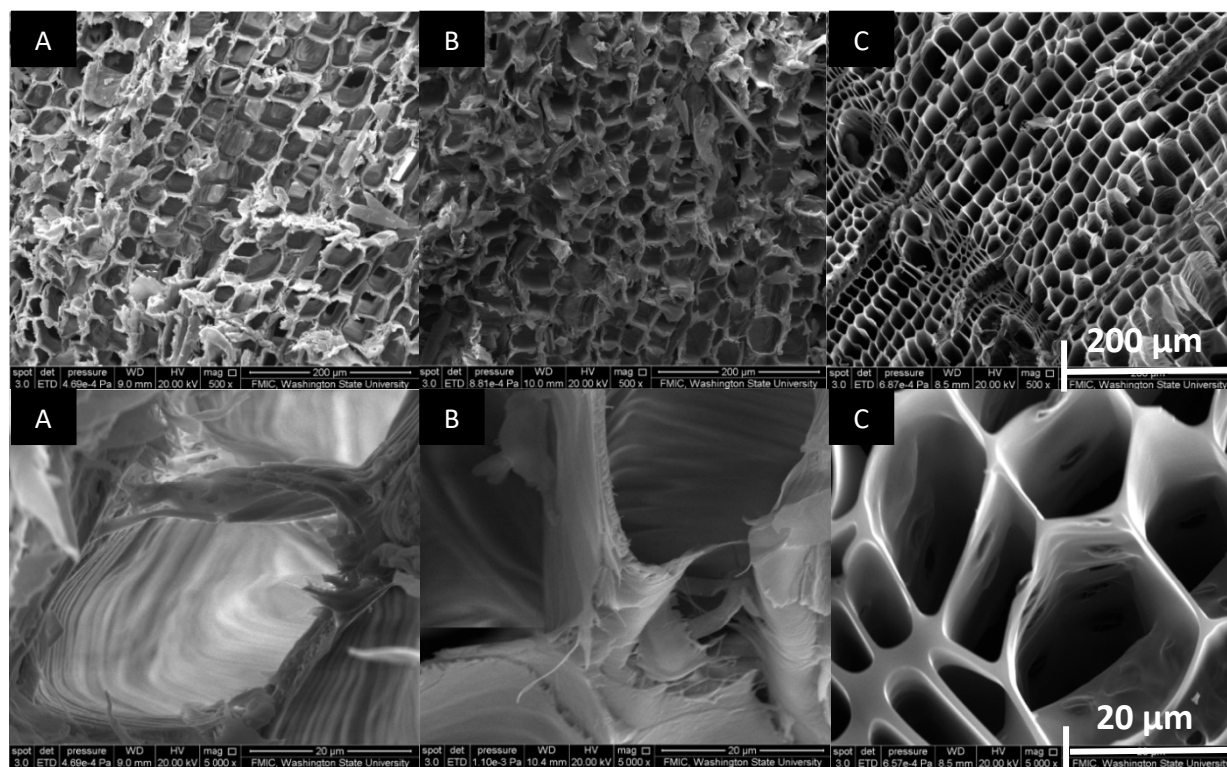


Figure 9. SEM micrographs at 500-x magnification (top row) and 5000-x magnification (bottom row) for A) raw wood, B) torrefied wood, and C) biochar.

3.2 Media Surface Chemistry

Thermal treatment degrades hemicellulose (200-260 °C), cellulose (240-350 °C), and lignin (280-500 °C) in wood cell walls.⁵⁹ At treatment temperatures above 240°C, the carbohydrate fraction of the wood decreases, and the aromatic fraction present in lignin increases. Ether (R-O-R') bonds that link guaiacyl rings (Figure 10) in lignin are thermally cleaved and newly formed C-C

direct bonds are thought to increase the guaiacyl ring density (Park et al., 2013) and surface area available for adsorption sites increases with increased aromatic density in wood cell walls.⁶¹ Metal adsorption is also enhanced on sorbents containing carboxyl functional groups (Figure 10) that provide sites for ion exchange. The formation of carboxyl groups is a result of the degradation of carbohydrates in cellulose, and can be improved through oxygenation during or after thermal treatment.⁶²

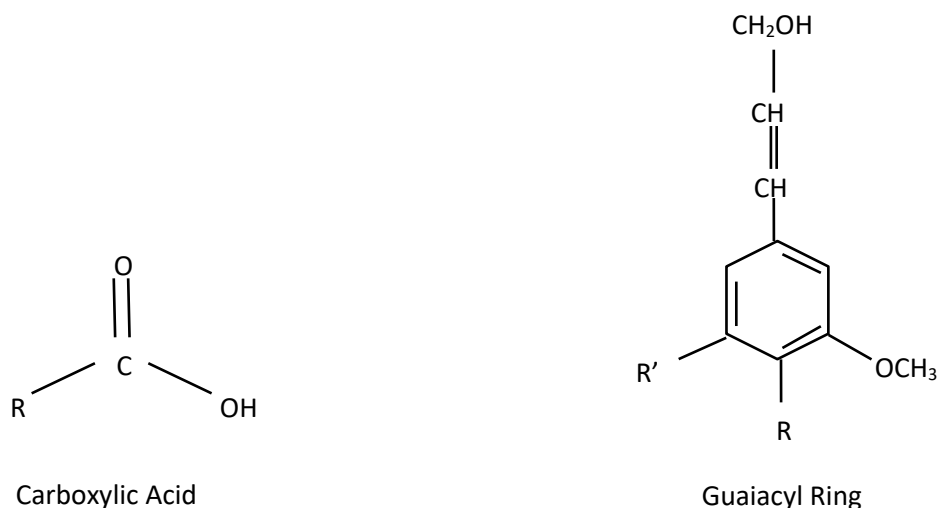


Figure 10. Structures of carboxylic acid and guaiacyl rings. Guaiacyl rings are the backbone of lignin.

Results from FTIR analysis of raw wood, torrefied wood, and biochar, presented in Figure 11, indicate the stretching of a C=C bond in guaiacyl rings (1510 and 1600 cm^{-1}). While there is no observed difference between treatments at 1510 cm^{-1} , the peak absorbance at 1600 cm^{-1} was more intense for torrefied wood and biochar than for raw wood crumbles. Differences in peak intensity indicate an increased aromatic density in torrefied wood and biochar.^{59, 60} The fraction of cellulose, indicated by the presence of aliphatic C-O-C (1050 cm^{-1}) is typically inversely correlated to aromatic density. In this case, the peak was more intense in raw wood than in torrefied wood and was not present in biochar. The results agree with the findings of others that indicate as treatment temperature increases, cellulose degrades and the aromatic content of the wood cell wall increases (Park et al., 2013). Additionally, the peak describing the presence of carbonyl (R-COR') groups (1740 cm^{-1}) was only present in raw wood suggesting a removal of ester groups (R-COOR') from the hemicellulose fraction as treatment temperature increases above $200\text{ }^{\circ}\text{C}$ (Park et al., 2013). Carboxylic acid (1700 cm^{-1}) is only present in the torrefied wood and biochar samples. This agrees with the knowledge that as treatment temperature increases, the carbohydrate fraction of lignocellulosic biomass further degrades (Park et al., 2013). If surface functional groups were the only factor defining adsorption potential, the torrefied wood and biochar would be expected to outperform raw wood.

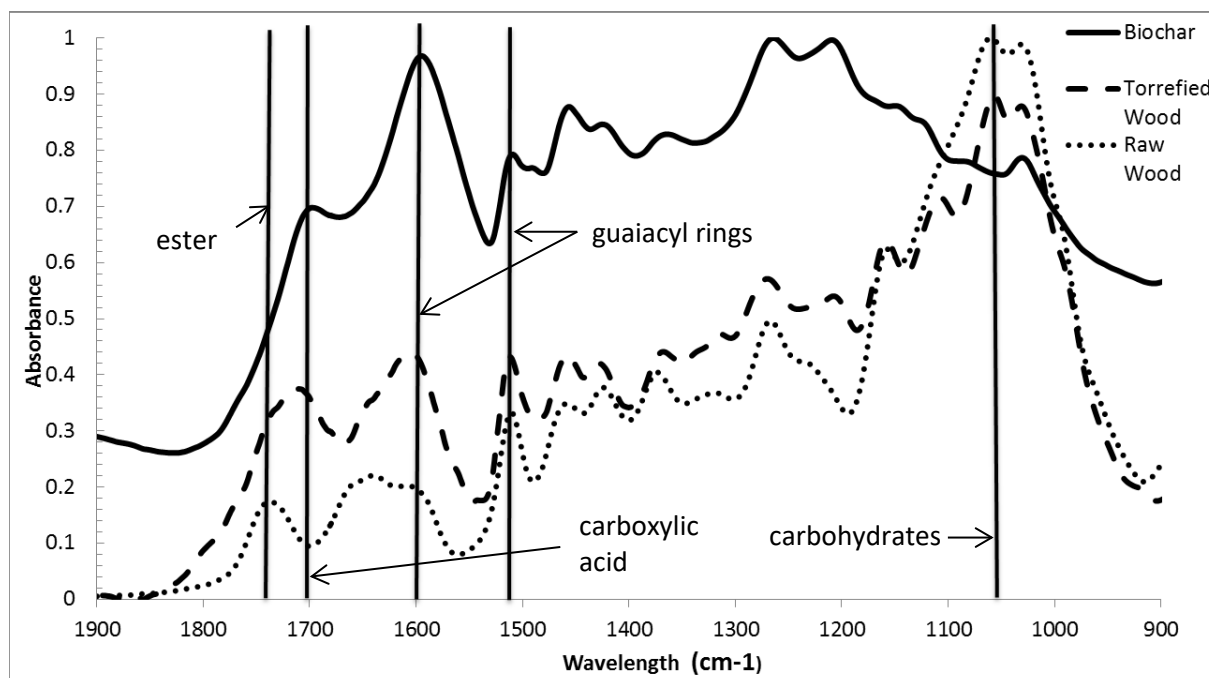


Figure 11. FTIR results for biochar, torrefied wood, and raw wood.

3.3 Single and Multi-Solute Isotherms

3.3.1 Single Solute Results

Both the Freundlich and Langmuir equations were evaluated for their ability to describe single solute isotherm data. It was found that the Freundlich equation provided the best fit of the data over the range of concentrations studied. Values of the Freundlich equation fitting constants, K_F and $1/n$, are presented in Table 4.

Table 4. Freundlich equation fitting constants.

Media	Cu		Zn	
	K_F	$1/n$	K_F	$1/n$
Biochar	0.509	0.374	0.136	0.789
Torrefied Wood	0.412	0.579	0.317	0.468

The data in Figure 12 indicate that copper has a higher affinity for biochar than torrefied wood. Conversely, the data in Figure 13 show that zinc has a greater affinity for biochar compared to copper.

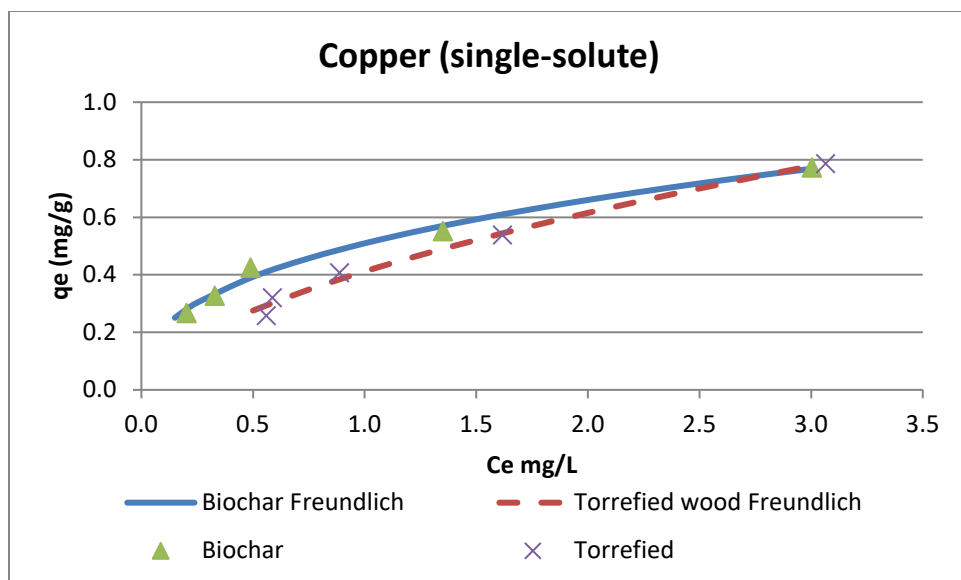


Figure 12. Comparison of biochar and torrefied wood copper adsorption data.

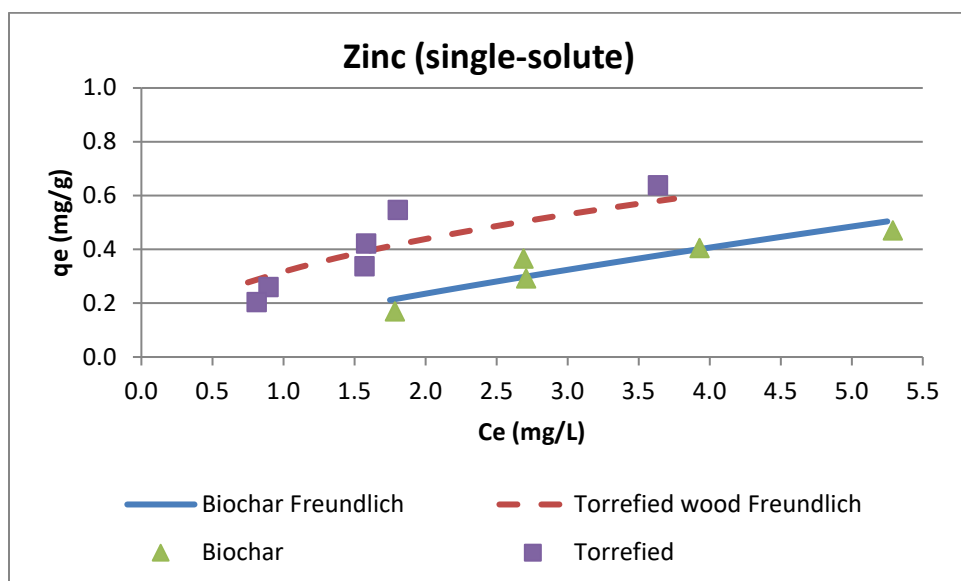


Figure 13. Comparison of biochar and torrefied wood zinc adsorption data.

3.3.2 Multi-Solute Results

Multi-solute isotherm data was plotted along with the single solute Freundlich equation predictions in Figure 14 and Figure 15. The multi-solute data generated from sorption to biochar and torrefied wood shows that for both sorbents, copper out competes zinc for sites of

adsorption under the conditions studied. Solid phase capacity for copper on biochar in a multi-solute system remained essentially the same as in the single-solute system. Conversely, zinc sorption to biochar was negatively affected by the presence of copper, evidenced by the data falling below the single-solute Freundlich equation prediction line. Similar results are shown for the torrefied wood (Figure 15). Copper outcompeting zinc for adsorption sites is a significant advantage considering that zinc exists at significantly higher concentrations in stormwater than copper and the allowable discharge limit of copper is over an order of magnitude less than for zinc (Table 1).

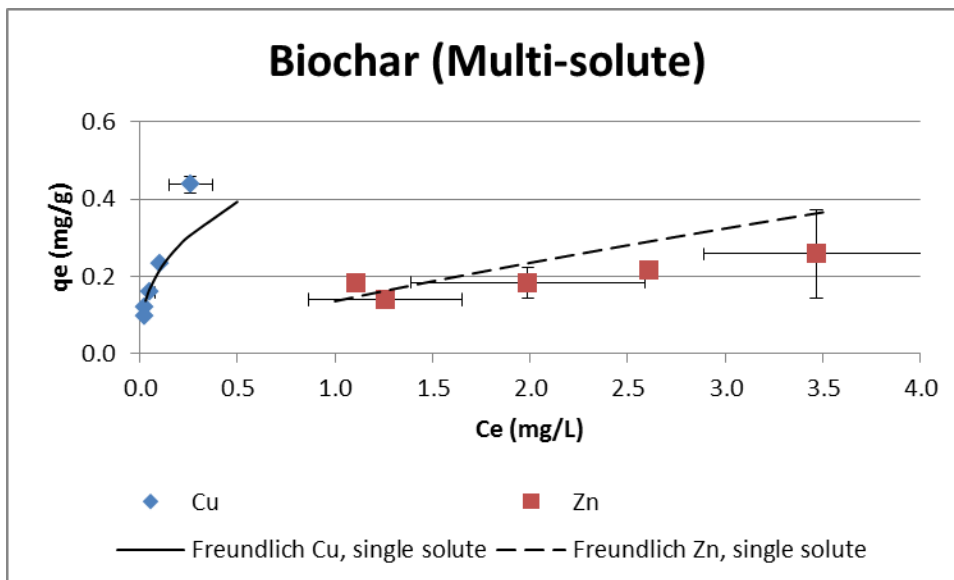


Figure 14. Biochar multi-solute isotherm data and single solute Freundlich equation predictions. Initial copper and zinc concentrations were 2.5 and 4.5 mg/L, respectively. Error bars represent 95% confidence intervals.

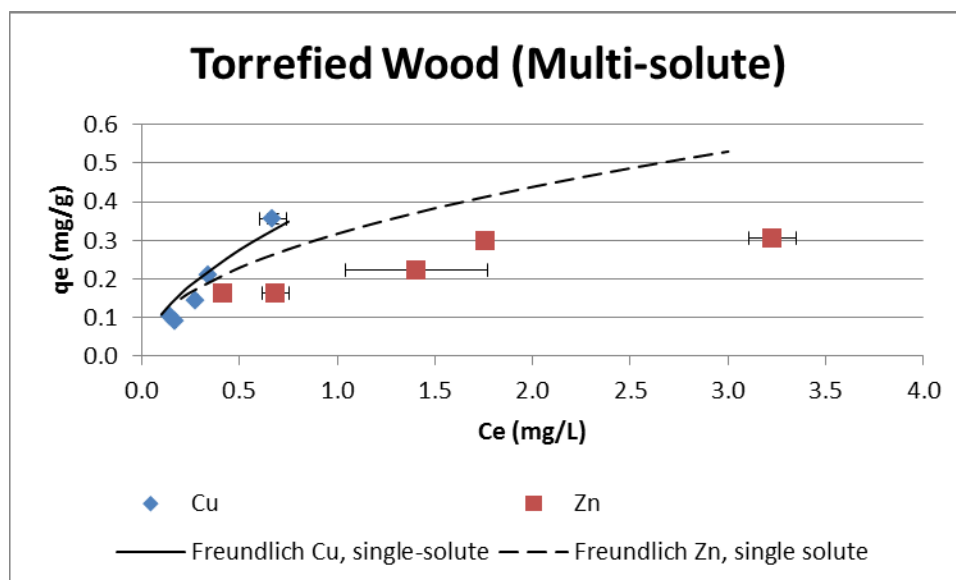


Figure 15. Torrefied wood multi-solute isotherm data and single solute Freundlich equation predictions. Initial copper and zinc concentrations were 2.5 and 4.5 mg/L, respectively. Error bars represent 95% confidence intervals.

3.3.3 Adsorption Kinetics

The rate of copper and zinc adsorption to biochar and torrefied wood was tested to assess if the 24-hour equilibrium period was sufficient to obtain useful data. Results are presented in Figure 16 Figure 17. After 24-hour equilibration, 88% of copper and 71% of zinc were adsorbed by biochar when compared to a 72 hour equilibration period. After 24 hours, 91% of copper and 90% of zinc were adsorbed by torrefied wood when compared to 72 hours. It was determined that while equilibrium had not been fully achieved, a 24 hour mixing period was sufficient to make relative comparisons between the performance of biochar and torrefied wood and to gain useful multisolute sorption data regarding competitive adsorption effects on both biochar and torrefied wood.

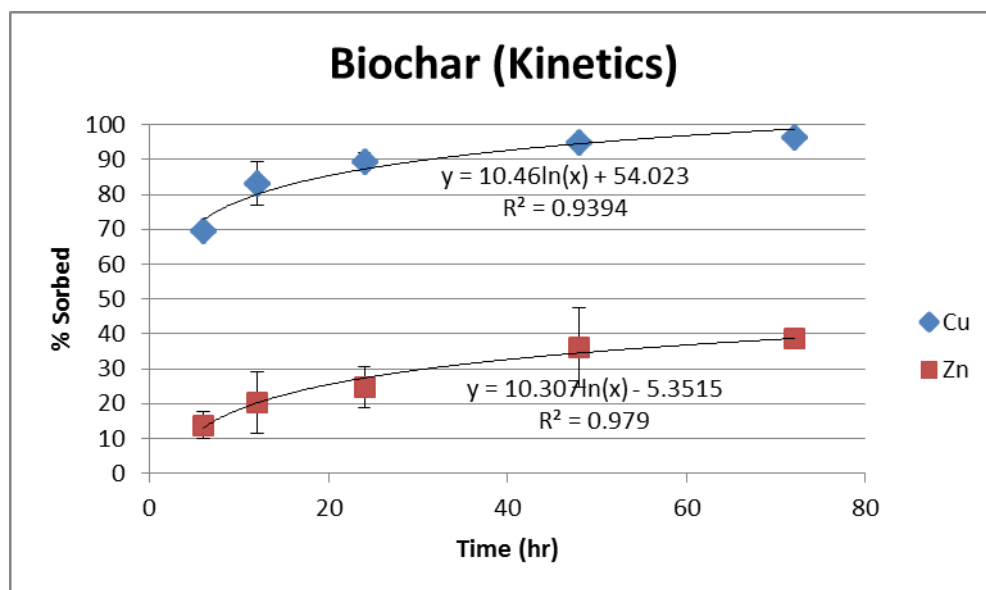


Figure 16. Biochar adsorption kinetics. Initial copper and zinc concentrations were 2.5 and 4.5 mg/L, respectively. Error bars represent 95% confidence limits.

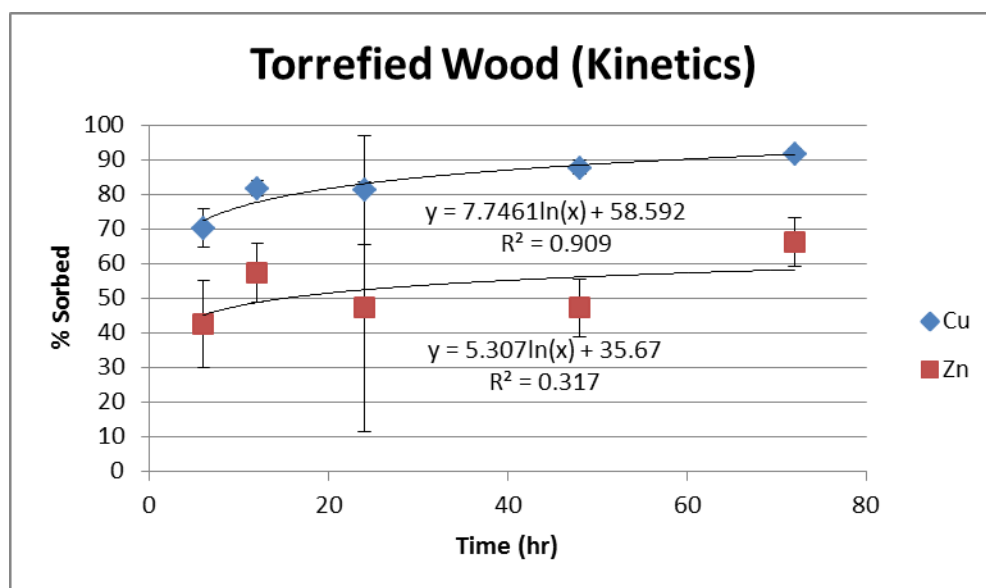


Figure 17. Torrefied wood adsorption kinetics. Initial copper and Zn concentrations were 2.5 and 4.5 mg/L, respectively. Error bars represent 95% confidence limits.

3.4 Phase I & II Bench Scale Testing

3.4.1 General Long-Term Trends

Influent and effluent zinc and copper concentration data are shown in Figure 18 and Figure 19 for biochar and torrefied wood columns. Each effluent data point represents an average from three replicate columns. Each influent data point in Phase I represents an individual sample taken – several of which originated from the same influent batch. Phase II influent data points represent an average of 3 samples taken from the same influent batch. The difference between Phase I & II was duration of each test event. Phase I column loading events lasted 20 minutes while Phase II events were 80 minutes in duration. The detailed behavior exhibited by each effluent concentration profile will be discussed later in Section 3.4.2 Short-Term Trends. Here the focus is on evaluating general, long-term data trends.

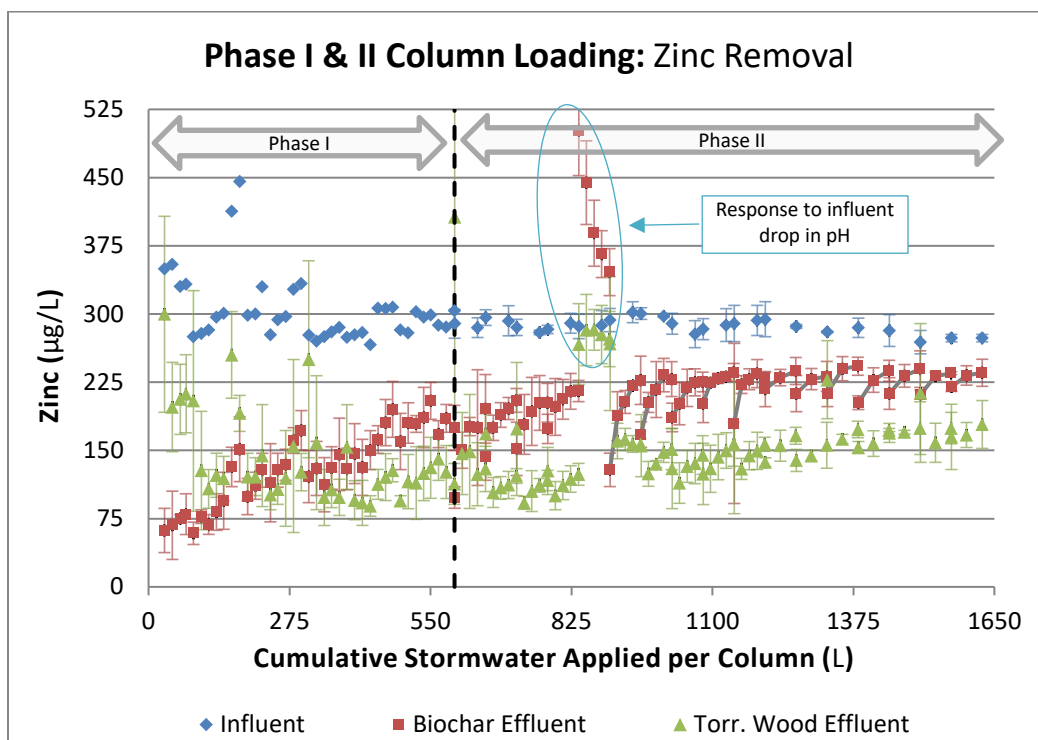


Figure 18. Zinc concentrations for the influent and effluent during Phase I & II column loading experiments. Error bars represent 95% confidence intervals.

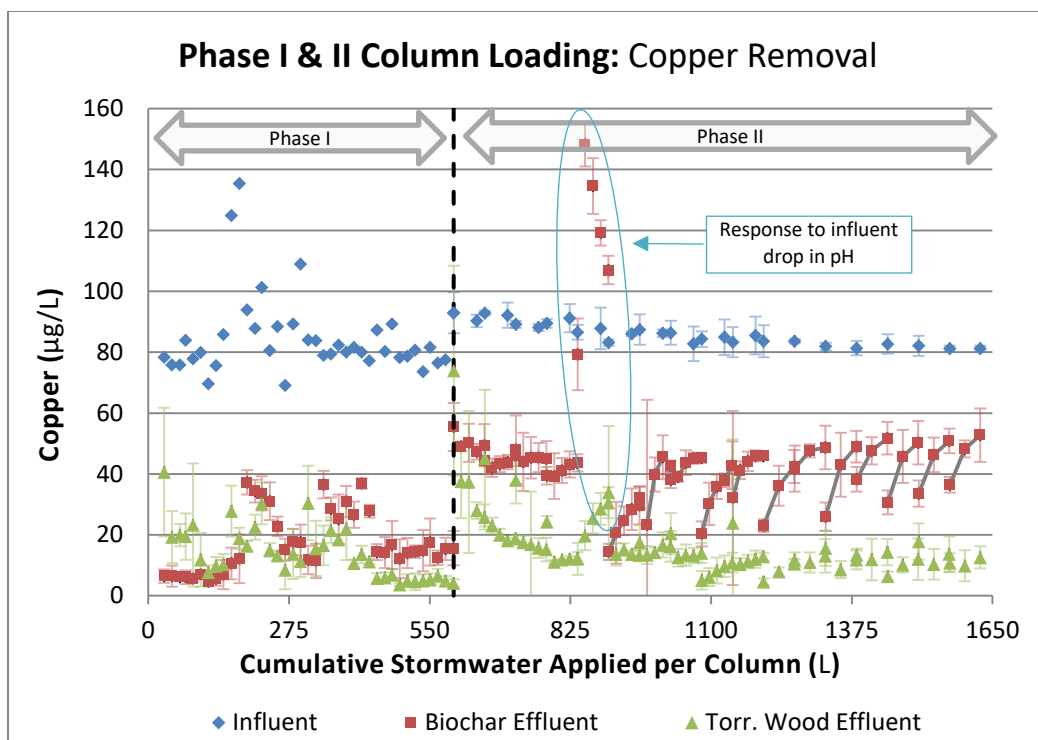


Figure 19. Copper concentrations for the influent and effluent during Phase I & II column loading experiments. Error bars represent 95% confidence intervals.

The influent and effluent data for Phase I testing exhibits more scatter than the Phase II data (Figure 18 and Figure 19). This is due to greater experimental error experienced during start-up of the column tests. The only effluent concentration profile that shows a discernable long term trend is that for zinc on biochar columns (Figure 18). The concentration is observed to increase from about 75 µg/L to 175 µg/L during Phase I. This is typical behavior for most sorbents in adsorption systems; as available sorption sites become occupied, the contaminant removal efficiency decreases and effluent concentration increases.

An interesting trend can be observed in the torrefied wood column effluent data at the early stage of operation (up to about 100 L). The effluent zinc data in Figure 18 shows a decreasing concentration during this period of operation. It is believed that this behavior is related to the changing moisture content of the media as testing progresses. At the initiation of Phase I testing, the moisture content of torrefied wood (4%) was well below the fiber saturation point (fsp) that is 25 – 30% for most wood species.⁴⁹ As column testing progressed, the torrefied wood crumbles swelled with hydration, opening capillary structure and allowing metals to access additional sites of adsorption through diffusion.²¹ Once inside the cell structure, the metals are removed from solution by electrostatic bonding with hydroxyl groups associated with wood polymers.⁵⁰

In Phase II, the overall effluent zinc concentration continued to increase for both media as cumulative stormwater throughput increased (Figure 18). For biochar, effluent zinc concentration stabilized at an average value of approximately 230 µg/L at stormwater

throughput greater than 1325 L. Torrefied wood columns also showed a gradual increase in effluent zinc concentration. At the end of phase II testing (1628 L total stormwater throughput), effluent zinc concentration for torrefied wood was approximately 160 µg/L. Overall, both media exhibited decreased percent zinc removal with increased cumulative stormwater throughput during Phase II.

The data presented in Figure 19 indicate that the long-term Phase II effluent copper concentration for biochar is stable at approximately 45 µg/L. The torrefied wood effluent data shows an initial decrease in copper concentration from the initiation of Phase II to a throughput of approximately 870 Liters (230 gal.). This is likely attributed to a significant column rest period that occurred between Phase I and II, resulting in decreased moisture content of the media and resulting decrease in adsorption site availability. As throughput volume increased across Phase II, torrefied wood effluent copper concentration stabilized at an average concentration of about 12 µg/L.

The overall removal for both Phase I and II was determined by calculating total mass of zinc and copper adsorbed using influent and effluent concentration and flow data. After 1628 Liters of synthetic stormwater passed through the columns, the respective total mass of zinc and copper removed from solution by biochar was 163 and 78 mg and by torrefied wood was 231 and 114 mg. This equates to an overall percent removal of 34% zinc, 57% copper for biochar and 48% zinc, 83% copper for torrefied wood. It is clear that, for the conditions studied, torrefied wood outperformed biochar with regard to lower effluent metal concentration and higher percent removals.

The pH data shown in Figure 20 indicates that the biochar column increased the simulated stormwater pH during Phase I while torrefied wood lowered the pH, which is expected behavior for each media. Most woods originating from temperate zones are inherently acidic, including Douglas-fir and members of the *Pinus* genus.⁵¹ When wood, including torrefied wood, is in contact with water, free acids and acidic groups (primarily acetic acid, formic acid, and acetyl groups) are released into solution lowering the pH.^{29,51} During complete pyrolysis, acidic chemical compounds are released from the wood along with the desired sugar polymers, leaving behind a char that is typically alkaline.²⁹

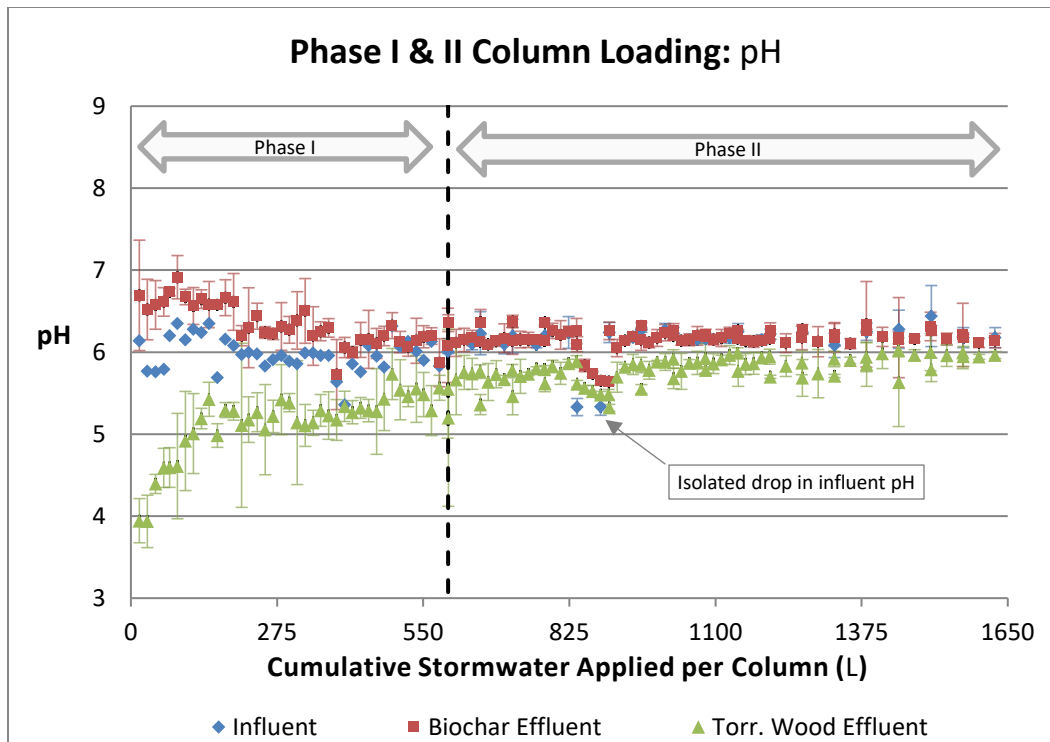


Figure 20. Influent and effluent pH values are shown during Phase I & II column loading. Error bars represent the 95% confidence interval.

At the end of Phase I and continuing through Phase II, influent and effluent pH were the same for biochar. Torrefied wood effluent pH was lower through Phase II, but was observed to gradually approach influent pH.

3.4.2 Short-Term Trends

Short term trends refer to effluent concentration profiles (Figure 18 and Figure 19) within and between single storm events. One of the most interesting single event concentration profiles occurs in phase II at a cumulative application volume of 230 gal. These profiles are the result of an unexpected low influent pH caused by a failure in the house deionized water system. The data in Figure 20 show that the pH decreased from a desired value of 6.1 to 5.2. The decrease in pH resulted in a significant increase in column effluent metal concentration. In fact, as can be seen in Figure 18 and Figure 19, the effluent zinc and copper concentrations during this event were greater than the influent for the biochar columns. Effluent concentrations from the torrefied wood columns also increased, but not as dramatically as for biochar. These concentration increases indicate the importance of pH on adsorption, particularly with regard to the adsorption of metals.

Excluding the isolated pH anomaly, most of the single event effluent concentration data show an interesting profile for both zinc and copper, regardless of media. These effluent concentration profiles are most evident in phase II where it can be seen that at the beginning of each simulated stormwater runoff event, the effluent concentration is relatively low and as the

event proceeds, the effluent concentration increases. For example, consider the event that begins at a cumulative stormwater volume of 900 L (Figure 18). The initial effluent zinc concentration is 129 µg/L and as the event progresses the concentration increases to 225 µg/L. This pattern is repeated following each 12-24 hour rest period, that is, lower initial effluent concentration with concentration increasing throughout the event. These “r-shaped” profiles are the result of intra-particle metal concentration decreasing between storm events (no flow period) as metals access harder to reach sites of adsorption, decreasing intra-particle and inter-particle pore water concentrations. Therefore, at the initiation of a run following a no-flow period, a high concentration gradient exists between the influent stormwater and the intra-particle pore water, resulting in increased rate of diffusion and lower effluent concentrations.

3.4.3 Supplementary Effluent Sample Testing

In addition to composite sample soluble metal quantification, supplementary testing was performed to evaluate effluent total suspended solids concentrations. In addition, discrete vs. composite metal concentrations were determined for quality control. Low total suspended solids (TSS) concentrations (< 3 mg/L) were observed in the effluent for a short duration at the initiation of Phase I testing. The effluent TSS were likely a result of loose fines being flushed off the media. After application of a total stormwater volume of about 90 L, TSS concentrations fell to less than 0.5 mg/L and remained there for the remainder of testing for both biochar and torrefied wood.

For selected events in Phase I, discrete effluent samples (80 mL) were taken simultaneously with the composite samples. The resulting discrete metal concentrations were then compared against the composite sample concentrations as a means of checking analytical technique. Discrete sample concentrations supported the macro trends described by the composite samples. This extra step confirmed laboratory techniques and assisted in validating metal quantification.

Following the end of Phase II, biochar and torrefied wood columns were subjected to increased flow testing. Column effluent metal concentrations and pH values during the increased flow tests are shown graphically in Figure 21 through Figure 23. Averages are provided in Table 5 for comparison.

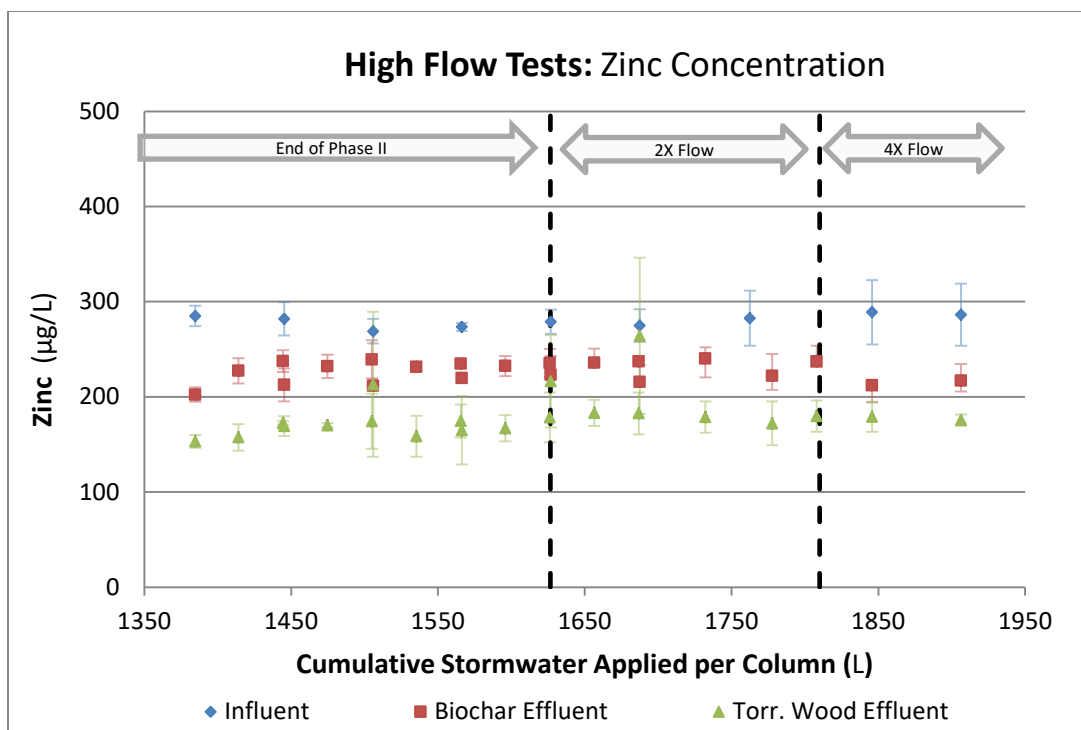


Figure 21. Zinc influent and effluent concentrations during high flow tests.

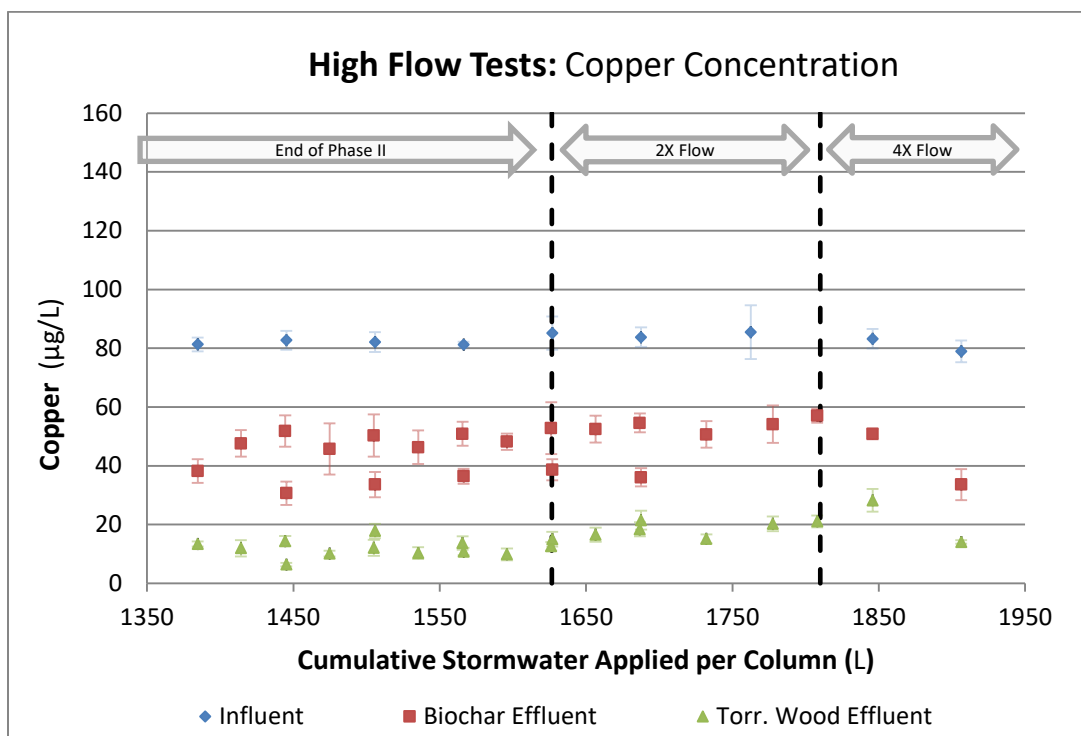


Figure 22. Copper influent and effluent concentrations during high flow tests.

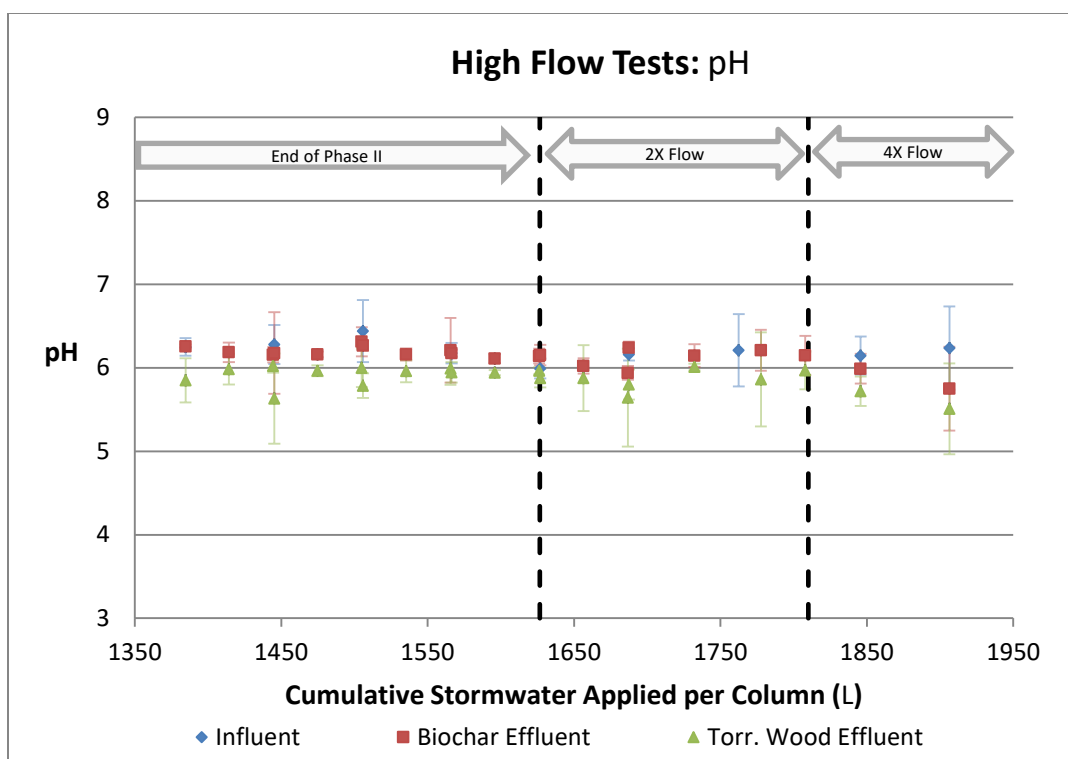


Figure 23. Influent and effluent pH values during high flow tests.

Table 5. Average effluent metal concentrations from torrefied wood and biochar columns when exposed to increasing influent flow rates of 0.76, 1.51, and 3.03 liters per minute.

Media / Metal		End of Phase II ($\mu\text{g/L}$)	2x Flow ($\mu\text{g/L}$)	4x Flow ($\mu\text{g/L}$)
Biochar	Zn	227 ± 7	230 ± 4	215 ± 7
	Cu	44 ± 5	49 ± 4	42 ± 10
Torrefied Wood	Zn	171 ± 9	195 ± 15	177 ± 6
	Cu	12 ± 2	18 ± 1	21 ± 9

It can be seen that increasing the flow rate resulted in no significant increase in effluent metal concentrations or change in pH over the range of flows studied. The shows that metal adsorption is stable over a relatively wide range of flow. The influence of flow on removal is important with regard to stormwater treatment applications due to highly variable flows experienced in the field.

After increased flow testing was complete, the biochar and torrefied wood columns were subjected to a deicer flush. The column influent contained calcium chloride with Boost™ (CCB) ($0.40 \text{ g CaCl}_2/\text{L}$) and no added copper or zinc. Flow through the columns was maintained at 0.76 lpm. Low concentrations of zinc and copper were detected in the influent and attributed to residual metals on the feed barrel walls. The 61 liter per column deicer flush was followed by an

equal volume standard stormwater influent batch with influent metal concentrations adjusted to 300 µg/L zinc and 100 µg/L copper and the pH adjusted to 6.1 ± 0.1 . The stormwater application rate remained at 0.76 lpm. Influent and effluent metal concentrations for the deicer tests are shown in Figure 24 and Figure 25.

Both media released metals when exposed to the deicer solution, resulting in significant increases in effluent concentration. The biochar column peak effluent metal concentrations were 1936 µg/L zinc and 526 µg/L copper. The torrefied wood column peak effluent metal concentrations were 4873 µg/L zinc and 395 µg/L copper. The calcium chloride concentration in the simulated deicer runoff was three orders of magnitude greater than previous influent zinc and copper concentrations. The high concentration resulted in a cation exchange phenomena, displacing sorbed copper and zinc ions from the media.

At the beginning of the deicer flush, the most accessible and exchangeable copper and zinc were replaced by calcium, resulting in the highest effluent concentrations (Figure 24 and Figure 25). As the deicer testing progressed, biochar and torrefied wood columns exhibited a decrease in metal effluent concentration. This is likely a result of easily accessible metals being displaced early in the run followed by the release of metals at a rate controlled by intra-particle diffusion.

When standard stormwater influent (300 µg/L zinc, 100 µg/L copper, pH = 6.1, and Q = 0.76 lpm) was resumed following a 24 hour rest period, the initial effluent zinc concentrations in both media columns increased when compared to the last samples collected at the end of the deicer flush (Figure 24). The last sample collected during the deicer flush for biochar and torrefied wood had a respective zinc concentration of 167 ± 22 µg/L and 347 ± 18 µg/L and the first sample collected after resuming a standard stormwater run yielded a concentration of 355 ± 182 µg/L and 3915 ± 518 µg/L. This behavior is due to continued cation exchange occurring in the intra-particle pore water during the rest period. When testing resumed after the rest period the zinc concentration gradient was initially reversed and zinc moved from the intra-particle pore water into the inter-particle water. The zinc concentration spike at standard influent initiation was more pronounced in torrefied wood compared to biochar, likely because torrefied wood has more difficulty to reach adsorption sites. This behavior was not observed for copper (Figure 25), indicating the previously discussed competitive advantage of copper over zinc.

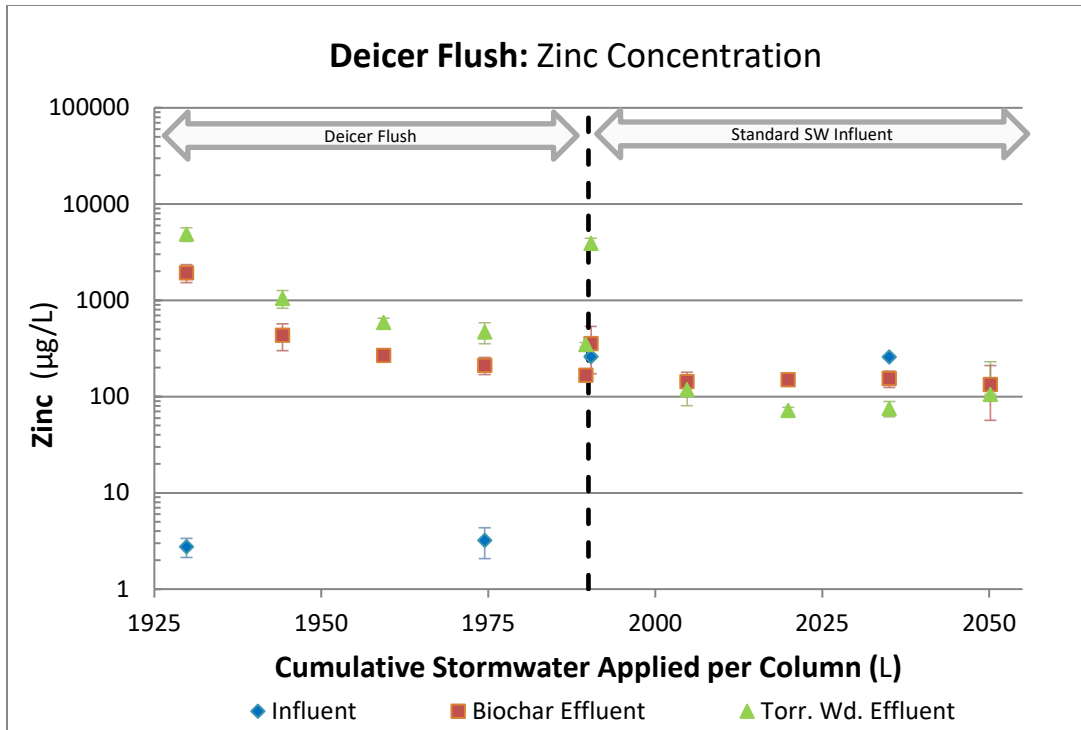


Figure 24. Influent and effluent zinc concentrations (log scale) during and following a deicer flush. Calcium Chloride with Boost™ was used as the anti-icing agent.

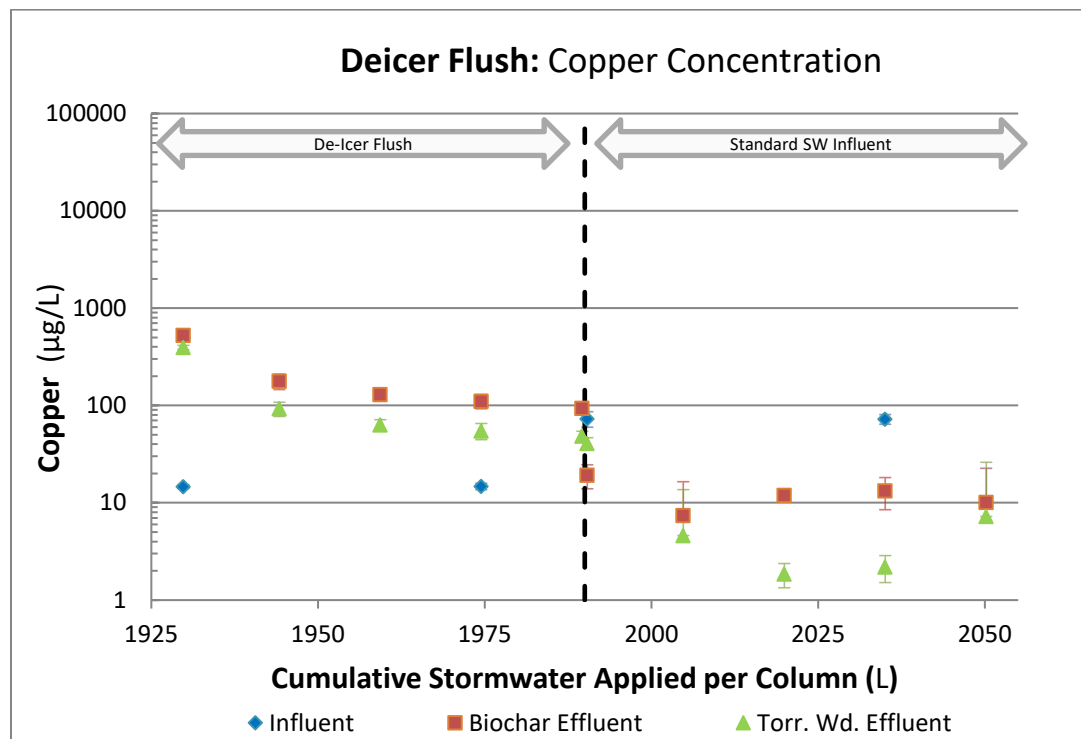


Figure 25. Influent and effluent copper concentrations (log scale) during and following a deicer flush. Calcium Chloride with Boost™ was used as the anti-icing agent.

The total mass of metals released during the salt flush for biochar and torrefied wood columns were 17.5 mg zinc, 8.0 mg copper and 40.0 mg zinc, 4.2 mg copper, respectively. When compared to the total mass of metals sorbed onto the media, the percentage of sorbed metals released by biochar and torrefied wood were 11% zinc, 10% copper and 17% zinc, 4% copper, respectively. The deicer tests indicate that steps may need to be taken to temporarily divert runoff from entering field columns if an anti-icing solution was applied prior to a runoff event.

3.4.4 Raw Wood and Pea Gravel

Based on the significant level of metal removal exhibited by torrefied wood, it was decided to test raw wood crumbles. Since pea gravel was used in the media columns it was also subjected to full column tests. Influent and effluent zinc and copper concentrations and pH values are shown in Figure 26 through Figure 28 for raw wood and pea gravel columns. Phase I & II biochar and torrefied wood 7-point moving average trend lines are also displayed on the graphs for a visual comparison between all four media.

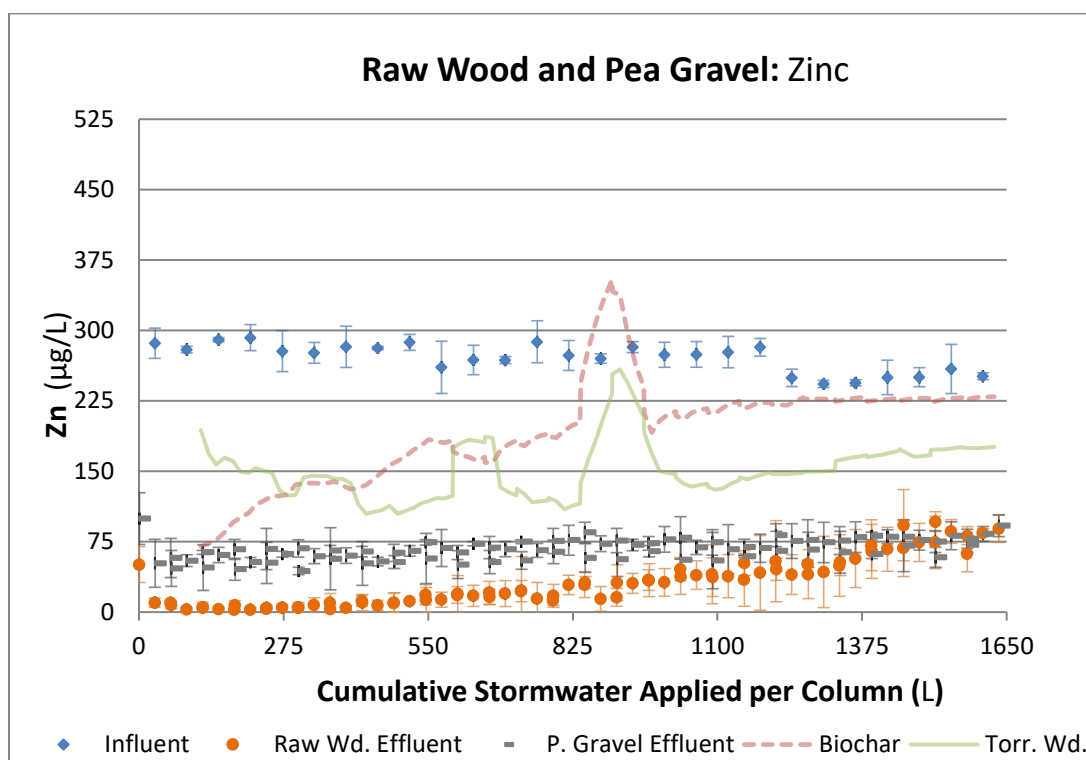


Figure 26. Influent and effluent zinc concentrations for raw wood and pea gravel columns. Phase I & II biochar and torrefied wood moving average trend lines are displayed for graphical comparison.

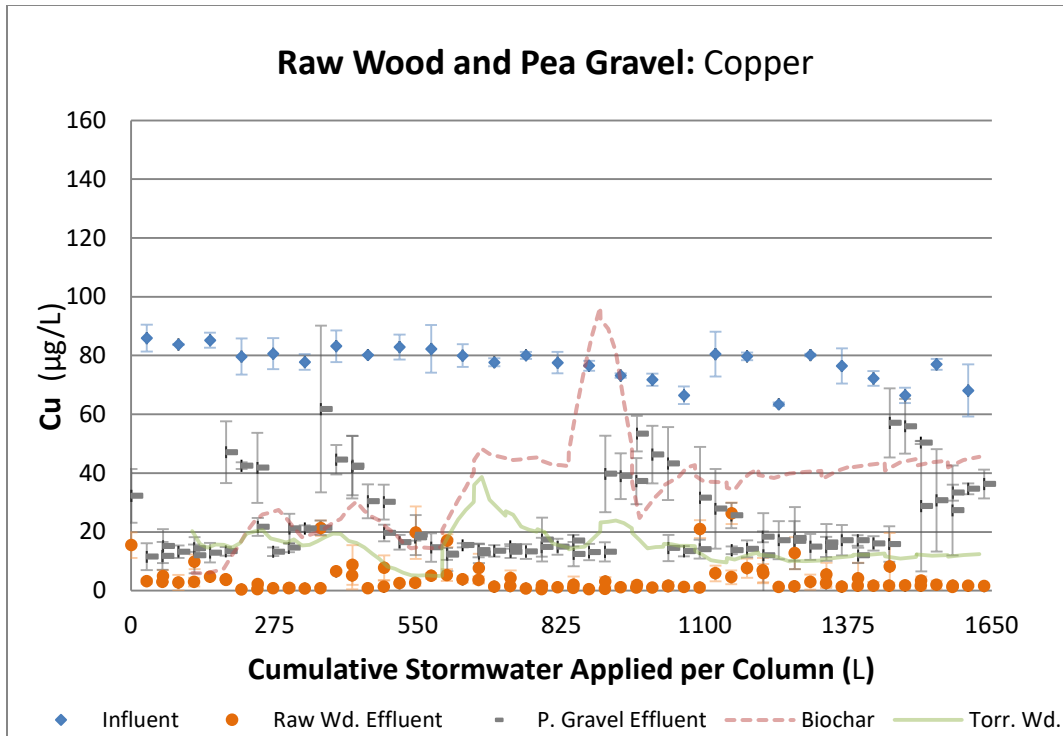


Figure 27. Influent and effluent copper concentrations for raw wood and pea gravel columns. Phase I & II biochar and torrefied wood moving average trend lines are displayed for graphical comparison.

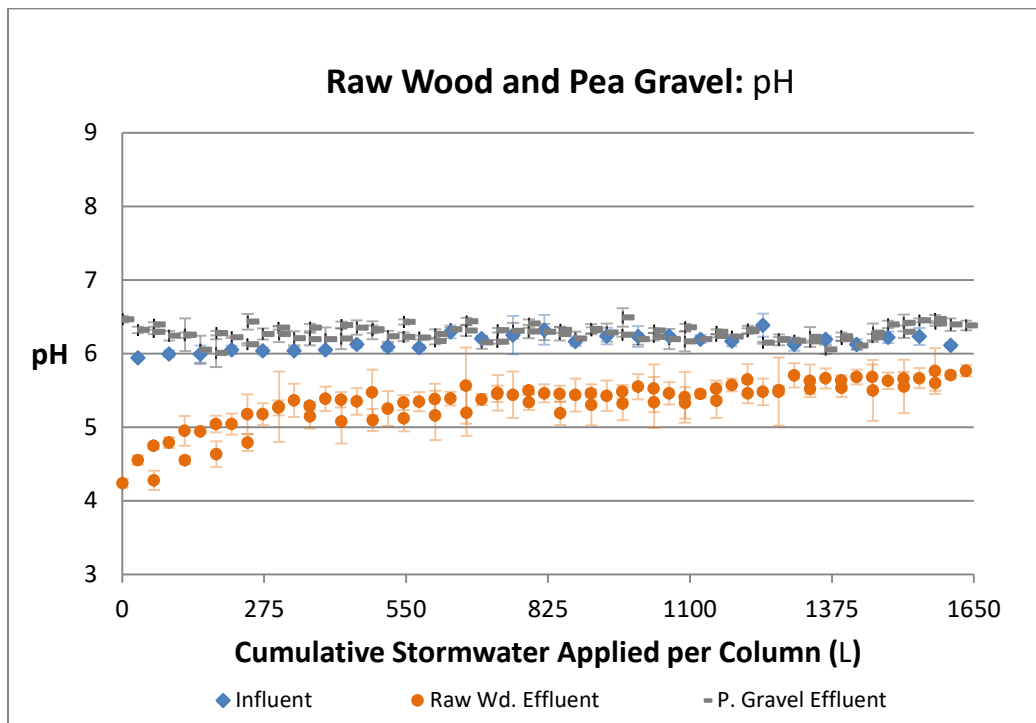


Figure 28. Influent and effluent pH values for raw wood and pea gravel columns.

Both raw wood crumbles and pea gravel exhibited significant metal removal ability when compared to biochar and torrefied wood. Torrefied wood's primary metal removal performance hinges on the inherent properties of the intact wood structure and therefore it is not surprising that raw wood proved to be an effective metal adsorbent. It is also well documented that sand and gravel filtration systems are highly effective at removing particulate-bound contaminants, the observed removal of soluble metal, however, was unexpected. The surface of the pea gravel must have complexation sites that result in copper and zinc sorption. Mechanisms of the observed removal were not evaluated, however.

While torrefied wood outperformed biochar, raw wood and pea gravel proved to be even more effective. Raw wood significantly outperformed all other investigated media in relation to copper by adsorbing 97% of the total exposed dissolved copper from the influent. At the end of 1630 Liters, the effluent exiting raw wood columns contained 2 µg/L copper which is below the Washington State maximum chronic discharge to marine waters limit of 3.1 µg/L (Figure 27). In relation to zinc, raw wood again outperformed all other investigated media by adsorbing 89% of the total exposed dissolved zinc from solution. The zinc effluent exiting raw wood and pea gravel columns were just reaching the maximum chronic discharge limit of 81 µg/L over 4 days at the end of testing (Figure 26).

Raw wood and pea gravel adsorbed 393 mg zinc, 123 mg copper and 328 mg zinc, 89 mg copper, respectively, during the 1630 Liter (430 gallon) testing period. Values reported in Table 6 are associated with 1630 Liters (430 gallons) of stormwater treated at target influent concentrations of 300 µg/L zinc and 100 µg/L copper. The biochar and torrefied wood values reported in Table 6 were calculated at the end Phase II and before supplementary tests (high flow and deicer flush) were performed. The percent metals adsorbed data indicate that for all media, copper outcompeted zinc for sites of adsorption, even though the copper feed concentration was 73% less than zinc.

Table 6. Summary table showing the mass of metals adsorbed onto filter media following the cumulative application of 1630 liters of synthetic stormwater.

Media /Metal	Biochar		Torrefied Wd.		Raw Wood		Pea Gravel	
	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu
Total mass of metals applied (mg)	477	138	477	138	443	127	443	127
Mass of metal removed by the media column (mg)	163	78	231	114	393	123	328	89
Percentage of total metal removed from influent	34%	57%	48%	83%	89%	97%	74%	70%
Mass of metal sorbed per mass of media (mg/g)	1.15	0.55	0.93	0.46	1.81	0.57	0.13	0.04

3.4.5 Solid Phase Acid Extraction

Acid extraction tests (EPA Method 200.7) were performed on biochar and torrefied wood column media after testing was complete to quantify the mass of metals sorbed onto the media and compare it against the mass of metals removed based on mass balance calculations using

flow and influent and effluent concentrations. The total mass of metals recovered in the acid extraction tests are reported for the entire column which includes metals from of the media and the upper layer of pea gravel. Through acid extraction, the respective mass of zinc and copper recovered from biochar columns was 121 ± 72 mg and 55 ± 12 mg and recovered from the torrefied wood columns was 211 ± 32 mg and 153 ± 24 mg. At the completion of all testing, mass balance calculations using influent and effluent concentrations and flow showed that biochar columns retained 169 mg zinc and 85 mg copper and torrefied wood columns retained 228 mg zinc and 135 mg copper. The percent difference of acid extraction values from mass balance values for biochar are 28% zinc, 35% copper and for torrefied wood -8% zinc, 12% copper. A positive percent difference indicates the acid extraction result was less than the mass balance calculation, with the opposite being true for a negative value.

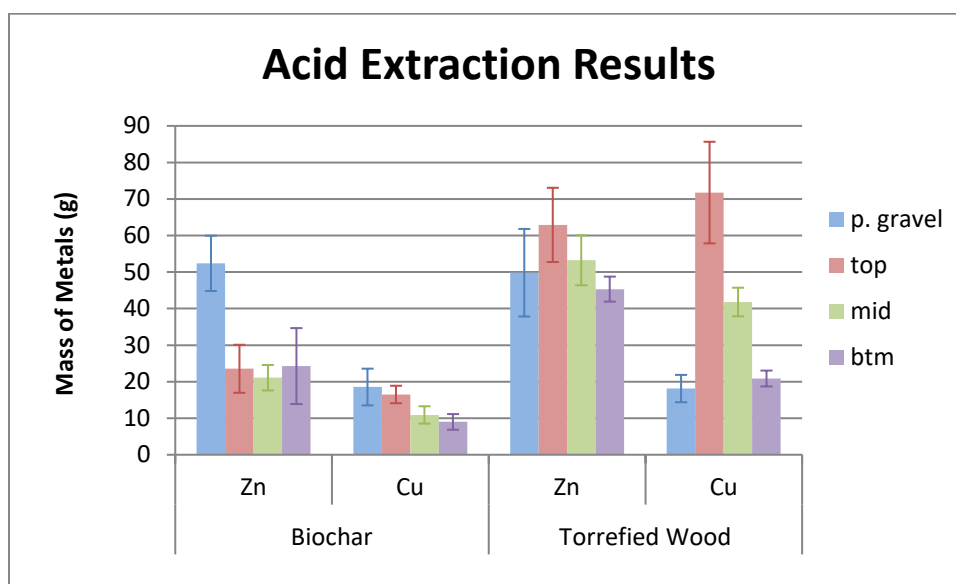


Figure 29. Column graph displaying stratified metal concentrations determined using the acid extraction method.

The data in Figure 29 represents the metal concentration profile through the media. With the exception of zinc on biochar, higher concentrations of metals are found in ascending layers of media because they are first to be exposed to the influent. As adsorption sites at the top become exhausted, the concentration profile moves down gradient until the entire column is exhausted. This behavior is commonly seen in gravity-flow columns used for sorption applications.²² The zinc profile for biochar shown in Figure 18 exhibits column exhaustion or near exhaustion which is consistent with the 14% zinc removal by biochar columns at the end of testing (Table 6).

When compared to the total mass of metals removed by the columns, the fraction retained by pea gravel, determined from acid extraction results, was considerable. While only occupying 20% of the total column media volume, pea gravel respectively adsorbed 43% and 34% of zinc

and copper in biochar columns. Still significant, although to a lesser degree, 24% zinc and 12% copper adsorption was attributed to the pea gravel overlying the torrefied wood crumbles.

3.5 Field Testing

3.5.1 Field Column Results: August – October 2015

Presentation of the field testing results has been divided into two groups based on the media used in the column. Biochar was used during the August – October 2015 period while raw wood crumbles were used during the January – April 2016 period. Three stormwater runoff events resulted in column flow-through and sample collection on August 14th, August 29th, and October 10th (Figure 30 through Figure 32). A submersible pump was used inside the subsurface vault to supply stormwater influent to the field column during the August 14th and 29th events. Clogging of the column occurred as a result of fine particulates being introduced by the pump which prompted its removal after the Aug. 29th storm event. The top layer of pea gravel was rinsed clean and permeability through the column was regained.

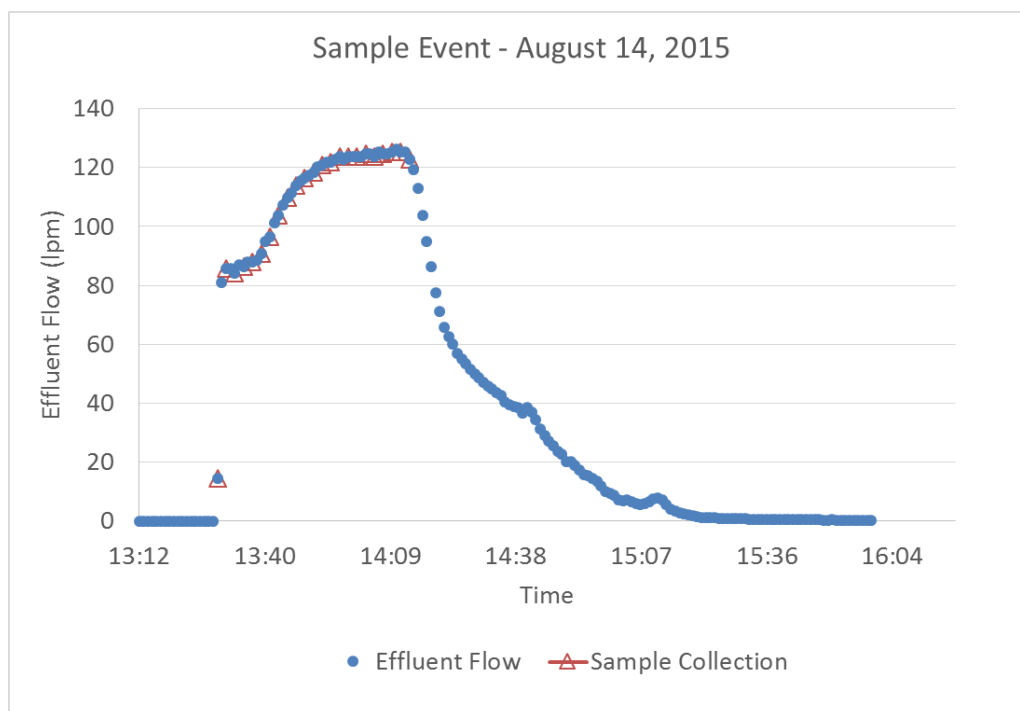


Figure 30. Column effluent flow and sample collection time during the August 14 event.

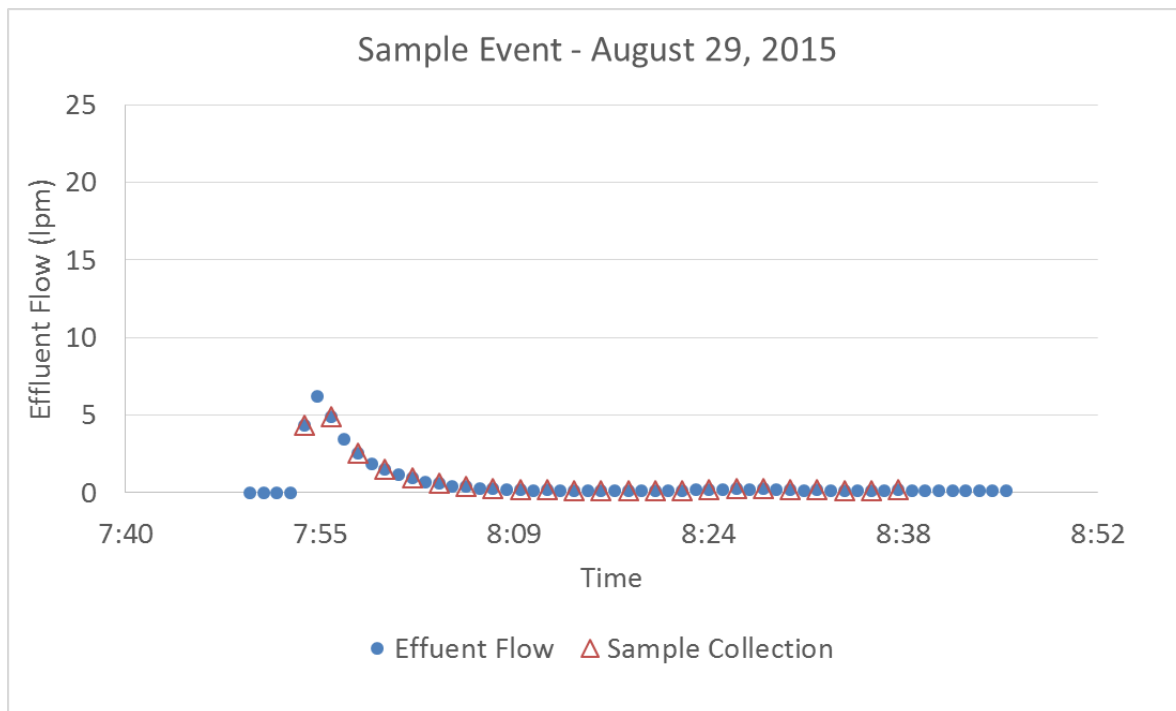


Figure 31. Column effluent flow and sample collection time during the August 29 event.

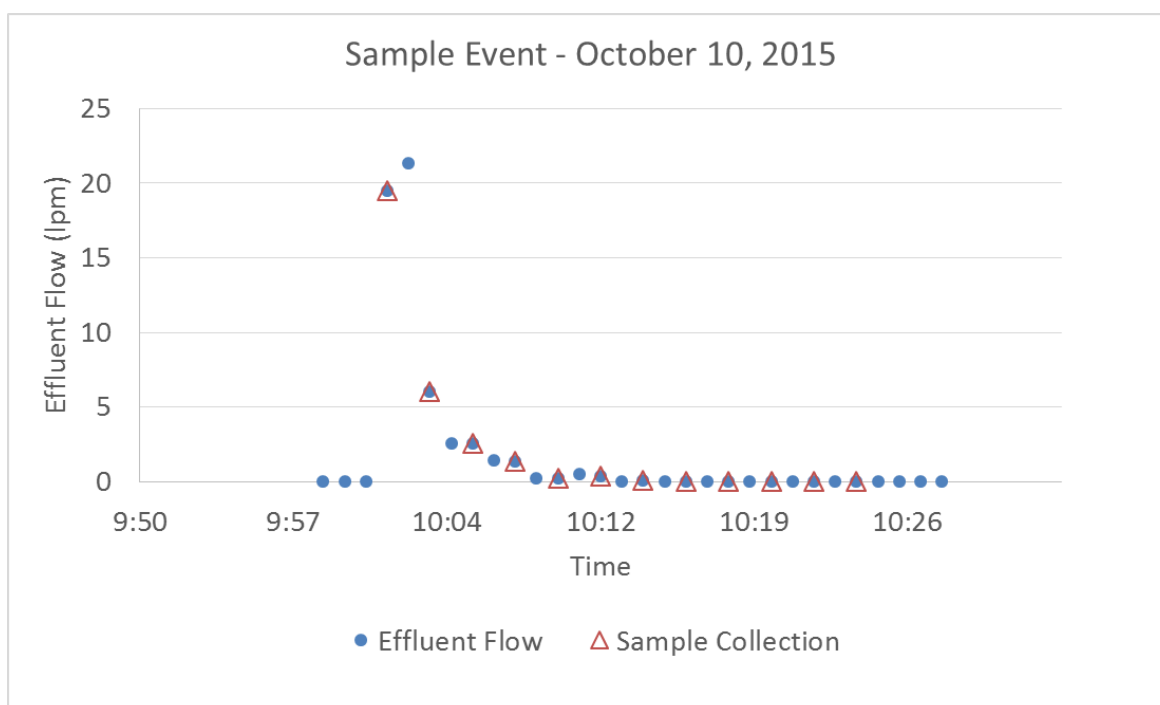


Figure 32. Column effluent flow and sample collection time during the October 10 event.

During each monitored storm event, discrete samples were programed to be collected every 2 minutes. Up to 24 samples could be collected for each event, if the duration of the event was

sufficient (≥ 48 min). The first half and the second half of the discrete samples for each event were mixed to make two composite samples. These composite samples were then analyzed for total and soluble metals (zinc and copper), TSS, TVSS, and pH. The metal concentration data shown in Table 7 summarize the results of three storm events. To simplify presentation, metal and TSS concentration data for each event are presented as an overall composite average. Detailed sample event data can be found in the Appendix.

Table 7. Influent and effluent constituent concentration averages for the field column containing biochar.

Constituent		Event 1 (August 14th)			Event 2 (August 29th)			Event 3 (October 10)			Average All Events		
		Avg Influent	Avg Effluent	Conc Reduction (%)	Avg Influent	Avg Effluent	Conc Reduction (%)	Avg Influent	Avg Effluent	Conc Reduction (%)	Influent	Effluent	Conc Reduction (%)
TSS (mg/L)		141	88	38	100	22.5	78	313	130	58	185	80	57
Total Metals ($\mu\text{g/L}$)	Cu	45	50	-11	21	13	40	38	15	61	35	26	25
	Zn	270	184	32	131	36	73	143	78	45	181	99	45
Dissolved Metals ($\mu\text{g/L}$)	Cu	17	18	-8	6.1	8.2	-34	3.0	2.6	13	8.8	9.8	-11
	Zn	116	99	14	46	15	68	45	28	38	69	47	31

The data from the August 14 event indicate a relative low level of constituent percent removal compared to the other two field events and compared to laboratory column testing using biochar (Table 7). The lower observed removal efficiencies are likely a result of the high flow and influent concentrations observed during the August 14 event. The peak flow, normalized to the column surface area, was about 0.078 lpm/cm² compared to respective peak flows of 0.004 lpm/cm² and 0.014 lpm/cm² for August 29 and October 10. The highest applied flow during laboratory testing was 0.042 lpm/cm². In general, higher flows that result in significantly lower column contact times is known to decrease constituent removal in continuous flow columns. The minimal or, in some cases, negative soluble copper removal is a result of very low influent soluble copper concentrations and possible interference from MCE filter membranes used to remove particulates from the sample prior to ICPMS testing.

The average influent TSS concentration for the three storm events was 159 mg/L. Washington State has a stormwater quality treatment goal of 80% TSS removal for facilities that produce TSS within the 100-200 mg/L range.¹⁹ Average TSS removal was 57%, less than the 80% goal. It is also noteworthy that the field column containing biochar exceeded the marine discharge limits for copper during all three events. The discharge limits for zinc was violated during the August 14, 2015 event.

3.5.2 Sludge Characterization

As discussed previously, significant solids were observed in the stormwater vault. A sample of these solids was collected from inside the main chamber of the vault and characterized for dry weight metal concentrations and particle size distribution. The sludge particle size distribution

is shown in Figure 33. The mean particle size of the sludge sample was 53.1 μm which falls within the silt classification range.

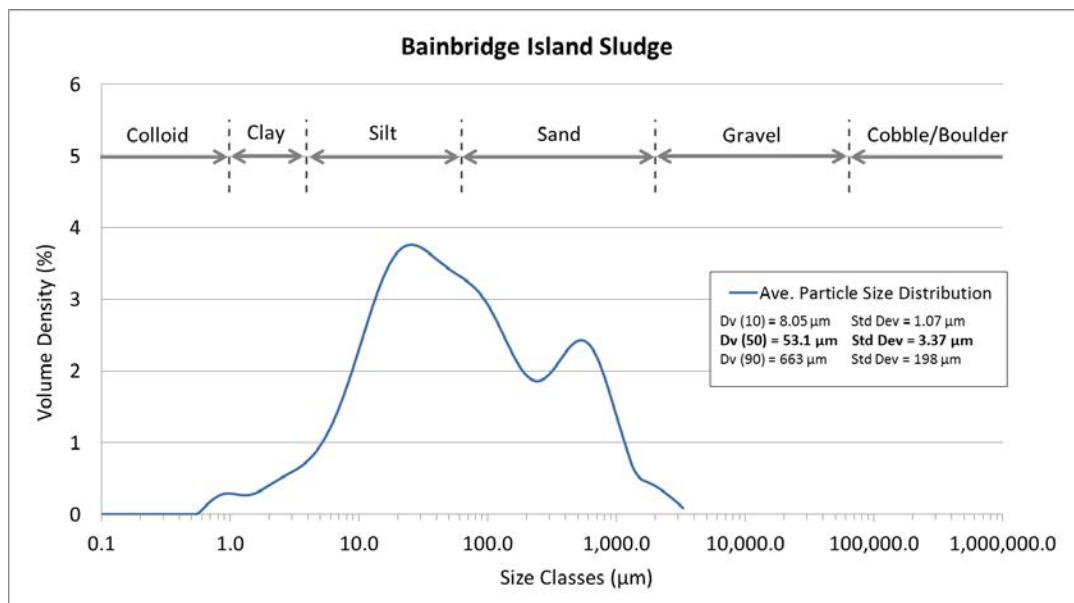


Figure 33. Stormwater vault sludge particle size distribution.

The solids contained an average concentration of 731 ± 132 mg/kg zinc and 107 ± 35 mg/kg copper and was comprised of 33% volatiles. Washington State marine sediment quality standards limit zinc and copper concentrations to 410 mg/kg zinc and 390 mg/kg copper.⁵³ While the sludge sample taken contained almost 80% more zinc than allowed, it was a single sample and several more tests should be performed to determine a more seasonally or annually representative mean.

3.5.3 Field Column Results – January - April 2016

As a result of the performance of raw wood crumbles during laboratory testing, the field column media was changed from biochar to raw wood crumbles following the October 2015 event. Influent and effluent samples were collected and analyzed for nine storm events during the January – April field testing period. The 24 influent and 24 effluent sample bottles, collected at 2 minute intervals, were composited prior to analysis. Three composite samples were produced for each 24-bottle sample set using bottles 1-8, 9-16, and 17-24. The column effluent flow hydrograph for the second phase of field data collection is shown in Figure 34. Constituent concentrations from nine storm events are summarized in Table 8.

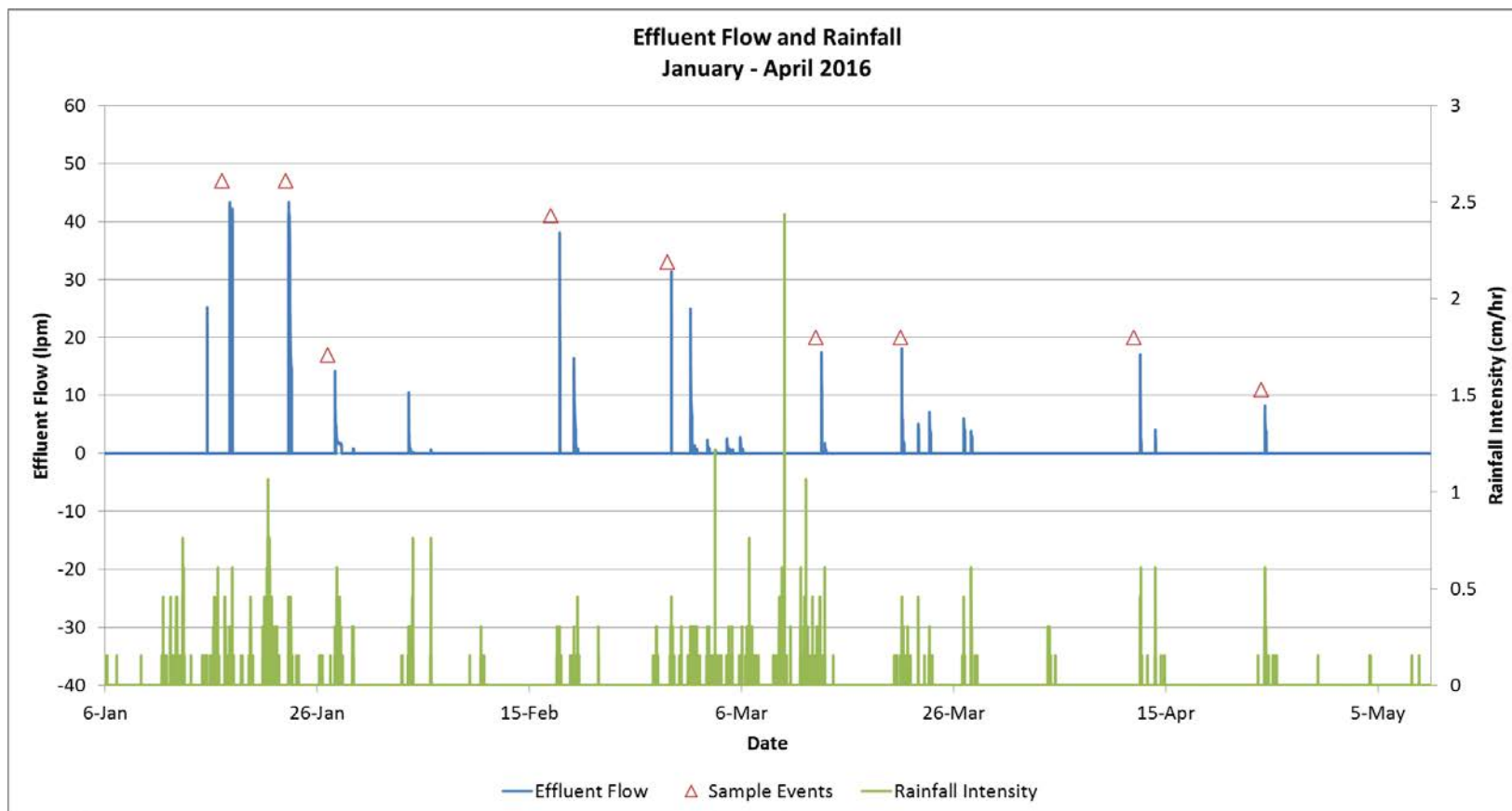


Figure 34. Field column effluent flow, rainfall intensity, and sample collection event during field testing of raw wood crumbles.

Table 8. Influent and effluent constituent concentration averages for the field column containing raw wood crumbles.

Constituents		Event 1 (January 17)			Event 2 (January 23)			Event 3 (January 27)			Event 4 (February 17)			Event 5 (February 28)			Event 6 (March 13)			Event 7 (March 21)			Event 8 (April 12)			Event 9 (April 24)		
		Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)	Avg. Inf.	Avg. Eff.	Conc. Reduc. (%)
TSS (mg/L)		37	12	69	29	9	69	63	16	74	38	10	73	28	10	64	28	10	64	51	13	74	141	56	60	44	11	74
pH		7.3	7.4	-	7.5	7.5	-	7.2	7.0	-	7.0	6.8	-	6.9	6.8	-	6.9	6.8	-	7.1	7.1	-	6.7	6.8	-	6.8	7.1	-
Total Metals (µg/L)	Cu	8.4	4.8	43	8.1	3.8	53	16.8	6.1	63	7.8	3.9	50	6.5	4.2	36	6.5	4.2	36	12.5	6.7	47	43.3	34.6	20	14.6	7.8	46
	Zn	81	42	48	91	36	61	169	55	68	79	42	47	51	35	32	51	35	32	118	57	51	265	192	28	82	49	40
Dissolved Metals (µg/L)	Cu	2.0	1.8	6.8	3.0	2.7	11.1	2.8	2.4	14.1	1.8	1.7	3.8	2.2	2.3	-1.5	2.2	2.3	-1.5	3.2	3.3	-2.1	17.0	21.6	-27.3	5.6	5.4	2.4
	Zn	40	19	54	57	29	49	57	32	44	36	23	37	30	25	15	30	25	15	59	41	31	152	129	15	45	36	21

For ease of presentation of overall data trends, the constituent concentration data in Table 8 are averages of the three composite sample concentrations. Individual composite concentrations will be presented in the following section to show concentration trends during individual storm events. Stormwater runoff water quality (column influent concentrations) exhibited typical behavior at the Bainbridge Island ferry terminal site. In general, concentrations were affected by antecedent dry period. During periods of frequent rainfall, constituent concentrations were lower than those concentrations observed during infrequent rainfall. For example, most of the constituent influent concentrations for Event 2 and 6 that followed frequent periods of rain, are lower than other events. Conversely, Event 8 that follows a dry period (March 28 – April 12) that was interrupted by only two low intensity rain events on April 3 and April 4, exhibited the highest constituent concentrations. These results are due to the build-up of contaminants on the parking surface during dry periods which are then transferred to runoff during a rain event.

Both total and dissolved metal concentrations were observed to be proportional to TSS concentration. The TSS – metal concentration correlation is shown in Figure 35 through Figure 38. With the exception of the April 12 runoff event, effluent soluble zinc concentrations remained below the marine discharge limit of 90 µg/L for acute toxicity and 81 µg/L for chronic toxicity.⁶ Effluent soluble copper remained below the acute concentration limit of 4.8 µg/L for all but the April 12 event and below the chronic limit of 3.1 µg/L limit for six of nine events (Table 8). Not surprisingly, the April 12 event copper concentration, following a long antecedent dry period, was above both the chronic and acute limits.

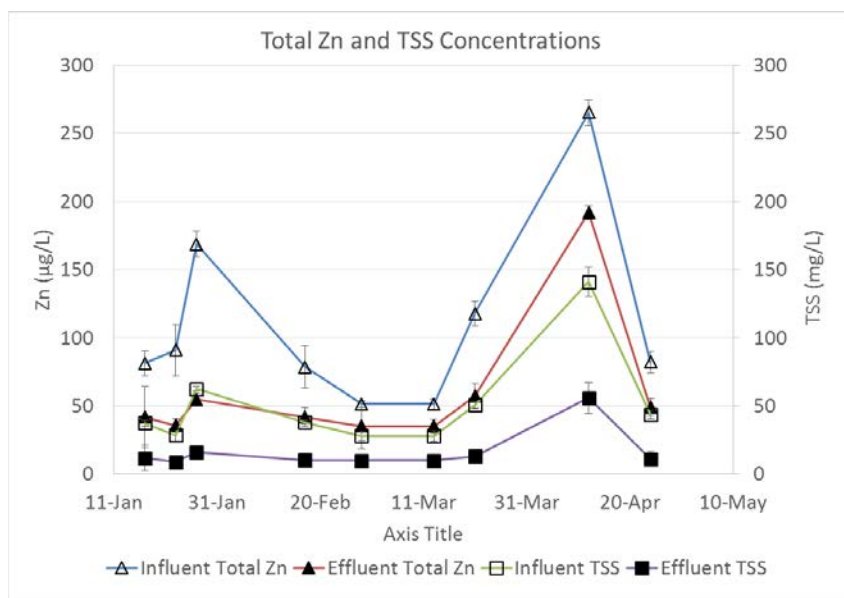


Figure 35. Column influent and effluent total zinc and TSS concentrations. Error bars represent 95% confidence limits.

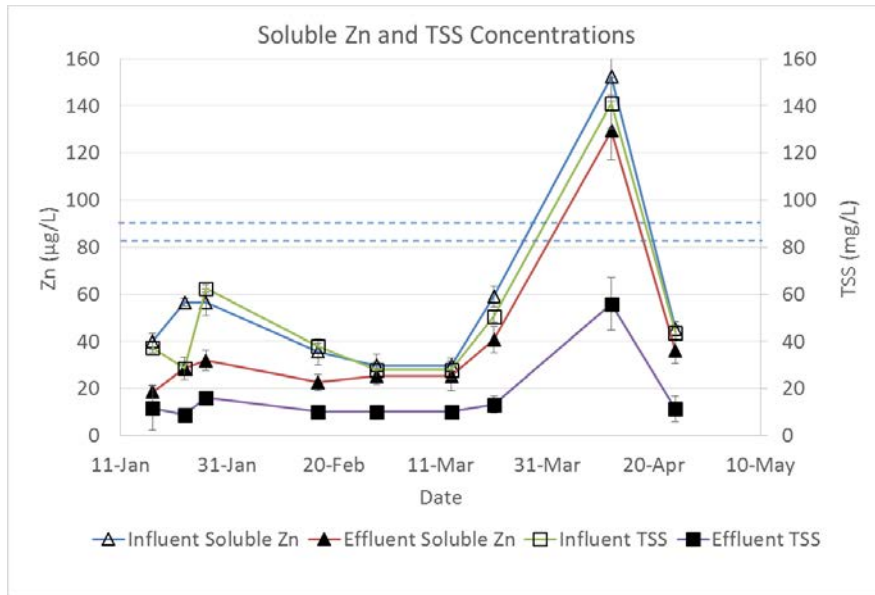


Figure 36. Column influent and effluent soluble zinc concentrations. The dashed horizontal lines are the acute and chronic marine discharge limits.⁶ Error bars represent 95% confidence limits.

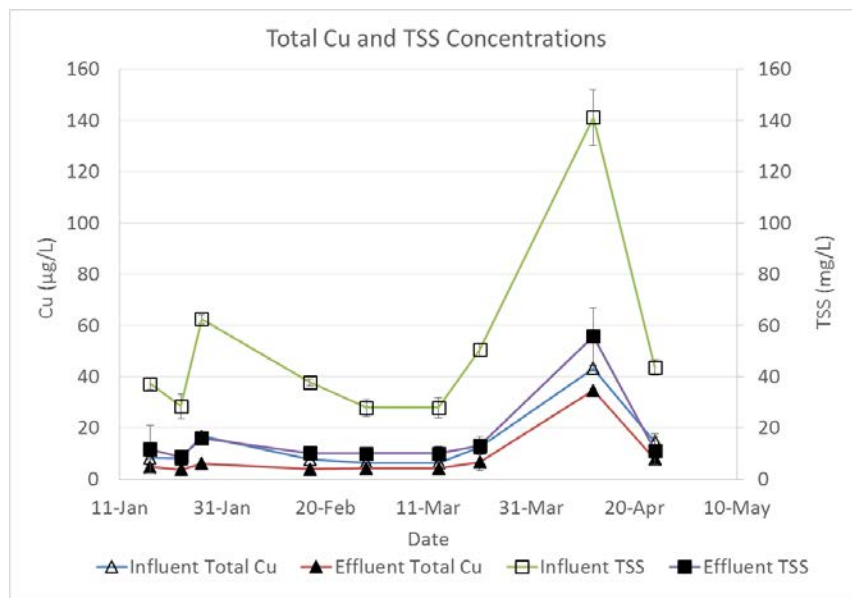


Figure 37. Column influent and effluent total zinc and TSS concentrations. Error bars represent 95% confidence limits.

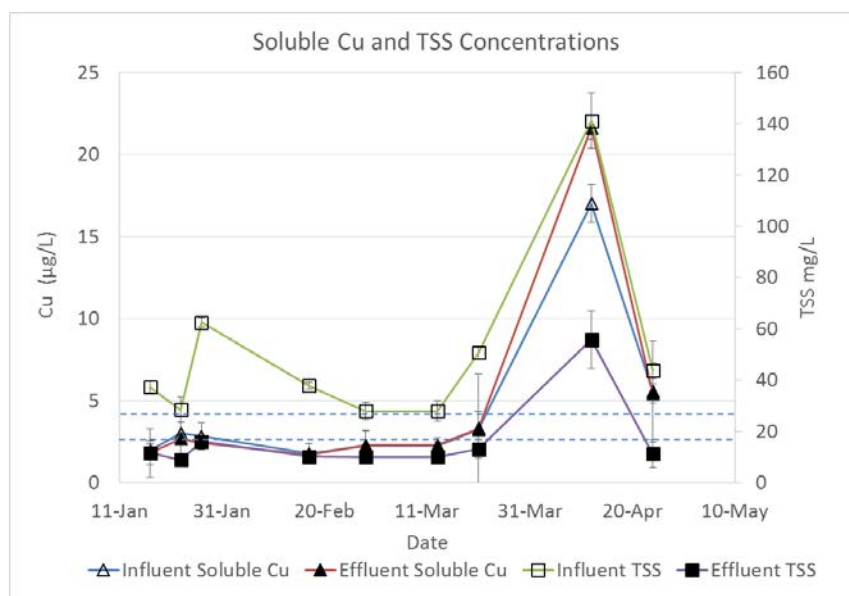


Figure 38. Average column influent and effluent soluble copper and TSS concentrations. The dashed horizontal lines are the acute and chronic marine discharge limits.⁶ Error bars represent 95% confidence limits.

Comparisons between biochar and raw wood column performance is presented in Table 9. It can be seen that the average effluent concentrations for all constituents are less for the column containing raw wood crumbles. The average effluent soluble copper concentration for raw wood column was 4.8 µg/L, matching the acute concentration discharge limit to marine waters, while the biochar column effluent average was 10 µg/L. Both column media exhibited soluble zinc concentrations less than the acute and chronic discharge limit of 90 and 81 µg/L, respectively. These results reflect the finding in the laboratory scale testing. Column testing using raw wood crumbles yielded significantly lower effluent metal concentrations (Figure 26 and Figure 27). However, it is important to note that the field stormwater copper concentrations were in the low ppb range and no significant reduction in copper concentration was observed for either biochar or raw wood crumbles.

Table 9. Biochar and raw wood column overall average constituent concentration data, including percent concentration reduction.

Constituents		All Event Summary - Raw Wood Crumbles									All Event Summary - Biochar								
		Avg. Inf.	Max.	Min.	Avg. Eff.	Max.	Min.	Avg. Conc. Reduc. (%)	Max. Reduc. (%)	Min. Reduc. (%)	Avg. Inf.	Max. Inf.	Min. Inf.	Avg. Eff.	Max. Reduc. (%)	Min. Reduc. (%)	Avg. Conc. Reduc. (%)	Max. Reduc. (%)	Min. Reduc. (%)
TSS (mg/L)		51	141	28	16	56	9	34	74	60	185	313	100	80	130	23	57	78	38
Total Metals (µg/L)	Cu	14	43	6.5	8.5	35	3.8	11	63	20	35	45	21	26	50	13	25	61	-11
	Zn	110	265	51	60	192	35	85	68	28	181	270	131	99	184	36	45	73	32
Dissolved Metals (µg/L)	Cu	4.4	17	1.8	4.8	22	1.7	5	14	-27	9	17	3.0	10	18	3	-11	13	-34
	Zn	56	152	30	40	129	19	48	54	15	69	116	45	47	99	15	31	68	14

Field column influent and effluent concentration variation during an individual storm event is shown in Figure 39. The January 27, 2016 event is representative of the trends observed during all storm events (presented in the Appendix). Twenty-four sample bottles were filled during each storm event at two minute intervals. Each composite was produced by mixing sequential eight bottle sets and analyzing for the desired constituent. The first composite constituent concentrations, therefore, represent the first 16 minutes of the storm event while the third composite constituent concentrations represent the last 16 minutes. Both influent and effluent concentrations for all constituents are shown to decrease as the storm event progresses in time. Stormwater runoff (referred to as column influent) concentration is typically greater at the beginning of a storm event and, as the runoff event continues, the concentrations decrease as the contaminants are removed from the surface.

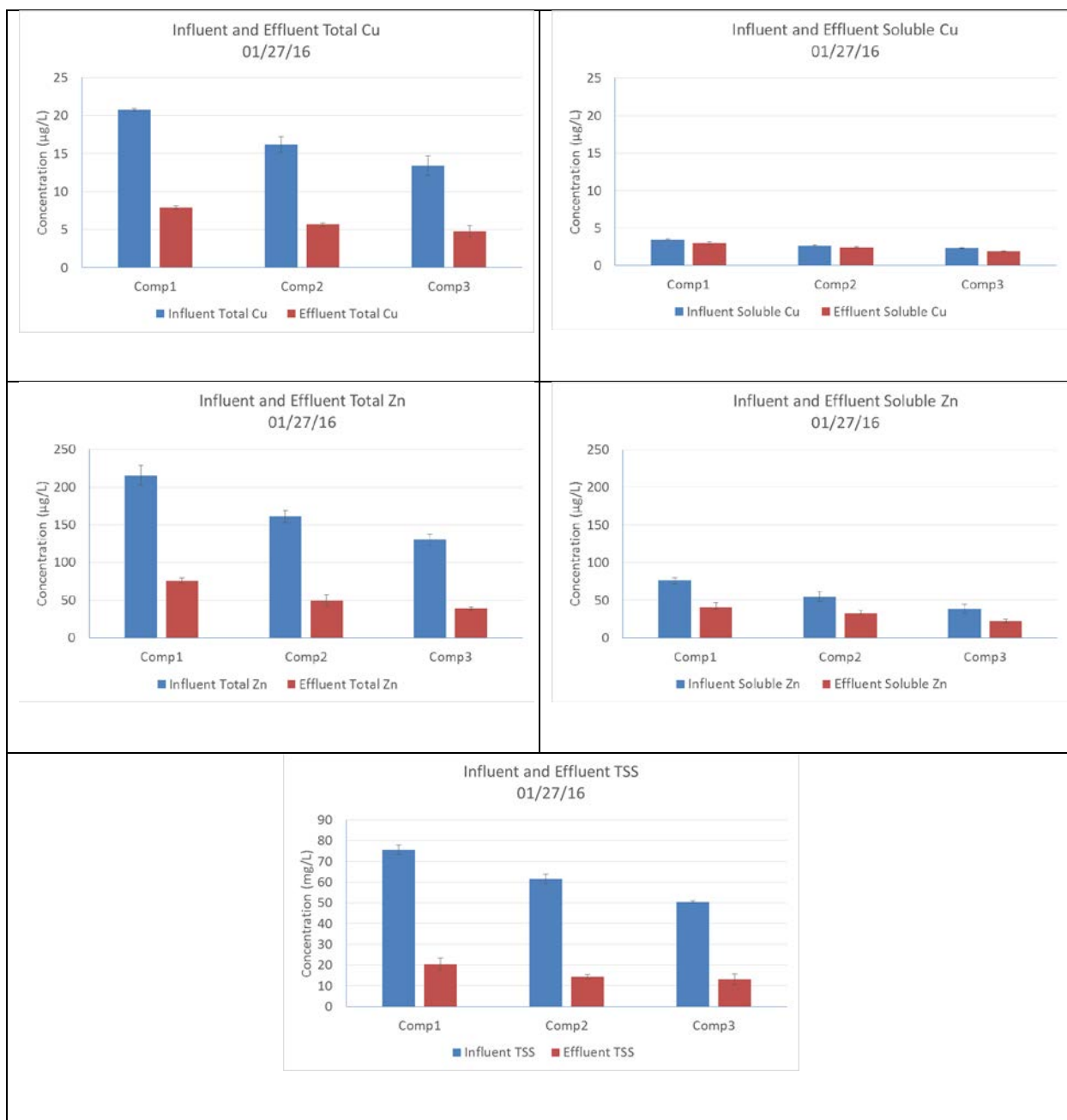


Figure 39. Average field column influent and effluent constituent concentrations for each of three composites developed from the January 27, 2016 storm event samples. Error bars are 95% confidence intervals.

4. SUMMARY AND CONCLUSIONS

Three primary media (raw wood crumbles, torrefied wood crumbles, and biochar) were evaluated for their ability to adsorb copper and zinc that are constituents of concern in stormwater runoff. Single and multi-solute laboratory adsorption isotherm experiments were performed as a screening tool to evaluate the potential of torrefied wood and biochar for field

application. Single solute isotherm data indicated that torrefied wood had a greater capacity for zinc while biochar exhibited a greater capacity for copper. However, the multisolute adsorption equilibrium data showed that copper outcompeted zinc for sites of adsorption on both media.

Multi-solute continuous flow column experiments were performed using raw wood crumbles, torrefied wood crumbles, biochar and pea gravel to assess their ability to adsorb soluble copper and zinc. Torrefied wood outperformed biochar by adsorbing 83% of the applied copper and 48% of the applied zinc, compared to 57% and 34% for biochar. However, raw wood crumbles outperformed all other media evaluated by adsorbing 97% copper and 89% of zinc. Interestingly, pea gravel outperformed biochar, removing 70% copper and 74% zinc from the influent. Peak sorption performance for torrefied wood and raw wood was not realized until the media was hydrated past the fiber saturation point allowing metals to diffuse more readily into the wood cellular structure. Even though torrefaction was shown to increase metal bonding surface functional groups from hemicellulose degradation, it proved to be insignificant when compared to preserved intercellular adsorption sites attributed to the intact hemicellulose fraction of raw wood.

Not surprisingly, pH proved to be a significant factor for metal adsorption and retention onto the sorbents. Torrefied wood showed greater resilience to pH fluctuation than biochar. Raw wood and pea gravel were not tested for pH sensitivity, however, it is likely that raw wood will exhibit the same resilience to pH based on similar characteristics with torrefied wood. A significant decrease in raw wood effluent pH was observed during column tests but both copper and zinc effluent concentrations remained below that for biochar and torrefied wood. These data show that raw wood crumbles maintain a high sorption potential even under relatively low pH conditions. Field tests showed no pH decrease for either biochar or raw wood due to the natural buffer capacity of stormwater runoff at the Bainbridge ferry terminal site.

Laboratory column experiments indicated that flow rate had no effect on metal effluent concentration over the range evaluated. This is promising for stormwater applications where flow rates can vary widely. The deicer flush through the media resulted in a significant increase in effluent metal concentrations due to the displacement of zinc and copper by calcium. Both media resumed zinc and copper adsorption after the salt flush, indicating that it may be possible to continue use following deicer application in the field. However, the significant increase in column effluent metal concentration during simulated deicer flush tests show that consideration should be given to bypassing field columns during periods of deicer application.

The Bainbridge Island ferry terminal field site data is more challenging to interpret due to the highly variable conditions compared to laboratory tests. The presence of suspended solids, not present in the laboratory testing, affects metal concentration data as well. In spite of expected operating condition variability, the field column data indicated that raw wood crumbles yielded consistently lower soluble metal copper and zinc concentrations compared to torrefied wood. The column containing biochar violated marine discharge limits for zinc for one of the three runoff events. Copper concentration discharge limits were violated for each of the three events.

Conversely, with the exception of the April 12 runoff event, effluent soluble zinc concentrations remained below the marine discharge limit of 90 µg/L for acute toxicity and 81 µg/L for chronic toxicity for the column containing raw wood crumbles.⁶ Effluent soluble copper for the raw wood crumble column remained below the acute concentration limit of 4.8 µg/L for all but the April 12 event and below the chronic limit of 3.1 µg/L limit for six of nine events. The April 12 event copper concentration, following a long antecedent dry period, was above both the chronic and acute limits.

5. RECOMMENDATIONS

Based on the performance of the raw wood crumbles in both laboratory and field scale testing consideration should be given to using raw wood as a filter sorbent for the reduction of total and soluble metal concentration in stormwater runoff. Prior to full implementation, however, additional information would be required. Long term performance related to the ability of raw wood to maintain its' structural integrity needs to be evaluated. Two questions need to be answered: (i) does raw wood deteriorate with time due to fungal and/or bacterial degradation and (ii) if degradation occurs, is soluble metal sorption compromised? Raw wood samples were collected during the decommissioning of the field column and no visible degradation was observed, however, the raw wood was exposed to field conditions for about 4 months. Degradation and sorption studies should be carried out for at least a year. This study should be conducted in the field as it would not be possible to adequately mimic the chemical, biological and physical nature of stormwater in a laboratory setting. A long term study would also allow for the collection of additional data regarding metal concentration reduction performance following extended antecedent dry periods. These data would be important as stormwater metal concentrations were shown to be greatest following these periods.

During the field column installation process it became apparent that the existing filter columns in the stormwater vault require significant time and effort to remove and replace. All stormwater treatment systems require routine maintenance to maintain effectiveness and a maintenance routine is more likely to be kept if the process is relatively quick and easy. Effort should be focused on the design of a filtration system that can be efficiently maintained, regardless of the filter media used. For example, if exhausted filter media could be removed and replaced in-situ without the removal of the filters themselves, the process might be greatly simplified. With a proper design, it might be possible to use a vacuum truck to remove media and replacement accomplished by simply pouring new media into the filter structure. Ease of maintenance would affect not only the long term efficacy of the treatment system, but also overall cost of operation.

Although this project was focused on metal removal, stormwater solids are also an important factor that should be considered in any filter design. As noted in the Results section of the report, clogging of the field column occurred on a couple of occasions. This was elevated by raising the column feed pump off the bottom of the stormwater vault by about 35 cm. the

stormwater vault acted as a pre-sedimentation basin, effectively reducing the concentration of solids entering the column.

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7. APPENDIX

The information in the appendix presents added detail to the data and figures in the main body of the report. Additional detailed information is available from two theses generated as a result of this work: Assessing Copper and Zinc Adsorption to Thermally Treated Lignocellulosic Biomass, by Joseph Smith, August 2015 and Assessment of Copper and Zinc Adsorption Lignocellulosic Filtration Media using Laboratory and Field Scale Column Tests for the Purpose of Urban Stormwater Remediation, by Vincent McIntyre, December 2015.

7.1 - Weir box Dimensions and Calibration

Detailed dimensions of the weir box, used to quantify field column effluent flow, are presented in Figure 40.

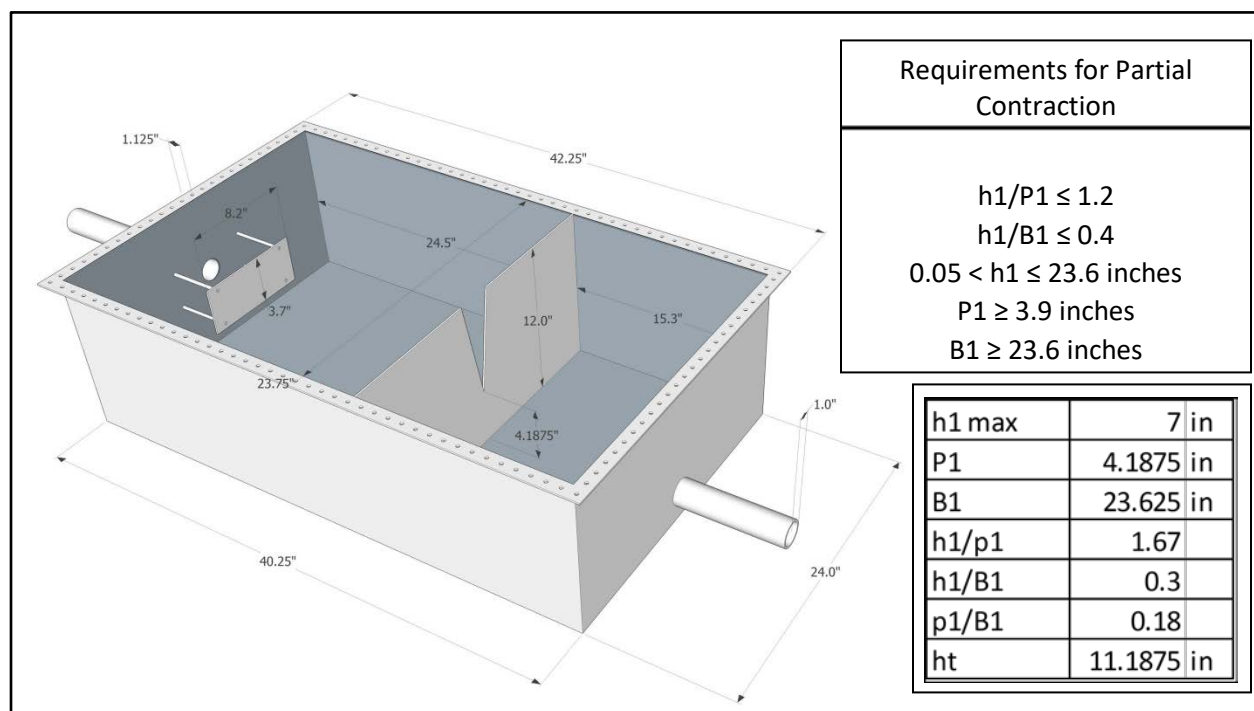


Figure 40. Weir box dimensions and partial contraction verification.

Table 10. 20° Weir plate calibration table.

Plate 2: $\theta = 20^\circ$								
Height (in)	t (sec)	vol (mL)	Q (mL/s)	Stdev (mL/s)	Stdev (gpm)	Q _{ave} (mL/s)	Q (gpm)	Q (cfs)
4	3.16	3340	1057.0	66.2	1.05	1050.1	16.6	0.037
	2.13	2370	1112.7					
	2.08	2040	980.8					
3	2.6	1600	615.4	19.4	0.31	593.0	9.4	0.021
	2.81	1630	580.1					
	2.57	1500	583.7					
2	3.64	880	241.8	2.5	0.04	243.5	3.9	0.009
	3.3	800	242.4					
	3.49	860	246.4					

7.2 - Laboratory Column Data

Table 11. Phase I laboratory column data for composite samples.

Phase I - Non filtered				Influent			Ave. Biochar												Ave. T.W.											
Day	Event	Ave. Cum. Vol.		Zn	Cu	pH	Zn				Cu				pH				Zn				Cu				pH			
		Gal.	Liter	(ppb)	(ppb)	(pH)	(ppb)	(stdev)	(95% CI)	% Rmv	(ppb)	(stdev)	(95% CI)	% Rmv	(pH)	(stdev)	(95% CI)	(ppb)	(stdev)	(95% CI)	% Rmv	(ppb)	(stdev)	(95% CI)	% Rmv	(pH)	(stdev)	(95% CI)		
1	1	4.2	16.0	-	-	6.14	-	-	-	-	-	-	-	-	6.69	0.3	0.7	-	-	-	-	-	-	-	-	3.94	0.1	0.3		
2	2	8.2	30.9	349.7	78.3	5.77	62.0	9.8	24.4	0.8	6.5	0.9	2.2	0.9	6.52	0.1	0.4	299.9	43.4	107.7	0.1	40.6	8.5	21.1	0.5	3.94	0.1	0.3		
3	3	12.3	46.5	354.5	75.8	5.76	67.8	15.1	37.6	0.8	6.4	1.4	3.5	0.9	6.58	0.1	0.3	197.8	19.8	49.2	0.4	19.2	3.5	8.6	0.7	4.39	0.0	0.1		
4	4	16.4	62.0	330.2	75.8	5.79	75.2	1.6	3.9	0.8	6.1	0.2	0.4	0.9	6.61	0.1	0.2	206.3	15.6	38.6	0.4	19.9	1.5	3.7	0.7	4.59	0.1	0.2		
5	5	19.3	72.9	332.7	83.9	6.2	79.9	9.0	22.3	0.8	6.1	0.9	2.2	0.9	6.73	0.0	0.0	212.1	17.3	42.9	0.4	19.4	3.0	7.6	0.8	4.59	0.1	0.2		
8	6	23.2	87.7	275.1	77.8	6.35	59.0	5.0	12.3	0.8	5.6	0.4	1.1	0.9	6.91	0.1	0.3	204.5	48.8	121.1	0.3	23.2	8.1	20.2	0.7	4.61	0.3	0.6		
9	7	27.1	102.7	278.5	79.9	6.15	77.2	3.0	7.5	0.7	7.0	0.3	0.6	0.9	6.67	0.0	0.1	127.9	26.3	65.2	0.5	11.8	3.6	8.8	0.9	4.92	0.2	0.6		
10	8	31.1	117.6	282.6	69.6	6.28	68.7	4.4	10.9	0.8	4.7	0.5	1.1	0.9	6.56	0.1	0.2	107.8	8.5	21.1	0.6	7.7	0.9	2.4	0.9	5.01	0.2	0.5		
11	9	35.0	132.6	296.6	75.6	6.24	82.3	8.0	20.0	0.7	5.6	0.9	2.3	0.9	6.65	0.0	0.1	122.9	9.8	24.3	0.6	9.8	1.2	2.9	0.9	5.19	0.1	0.1		
12	10	38.8	146.9	300.6	85.8	6.35	94.7	12.6	31.3	0.7	6.9	1.9	4.8	0.9	6.58	0.1	0.3	119.1	9.9	24.5	0.6	10.2	1.4	3.4	0.9	5.43	0.1	0.2		
15	11	42.9	162.4	412.8	124.9	5.69	131.9	8.8	21.8	0.7	10.6	2.1	5.2	0.9	6.58	0.0	0.0	255.1	19.1	47.5	0.4	27.8	3.4	8.4	0.8	4.98	0.1	0.1		
16	12	47.0	177.9	445.8	135.5	6.16	151.3	14.4	35.7	0.7	12.2	3.2	8.0	0.9	6.66	0.1	0.2	190.8	8.0	19.8	0.6	18.8	1.4	3.5	0.9	5.29	0.0	0.1		
17	13	51.0	193.2	298.5	93.9	6.08	99.3	8.0	20.0	0.7	37.3	1.6	4.0	0.6	6.61	0.1	0.3	121.0	10.5	26.0	0.6	16.4	0.7	1.7	0.8	5.28	0.0	0.1		
18	14	55.1	208.6	300.1	87.8	5.97	111.3	6.0	14.9	0.6	34.4	1.5	3.7	0.6	6.20	0.0	0.1	121.1	8.4	20.8	0.6	22.5	1.6	4.1	0.7	5.11	0.4	1.0		
19	15	58.6	221.7	330.1	101.3	6	128.3	7.5	18.6	0.6	33.6	2.3	5.6	0.7	6.30	0.2	0.5	144.3	22.6	56.0	0.6	30.3	2.7	6.8	0.7	5.18	0.1	0.3		
20	16	62.8	237.6	277.0	80.5	5.98	114.4	17.3	43.0	0.6	31.1	2.5	6.2	0.6	6.44	0.1	0.2	101.2	6.7	16.6	0.6	15.0	0.9	2.3	0.8	5.27	0.1	0.2		
21	17	66.7	252.4	293.7	88.4	5.83	128.4	7.5	18.6	0.6	22.8	1.3	3.2	0.7	6.24	0.0	0.1	107.3	6.6	16.5	0.6	13.1	0.6	1.5	0.9	5.05	0.2	0.6		
22	18	70.7	267.7	297.1	69.1	5.91	134.3	6.9	17.1	0.5	15.1	1.4	3.6	0.8	6.22	0.0	0.1	119.4	21.2	52.6	0.6	8.4	2.5	6.3	0.9	5.22	0.1	0.2		
23	19	74.8	283.1	327.2	89.3	5.96	160.9	5.7	14.1	0.5	17.7	1.7	4.3	0.8	6.31	0.1	0.3	154.9	38.3	95.1	0.5	13.7	3.3	8.2	0.8	5.42	0.2	0.4		
24	20	78.7	297.9	333.3	108.9	5.89	172.0	8.8	21.8	0.5	17.6	2.3	5.7	0.8	6.27	0.1	0.2	126.2	8.3	20.7	0.6	11.3	2.1	5.2	0.9	5.38	0.0	0.1		
35	21	82.6	312.7	276.8	84.0	5.86	121.3	11.6	28.8	0.6	11.7	1.9	4.6	0.9	6.39	0.1	0.3	250.1	43.6	108.2	0.1	30.5	4.9	12.2	0.6	5.14	0.3	0.8		
36	22	86.6	327.8	270.2	83.8	5.99	130.3	12.0	29.7	0.5	11.5	2.3	5.6	0.9	6.50	0.2	0.4	158.4	29.6	73.6	0.4	15.5	3.7	9.1	0.8	5.11	0.1	0.3		
37	23	90.5	342.7	275.2	79.0	5.99	112.2	12.0	29.8	0.6	36.5	1.8	4.5	0.5	6.20	0.1	0.4	98.4	12.4	30.9	0.6	16.6	2.6	6.5	0.8	5.14	0.1	0.2		
38	24	94.3	357.1	280.4	79.4	5.96	130.7	9.4	23.3	0.5	28.5	1.5	3.8	0.6	6.25	0.0	0.1	106.8	7.9	19.7	0.6	21.5	1.7	4.2	0.7	5.29	0.1	0.2		
39	25	98.3	372.1	285.2	82.3	5.96	145.7	16.1	39.9	0.5	25.2	3.3	8.1	0.7	6.30	0.0	0.1	98.6	8.0	20.0	0.7	18.4	0.6	1.4	0.8	5.23	0.1	0.3		
42	26	102.3	387.2	274.3	80.0	5.64	129.6	9.2	22.9	0.5	30.9	2.1	5.1	0.6	5.73	0.2	0.4	153.7	18.7	46.5	0.4	22.0	4.2	10.4	0.7	5.17	0.1	0.2		
43	27	106.3	402.3	277.2	81.6	5.36	146.5	13.3	32.9	0.5	26.6	1.7	4.3	0.7	6.06	0.0	0.1	95.1	8.6	21.5	0.7	10.6	0.5	1.3	0.9	5.34	0.1	0.2		
44	28	110.2	417.0	279.6	80.0	5.86	131.4	12.4	30.9	0.5	36.9	0.7	1.7	0.5	6.00	0.0	0.1	92.4	10.0	24.8	0.7	13.6	1.2	2.9	0.8	5.27	0.1	0.1		
45	29	114.2	432.3	266.2	77.2	5.76	150.3	8.6	21.4	0.4	27.8	0.8	2.1	0.6	6.15	0.1	0.2	89.0	4.5	11.1	0.7	11.2	0.4	1.0	0.9	5.32	0.1	0.1		
46	30	118.2	447.3	306.4	87.3	6.08	161.9	6.1	15.2	0.5	14.3	1.1	2.6	0.8	6.16	0.1	0.4	112.9	6.6	16.4	0.6	5.7	0.7	1.7	0.9	5.29	0.1	0.1		
47	31	122.2	462.5	306.0	80.2	5.95	180.6	10.3	25.5	0.4	14.2	2.1	5.1	0.8	6.11	0.1	0.2	120.6	10.4	25.7	0.6	6.0	0.7	1.7	0.9	5.28	0.2	0.5		
48	32	125.8	476.4	307.5	89.3	5.82	195.2	12.3	30.7	0.4	16.7	3.2	7.9	0.8	6.20	0.0	0.1	128.1	5.1	12.7	0.6	6.9	0.8	2.0	0.9	5.43	0.2	0.4		
49	33	129.9	491.6	282.5	78.2	6.32	159.8	12.5	31.0	0.4	12.2	2.6	6.4	0.8	6.32	0.1	0.2	94.7	2.2	5.5	0.7	3.6	0.2	0.5	1.0	5.73	0.1	0.3		
50	34	133.8	506.6	279.3	78.7	6.07	180.2	8.9	22.1	0.4	14.0	2.0	4.9	0.8	6.12	0.1	0.1	115.7	12.0	29.9	0.6	4.9	0.9	2.2	0.9	5.54	0.1	0.4		
51	35	137.8	521.8	302.5	80.7	6.13	179.1	3.7	9.1	0.4	14.5	0.8	2.1	0.8	6.06	0.0	0.1	114.2	16.0	39.8	0.6	4.6	1.1	2.8	0.9	5.46	0.1	0.1		
52	36	141.9	537.1	296.5	73.6	6.01	186.2	13.4	33.2	0.4	14.8	2.7	6.8	0.8	6.14	0.1	0.3	124.8	12.1	30.0	0.6	5.0	0.8	2.0	0.9	5.55	0.2	0.4		
53	37	145.5	550.8	299.1	81.6	5.9	204.6	8.2	20.3	0.3	17.6	3.1	7.7	0.8	6.19	0.1	0.1	131.1	13.5	33.5	0.6	5.3	0.8	2.0	0.9	5.48	0.1	0.3		
54	38	149.5	565.8	287.8	76.4	6.13	167.8	6.0	14.8	0.4	12.5	0.9	2.3	0.8	6.20	0.0	0.1	140.7	9.5	23.5	0.5	6.6	0.9	2.3	0.9	5.29	0.1	0.3		
55	39	153.4	580.8	285.5	77.5	5.83	185.3	6.1	15.2	0.4	15.4	1.5	3.7	0.8	5.87	0.1	0.3	126.2	11.7	29.1	0.6	4.9	0.6	1.6	0.9	5.57	0.1	0.2		
56	40	157.6	596.5	303.6	92.8	6.01	175.0	9.9	24.7	0.4	15.6	2.3	5.6	0.8	6.08	0.2	0.5	113.2	9.0	22.5	0.6	4.1	0.5	1.3	1.0	5.55	0.2	0.6		

The data in Table 12 through Table 14 show that, under the experimental protocol applied during laboratory column testing, the filters used sorb a significant quantity of zinc and copper at low ppb concentrations. Filtration was no required during column laboratory testing due to a lack of suspended solids in the samples.

Table 12. Phase I filtered and unfiltered discrete samples for evaluating metal sorption to filters.

Day	Biochar																	
	1 min						10 min						20 min					
	Not Filtered			Filtered			Not Filtered			Filtered			Not Filtered			Filtered		
	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)
4	31	45.7	5.5	32	40.0	4.2	33	89.1	7.6	34	84.3	4.9	35	78.1	4.8	36	68.8	2.9
11	117	62.1	5.0	118	139.2	10.7	119	86.2	6.1	120	75.8	3.5	121	88.6	4.9	122	87.0	3.4
18	45	82.8	33.4	46	87.8	2.3	47	112.7	35.4	48	104.5	2.6	49	112.9	32.6	50	118.4	4.3
23	131	122.5	12.8	132	114.7	3.6	133	149.8	15.5	134	147.6	4.9	135	173.1	17.3	136	155.3	6.2
39	59	114.0	18.7	60	106.2	3.4	61	136.9	22.6	62	133.0	5.5	63	156.2	23.4	64	141.4	7.1
46	145	143.0	11.2	146	143.9	4.8	147	169.5	15.4	148	163.9	12.4	149	171.4	13.9	150	156.1	9.7
51	9	155.7	8.0	-	-	-	10	161.7	11.3	-	-	-	11	173.1	12.6	-	-	-
Day	Torrefied Wood																	
	1 min						10 min						20 min					
	Not Filtered			Filtered			Not Filtered			Filtered			Not Filtered			Filtered		
	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)
4	43	405.7	42.3	44	397.3	40.4	45	143.7	11.0	46	125.0	9.1	47	153.3	12.5	48	137.4	10.2
11	129	212.0	17.0	130	73.7	4.9	131	89.8	6.7	132	2757.0	0.1	133	96.6	7.7	134	89.7	4.6
18	57	142.0	28.2	58	135.1	9.6	59	91.3	18.5	60	85.5	3.6	61	85.0	16.1	62	68.1	2.6
23	143	139.1	11.5	144	151.7	9.3	145	115.6	11.3	146	101.6	6.2	147	131.2	13.6	148	111.2	7.7
39	71	-	-	72	159.8	10.0	73	102.7	20.2	74	88.9	7.3	75	97.8	18.6	76	80.5	3.8
46	157	167.3	8.8	158	153.8	8.1	159	101.8	4.8	160	89.6	3.9	161	107.8	5.4	162	96.6	4.4
51	15	165.4	7.0	-	-	-	16	107.7	4.1	-	-	-	17	112.4	4.5	-	-	-

Table 13. Phase I filtered and unfiltered influent and biochar data for evaluating metal sorption to filters.

Event	Influent (Single Sample)						Biochar, Column 1 (Composite Samples)						Biochar, Column 2 (Composite Samples)						Biochar, Column 3 (Composite Samples)					
	Not Filtered			Filtered			Not Filtered			Filtered			Not Filtered			Filtered			Not Filtered			Filtered		
	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)	#	Zn (µg/L)	Cu (µg/L)
1	15	-	-	16	270.0	45.0	-	-	-	17	90.2	13.5	-	-	-	18	68.6	6.1	-	-	-	19	47.5	7.0
2	1	349.7	78.3	2	336.0	63.0	3	68.9	7.2	4	63.2	9.4	5	69.1	6.9	6	66.0	5.3	7	48.2	5.2	8	42.6	3.8
3	15	354.5	75.8	16	316.0	57.0	17	62.4	6.0	18	81.9	4.8	19	88.5	8.3	20	79.1	6.4	21	52.6	5.0	22	50.2	4.0
4	29	330.2	75.8	30	312.9	58.4	37	76.0	6.1	38	69.7	4.8	39	76.6	6.3	40	76.6	5.3	41	73.0	5.9	42	69.0	4.8
5	55	332.7	83.9	56	312.4	66.8	57	78.8	6.0	58	72.7	5.2	59	91.4	7.2	60	86.9	5.5	61	69.5	5.0	62	67.8	4.2
6	73	275.1	77.8	74	246.0	52.1	75	65.1	6.2	76	60.8	3.9	77	59.0	5.4	78	50.8	3.4	79	52.9	5.2	80	47.6	3.5
7	87	278.5	79.9	88	249.5	57.6	89	78.4	7.0	90	67.4	3.7	91	80.1	7.3	92	73.0	4.5	93	73.1	6.7	94	67.9	4.2
8	101	282.6	69.6	102	269.7	48.8	103	64.7	4.2	104	57.8	2.5	105	66.5	4.6	106	58.4	2.9	107	74.8	5.3	108	68.0	4.3
9	115	296.6	75.6	116	274.3	53.7	123	71.7	4.4	124	68.2	3.0	125	6.7	91.2	126	79.3	2.6	127	84.1	5.8	128	78.2	4.1
10	141	300.6	85.8	142	280.7	64.5	143	87.9	5.9	144	78.8	4.0	145	83.9	5.2	146	73.6	3.3	147	112.4	9.6	148	93.4	5.1
11	1	412.8	124.9	2	411.8	101.8	3	120.2	7.9	4	108.1	5.2	5	134.3	11.1	6	131.9	8.0	7	141.2	13.0	8	135.9	9.5
12	15	445.8	135.5	16	408.5	104.3	17	138.1	8.7	18	123.4	6.1	19	144.6	11.4	20	157.2	8.1	21	171.3	16.4	22	172.4	12.1
13	29	298.5	93.9	30	278.1	36.7	31	88.1	35.0	32	87.3	8.3	33	103.0	38.7	34	94.1	9.0	35	106.7	38.0	36	103.4	9.4
14	43	300.1	87.8	44	263.8	38.0	51	103.2	32.3	52	92.1	2.2	53	112.9	35.8	54	111.4	4.2	55	117.6	35.0	56	112.8	3.7
15	69	330.1	101.3	70	317.6	54.5	71	117.8	30.7	72	115.4	3.7	73	134.7	33.7	74	127.4	5.9	75	132.5	36.3	76	116.2	3.3
16	83	277.0	80.5	84	272.3	40.8	85	92.4	27.8	86	88.7	9.9	87	134.8	33.8	88	117.6	11.2	89	115.9	31.7	90	159.1	7.6
17	101	293.7	88.4	102	273.1	56.1	103	117.8	21.0	104	113.9	5.3	105	132.5	23.3	106	138.1	7.5	107	134.7	24.1	108	120.6	5.9
18	115	297.1	69.1	116	288.4	42.6	117	127.0	13.4	118	123.2	3.4	119	132.4	14.9	120	135.6	4.8	121	143.5	17.0	122	136.6	5.4
19	129	327.2	89.3	130	309.1	60.8	137	152.9	15.3	138	147.0	5.8	139	165.3	19.3	140	151.6	8.8	141	164.5	18.5	142	151.7	7.1
20	155	333.3	108.9	156	297.3	73.6	157	159.9	14.6	158	161.4	10.9	159	180.5	20.1	160	181.4	12.9	161	175.5	18.2	162	151.0	7.6
21	1	276.8	84.0	2	266.0	67.1	3	104.9	9.1	4	100.5	6.2	5	128.9	12.7	6	122.8	9.3	7	130.1	13.4	8	132.6	9.4
22	15	270.2	83.8	16	260.6	71.7	17	116.0	8.8	18	110.9	6.1	19	129.5	11.3	20	124.0	8.0	21	145.3	14.3	22	142.2	11.0
23	29	275.2	79.0	30	256.8	41.3	31	95.8	34.1	32	100.0	13.0	33	116.6	37.1	34	110.3	12.9	35	124.3	38.4	36	115.7	22.1
24	43	280.4	79.4	44	264.2	44.0	45	117.9	26.5	46	108.1	8.2	47	134.3	28.9	48	129.2	6.0	49	140.0	30.1	50	130.8	6.0
25	57	285.2	82.3	58	277.4	53.5	65	123.5	20.5	66	120.8	5.3	67	152.6	27.2	68	149.8	10.0	69	161.0	27.7	70	153.4	10.5
26	83	274.3	80.0	84	261.7	39.7	85	117.5	28.2	86	114.3	4.2	87	131.4	31.4	88	125.0	5.2	89	139.9	33.2	90	129.0	5.0
27	97	277.2	81.6	98	261.9	43.3	99	127.8	24.3	100	123.2	4.5	101	156.8	28.5	102	154.7	9.2	103	154.9	27.1	104	147.5	7.4
28	111	279.6	80.0	112	264.6	37.6	113	114.0	36.0	114	110.3	11.3	115	141.7	36.8	116	133.5	12.0	117	138.7	37.8	118	132.3	13.2
29	125	266.2	77.2	126	253.6	33.4	127	138.1	26.6	128	122.8	4.5	129	156.3	28.4	130	142.9	5.8	131	156.5	28.3	132	151.5	7.6
30	143	306.4	87.3	144	290.4	69.1	151	154.2	12.8	152	146.3	9.3	153	162.4	14.8	154	152.4	10.8	155	169.1	15.3	156	163.8	12.4
31	169	306.0	80.2	170	301.2	61.9	171	166.6	11.3	172	153.9	6.6	173	184.3	15.1	174	174.6	11.0	175	190.9	16.1	176	177.0	12.1
32	183	307.5	89.3	-	-	-	184	177.7	12.7	-	-	-	185	204.1	20.5	-	-	-	186	203.8	16.8	-	-	-
33	190	282.5	78.2	-	-	-	191	143.0	8.6	-	-	-	192	163.7	13.8	-	-	-	193	172.8	14.3	-	-	-
34	1	279.3	78.7	-	-	-	2	168.3	11.3	-	-	-	3	182.8	14.5	-	-	-	4	189.6	16.1	-	-	-
35	8	302.5	80.7	-	-	-	12	180.6	14.4	-	-	-	13	174.1	13.5	-	-	-	14	182.8	15.5	-	-	-
36	21	296.5	73.6	-	-	-	22	167.4	11.2	-	-	-	23	193.3	15.2	-	-	-	24	197.8	17.9	-	-	-
37	28	299.1	81.6	-	-	-	29	193.1	13.3	-	-	-	30	209.3	20.3	-	-	-	31	211.4	19.3	-	-	-
38	35	287.8	76.4	-	-	-	36	159.4	11.2	-	-	-	37	171.3	13.3	-	-	-	38	172.7	13.0	-	-	-
39	44	285.5	77.5	-	-	-	45	179.5	13.3	-	-	-	46	182.7	16.1	-	-	-	47	193.8	16.7	-	-	-
40	53	303.6	92.8	-	-	-	54	161.7	12.4	-	-	-	55	177.8	17.4	-	-	-	56	185.5	17.1	-	-	-

Table 14. Phase I filtered and unfiltered torrefied wood data for evaluating metal sorption to filters.

Event	Torrefied Wd., Column 1 (Comp. Samples)						Torrefied Wd., Column 2 (Comp. Samples)						Torrefied Wd., Column 3 (Comp. Samples)					
	Not Filtered			Filtered			Not Filtered			Filtered			Not Filtered			Filtered		
	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu
		(µg/L)	(µg/L)		(µg/L)	(µg/L)		(µg/L)	(µg/L)		(µg/L)	(µg/L)		(µg/L)	(µg/L)		(µg/L)	(µg/L)
1	-	-	-	20	209.3	23.7	-	-	-	21	220.3	34.3	-	-	-	22	201.7	34.0
2	9	240.3	29.5	10	247.4	31.8	11	317.2	42.1	12	314.9	42.2	13	342.2	50.1	14	341.4	48.8
3	23	178.2	15.4	24	162.2	13.9	25	224.9	23.8	26	233.2	23.2	27	190.3	18.4	28	209.3	16.5
4	49	218.1	19.5	50	223.2	18.8	51	216.5	21.9	52	206.0	20.4	53	184.3	18.3	54	176.9	16.4
5	63	188.2	15.1	64	193.6	14.6	65	228.5	21.8	66	212.1	20.2	67	219.7	21.3	68	214.8	20.4
6	81	164.5	14.5	82	157.6	15.2	83	273.1	34.1	84	266.1	32.9	85	175.9	21.0	86	181.0	20.4
7	95	92.6	7.0	96	79.3	5.5	97	155.4	15.5	98	133.6	13.1	99	135.7	12.8	100	137.0	12.1
8	109	98.0	6.5	110	94.8	6.2	111	106.6	7.7	112	106.8	7.1	113	118.7	8.9	114	110.5	7.8
9	135	120.1	9.1	136	118.5	8.8	137	136.0	11.4	138	123.3	9.9	139	112.5	8.8	140	101.1	7.6
10	149	132.3	12.1	150	117.1	10.4	151	108.5	8.7	152	207.3	8.7	153	116.6	9.9	154	105.3	8.6
11	9	228.2	23.1	10	218.7	21.5	11	266.8	31.2	12	253.5	30.0	13	270.4	29.0	14	273.0	28.0
12	23	180.0	17.4	24	182.7	16.4	25	198.9	20.8	26	190.3	19.6	27	193.6	18.3	28	175.8	16.7
13	37	126.3	15.5	38	131.6	9.7	39	130.3	17.1	40	116.2	10.5	41	106.3	16.5	42	104.5	7.7
14	63	111.7	21.6	64	87.2	7.0	65	119.6	21.1	66	101.9	7.7	67	132.1	24.8	68	120.4	10.0
15	77	113.7	26.4	78	125.9	4.4	79	167.5	32.5	80	158.2	15.2	81	151.6	32.0	82	127.1	12.2
16	91	93.9	13.8	92	89.4	8.6	93	110.1	16.0	94	91.6	8.0	95	99.6	15.1	96	86.3	8.0
17	109	110.6	13.7	110	102.7	10.6	111	113.4	13.4	112	102.7	10.4	113	98.1	12.3	114	86.8	8.7
18	123	93.6	5.9	124	73.3	3.4	125	145.4	11.9	126	126.7	8.3	127	119.1	7.6	128	98.4	4.9
19	149	117.8	10.0	150	114.3	7.2	151	139.2	13.1	152	131.1	8.8	153	207.6	18.0	154	187.4	14.7
20	163	118.7	10.1	164	107.4	7.5	165	137.8	14.3	166	127.5	11.4	167	121.9	9.6	168	100.9	6.2
21	9	192.5	23.9	10	173.9	22.1	11	297.8	35.8	12	291.9	35.7	13	260.0	31.6	14	236.2	29.3
22	23	176.0	17.5	24	164.9	16.8	25	182.5	18.7	26	161.0	17.2	27	116.7	10.4	28	106.5	9.5
23	37	94.7	14.0	38	88.5	9.8	39	115.1	20.2	40	102.2	12.2	41	85.3	15.5	42	74.9	11.8
24	51	101.4	21.5	52	92.8	9.2	53	118.0	23.6	54	108.5	12.2	55	101.0	19.5	56	86.8	8.5
25	77	108.7	18.9	78	98.0	8.9	79	98.0	18.7	80	83.4	6.9	81	89.0	17.6	82	80.0	7.9
26	91	127.5	16.1	92	117.8	9.5	93	163.5	24.8	94	146.2	16.0	95	170.0	25.1	96	155.6	16.8
27	105	103.8	10.2	106	93.5	5.3	107	98.2	11.3	108	73.7	4.5	109	83.3	10.2	110	70.8	3.8
28	119	85.1	11.9	120	76.5	4.8	121	106.5	14.7	122	92.7	8.9	123	85.7	14.0	124	75.6	6.6
29	133	95.2	10.7	134	88.4	4.3	135	85.1	11.3	136	74.7	4.1	137	86.6	11.7	138	77.4	4.1
30	163	117.7	5.8	164	106.3	4.9	165	117.4	6.5	166	107.5	5.8	167	103.6	4.8	168	87.5	3.8
31	177	122.6	6.6	178	111.3	5.3	179	132.2	6.3	180	110.0	5.5	181	107.0	5.0	182	87.1	4.0
32	187	133.3	7.2	-	-	-	188	129.8	7.6	-	-	-	189	121.1	5.7	-	-	-
33	194	97.7	3.5	-	-	-	195	93.7	3.9	-	-	-	196	92.6	3.4	-	-	-
34	5	119.2	5.0	-	-	-	6	128.3	6.0	-	-	-	7	99.5	3.8	-	-	-
35	18	110.9	4.6	-	-	-	19	135.2	6.0	-	-	-	20	96.4	3.3	-	-	-
36	25	129.0	5.0	-	-	-	26	137.0	5.9	-	-	-	27	108.3	3.9	-	-	-
37	32	146.7	6.1	-	-	-	33	132.7	5.6	-	-	-	34	113.8	4.1	-	-	-
38	39	129.0	5.3	-	-	-	40	152.2	7.5	-	-	-	41	141.0	7.0	-	-	-
39	48	136.3	5.3	-	-	-	49	132.6	5.4	-	-	-	50	109.8	4.0	-	-	-
40	57	103.3	3.6	-	-	-	58	125.2	4.8	-	-	-	59	111.2	3.9	-	-	-

Table 15. Phase II laboratory column data for composite samples.

Phase II - Non filtered		Average Influent										Average Biochar										Average Torrefied Wood									
Day	Event	Ave. Cum Vol		Zn			Cu			pH		Zn			Cu			pH		Zn			Cu			pH					
		Gal.	Liters	µg/L	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)				
1	1	157.8	161.6	289.4	6.404	15.91	92.9	2.713	6.74	6.07	0.037	0.091	98.23	4.705	11.69	55.45	3.173	7.881	6.353	0.041	0.102	406.5	101.1	251.3	73.97	13.88	34.48	5.2	0.12	1.078	
		161.6	165.4										150.3	8.001	19.88	49.06	0.603	1.498	6.113	0.066	0.165	146.6	18.17	45.14	37.54	4.873	12.1	5.663	0.172	0.429	
		165.6	169.4										176.2	4.042	10.04	50.21	2.527	6.277	6.15	0.057	0.142	148.9	25.22	62.65	37.33	9.404	23.36	5.753	0.084	0.208	
		169.6	173.4	284.9	4.339	10.78	90.3	0.824	2.047	6.10	0.029	0.073	175.1	25.59	63.56	47.27	1.035	2.57	6.173	0.038	0.094	123.7	13.94	34.64	27.98	1.088	2.703	5.737	0.076	0.188	
		173.6	177.4										195.8	15.18	37.7	49.46	2.794	6.941	6.127	0.021	0.051	129.7	10.07	25.02	25.81	1.662	4.129	5.763	0.033	0.082	
2	2	173.8	177.6	296.1	3.428	8.515	92.9	0.293	0.728	6.23	0.106	0.264	143	10.35	25.71	44.26	1.744	4.332	6.367	0.062	0.154	168.3	2.458	22.09	45.17	9.052	22.49	5.36	0.05	0.123	
		177.6	181.4										175	5.622	13.97	42.09	1.239	3.078	6.095	0.015	0.037	103.8	6.647	16.51	23.01	1.072	2.664	5.637	0.091	0.226	
		181.6	185.4										189	5.419	13.46	43.24	1.061	2.636	6.133	0.025	0.062	108.9	4.965	12.33	20.04	0.799	1.984	5.73	0.067	0.166	
		185.6	189.4	292.5	6.661	16.55	92.2	1.668	4.143	6.10	0.048	0.119	196.1	4.895	12.16	43.91	0.943	2.343	6.17	0.07	0.174	112	6.073	15.09	18.1	0.383	0.951	5.667	0.021	0.051	
		189.6	193.4										205.1	5.245	13.03	45.82	1.295	3.218	6.14	0.067	0.166	121.9	3.218	7.993	18.75	0.522	1.297	5.78	0.028	0.07	
3	3	189.8	193.6	285.3	3.592	8.923	89.2	0.458	1.137	6.20	0.083	0.207	151.8	11.84	29.4	48.01	4.528	11.25	6.373	0.031	0.077	173.6	29.46	73.19	38.01	3.093	7.684	5.46	0.091	0.226	
		193.6	197.4										178.7	13.22	32.84	43.95	3.853	9.57	6.153	0.041	0.102	92.59	2.867	7.123	17.56	0.843	2.094	5.707	0.084	0.208	
		197.6	201.4										192.9	15.06	37.42	45.35	2.754	6.841	6.15	0.037	0.093	105.3	2.492	22.39	16.82	1.929	17.33	5.733	0.009	0.023	
		201.6	205.4	279.7	1.058	2.628	88.2	0.464	1.152	6.09	0.017	0.042	202.3	12.11	30.08	45.41	1.93	4.795	6.147	0.019	0.047	111.8	3.006	7.467	15.67	1.32	3.28	5.8	0.008	0.02	
		205.6	209.4										202.5	8.556	21.25	44.95	2.365	5.875	6.137	0.021	0.051	117	4.551	11.31	15.13	1.565	3.888	5.793	0.017	0.042	
4	4	205.8	209.6	283.0	1.833	4.554	89.4	0.568	1.412	6.20	0.045	0.112	173.7	6.5	16.15	39.41	1.164	2.893	6.363	0.012	0.031	127.5	10.47	26	24.27	0.783	1.944	5.617	0.04	0.1	
		209.6	213.4										197.9	12.55	31.16	39.25	3.023	7.509	6.26	0.037	0.093	100.2	6.256	15.54	11.06	0.254	0.63	5.827	0.031	0.077	
		213.6	217.4										206.3	8.783	21.82	41.12	1.666	4.138	6.21	0.07	0.173	111.4	6.31	15.67	11.81	0.12	0.299	5.743	0.054	0.135	
		217.6	221.4	289.9	4.361	10.83	91.2	1.852	4.6	6.24	0.078	0.193	215.1	7.893	19.61	43.12	1.751	4.349	6.247	0.029	0.071	118.6	5.792	14.39	12.08	0.368	0.914	5.863	0.021	0.051	
		221.6	225.4										215.3	4.722	11.73	43.63	1.135	2.819	6.257	0.062	0.155	123.9	4.813	11.96	12.33	0.79	1.961	5.887	0.029	0.071	
5	5	221.8	225.6	286.4	5.44	13.51	86.6	0.972	2.414	5.33	0.042	0.105	501.4	19.8	49.2	79.29	4.724	11.73	6.097	0.037	0.091	266.8	17.9	44.47	12.1	2.117	5.258	5.613	0.017	0.042	
		225.6	229.4										444.4	18.49	45.94	148.3	2.935	7.292	5.837	0.031	0.077	282.4	15.8	39.24	19.72	1.93	4.794	5.563	0.012	0.031	
		229.6	233.4										388.9	14.6	36.27	134.6	3.69	9.165	5.733	0.012	0.031	282.7	8.975	22.3	25.48	1.973	4.902	5.523	0.029	0.071	
		233.6	237.4	287.5	6.562	16.3	87.8	2.734	6.792	5.33	0.041	0.102	365.8	10.35	25.71	119.2	1.678	4.168	5.65	0.016	0.041	277.5	12.9	32.05	28.5	2.114	5.252	5.48	0.016	0.041	
		237.6	241.4										346	10.39	25.8	107	1.879	4.667	5.64	0.016	0.041	272.4	12.25	30.43	30.52	2.051	5.095	5.483	0.025	0.062	
16	6	237.8	241.6	293.3	5.157	12.81	83.1	0.388	0.964	6.24	0.05	0.123	128.7	7.431	18.46	14.38	1.075	2.67	6.26	0.043	0.107	267.4	29.59	73.51	33.85	8.83	21.93	5.323	0.017	0.042	
		241.6	245.4										187.6	10.8	26.82	20.68	4.079	10.13	6.05	0.042	0.105	160.4	7.916	19.66	13.58	1.469	3.65	5.697	0.074	0.183	
		245.6	249.4										203.3	5.05	12.54	24.66	1.907	4.737	6.14	0.014	0.035	162.1	4.939	12.27	15.12	0.807	2.004	5.82	0.014	0.035	
		249.6	253.4	301.8	4.631	11.5	86.1	0.321	0.798	6.18	0.025	0.062	221.3	1.862	4.626	28.42	2.744	6.818	6.187	0.012	0.031	157.3	3.626	9.008	13.61	0.496	1.231	5.85	0.05	0.123	
		253.6	257.4										227.2	10.72	26.62	29.68	2.518	6.255	6.153	0.052	0.13	156.8	2.377	5.904	13.25	0.665	1.652	5.843	0.039	0.096	
17	7	253.8	257.6	300.5	2.52	6.261	87.4	2.014	5.003	6.27	0.012	0.031	167.4	5.639	14.01	32.24	1.407	3.496	6.32	0.016	0.041	155.1	13.74	34.14	17.43	2.325	5.775	5.55	0.022	0.054	
		257.6	261.4										202.9	1.223	10.99	23.34	16.51	41.02	6.117	0.026	0.065	124.4	5.476	13.6	13.4	1.195	2.968	5.78	0.043	0.107	
		261.6	265.4										217	12.37	30.72	39.83	2.279	5.662	6.173	0.041	0.102	135	1.512	3.756	14.2	0.651	1.618	5.88	0.008	0.02	
		265.6	269.4	297.7	0.534	1.327	86.2	0.491	1.221	6.27	0.031	0.077	232.8	7.428	18.45	45.52	2.908	7.224	6.237	0.04	0.1	148	4.484	11.14	16.66	1.674	4.159	5.88	0.041	0.101	
		269.6	273.4										228.4	7.711	19.16	42.56	0.722	1.794	6.197	0.019	0.047	151.2	9.07	22.53	16.2	2.03	5.042	5.917	0.045	0.112	
18	8	269.8	273.6	289.4	4.604	11.44	86.4	1.587	3.942	6.23	0.031	0.077	186.3	6.362	15.8	38.05	1.073	2.666	6.257	0.037	0.091	130.2	17.84	44.31	20.43	2.699	6.704	5.68	0.051	0.127	
		273.6	277.4										201.3	9.351	23.23	39.05	0.659	1.637	6.14	0.022	0.054	114.2	8.905	22.12	12.52	1.169	2.904	5.767	0.088	0.219	
		277.6	281.4										218.9	8.293	20.6	43.66	1.63	4.049	6.15	0.029	0.073	132.7	7.116	17.68	13.35	1.419	3.525	5.867	0.017	0.042	
		281.6	285.4	277.8	5.971	14.83	82.7	2.271	5.642	6.15	0.021	0.051	224.7	5.975	14.84	45.16	0.728	1.808	6.2	0.045	0.113	135.6	8.974	22.29	13.17	1.021	2.536	5.87	0.057	0.142	
		285.6	289.4										225.3	4.405	10.94	45.2	0.658	1.634	6.193	0.017	0.042	145	8.477	21.06	14.03	1.324	3.288	5.923	0.073	0.182	
19	9	285.8	289.6	283.3	4.654	11.56	84.3	1.046	2.599	6.16	0.021	0.051	201.6	8.442	20.97	20.35	1.647	4.092	6.21	0.028	0.07	124.3	14.31	33.8	5.102	1.225	3.044	5.78	0.016	0.041	
		289.6	293.4										224.4	1.15	2.858	30.2	2.782	6.91	6.153	0.026	0.065	130	10.45	25.96	6.138	1.189	2.954	5.86	0.040		

Table 16. High flow and deicer flush column data.

Tests After Phase II - Non filtered			Average Influent										Average Biochar										Average Torrefied Wood									
Type	Day	Event	Ave. Cum Vol		Zn		Cu		pH		Zn		Cu		pH		Zn		Cu		pH		Zn		Cu		pH					
			Gal.	Liters	µg/L	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	µg/L	(stdev)	(95%CI)	-	(stdev)	(95%CI)	
2X Flow	1	1	429.8	433.6	279.1	5.133	12.75	85.1	2.282	5.668	5.99	0.048	0.119	223.1	7.998	19.87	38.66	1.43	3.553	6.153	0.05	0.124	216.3	19.5	48.44	15.02	2.494	6.195	5.877	0.045	0.112	
			437.6	441.4											235.9	5.999	14.9	52.46	1.834	4.555	6.023	0.037	0.091	183.1	5.502	13.67	16.52	2.372	5.893	5.877	0.159	0.396
		445.6	449.4											237.1	2.221	5.516	54.58	1.293	3.212	5.94	0.033	0.081	182.7	8.855	22	18.38	2.386	5.926	5.643	0.236	0.587	
	2	2	445.8	449.6	274.9	6.867	17.06	83.8	1.333	3.312	6.16	0.029	0.073	215.6	7.196	17.88	36.07	1.257	3.122	6.24	0.029	0.073	264.1	33.03	82.06	21.48	3.181	7.901	5.8	0.073	0.18	
			449.6	453.4																												
			453.6	457.4																												
			457.6	461.4																												
			461.6	465.4																												
			465.6	469.4	282.8	11.64	28.91	85.5	3.69	9.167	6.21	0.175	0.434																			
			469.6	473.4																												
			473.6	477.4																												
			477.6	481.4												222.3	9.209	22.88	54.16	2.554	6.344	6.21	0.099	0.247	172.1	9.247	22.97	20.26	2.479	6.157	5.86	0.227
													237.2	6.641	16.5	57.06	0.967	2.403	6.15	0.094	0.234	179.7	6.605	16.41	21.08	2.017	5.011	5.97	0.091	0.226		
4X Flow	1	1	487.6	491.4	288.9	13.57	33.71	83.2	1.326	3.293	6.15	0.092	0.228	212.2	2.429	6.035	50.79	0.735	1.826	5.99	0.071	0.177	179.1	6.338	15.74	28.24	3.826	9.504	5.72	0.071	0.177	
			503.6	507.4	286.3	13.16	32.68	78.9	1.5	3.727	6.24	0.2	0.498	217	7.013	17.42	33.61	2.12	5.265	5.75	0.202	0.502	175.6	2.361	5.864	14.06	0.624	1.551	5.51	0.219	0.545	
Salt Flush	1	1	509.8	513.6	2.751	0.249	0.618	14.69	0.1	0.249	6.087	0.031	0.077	1936	164.9	409.6	526.3	26.8	66.57	6.187	0.109	0.27	4873	312	776	395	8.3	20.6	4.47	0.14	0.36	
			513.6	517.4											434.1	54.06	134.3	178	12.98	32.25	6.157	0.18	0.447	1048	87.04	216.2	92.7	6.272	15.6	5.11	0.62	1.55
			517.6	521.4											269	13.68	33.99	130.1	6.161	15.31	6.16	0.177	0.439	591	26.05	64.72	63.37	3.162	7.85	5.32	0.58	1.45
			521.6	525.4	3.2	0.453	1.126	14.74	0.576	1.43	6.13	0.091	0.226	212.1	17.24	42.84	110.8	7.489	18.6	6.173	0.218	0.542	467.3	46.12	114.6	54.88	4.206	10.4	5.45	0.59	1.47	
			525.6	529.4											167	8.984	22.32	93.49	4.831	12	6.173	0.169	0.419	347	7.388	18.35	48.63	2.385	5.92	5.55	0.57	1.42
Post Salt Flush	2	1	525.8	529.6	259.8	5.251	13.04	73.06	2.883	7.161	6.24	0.036	0.088	354.5	73.28	182	19.2	2.141	5.319	6.05	0.083	0.206	3915	208.3	517.5	40.81	2.699	5.64	5.02	0.11	0.27	
			529.6	533.4											143.6	14.47	35.96	7.417	3.625	9.006	5.983	0.026	0.065	118	15.21	37.78	4.597	3.634	9.03	5.91	0.13	0.33
			533.6	537.4											150.3	3.649	9.065	11.93	0.683	1.698	6.01	0.036	0.088	71.65	2.435	6.05	1.855	0.21	0.52	5.89	0.1	0.24
			537.6	541.4	258.7	3.293	8.181	72.49	0.584	1.451	6.167	0.049	0.122	154.4	11.99	29.78	13.31	1.947	4.838	6.05	0.008	0.02	75.2	5.543	13.77	2.188	0.271	0.67	5.95	0.07	0.17	
			541.6	545.4											133.6	30.88	76.72	10.11	5.051	12.55	6.013	0.052	0.13	105.6	49.74	123.6	7.226	7.617	18.9	6.07	0.03	0.07

Table 17. Acid extraction data for biochar (BC) and torrefied wood (TW). Crossed out values were considered outliers and omitted from calculations. "Rock" refers to the covering layer of pea gravel.

Column	Level	Mass (g)	MC	UnFiltered					Filtered				
				#	Zn (µg/L)	Cu (µg/L)	Zn (mg/g)	Cu (mg/g)	#	Zn (µg/L)	Cu (µg/L)	Zn (mg/g)	Cu (mg/g)
BC 1	Rock	15.1524	0.0	232	12564	4167	0.083	0.028	256	13205	4384	0.087	0.029
	Top	1.0056	0.45	233	2742	1848	0.496	0.334	257	2710	1843	0.490	0.333
	Mid	1.0071	0.45	234	2617	1232	0.472	0.222	258	2608	1235	0.471	0.223
	Btm	1.0104	0.45	235	2346	1060	0.422	0.191	259	2359	1070	0.425	0.192
BC 2	Rock	15.0311	0.0	236	13169	4648	0.088	0.031	260	13289	4655	0.088	0.031
	Top	1.0055	0.45	237	3149	2069	0.569	0.374	261	3148	2087	0.569	0.377
	Mid	1.0023	0.45	238	2076	1073	0.377	0.195	262	2228	1158	0.404	0.210
	Btm	1.0083	0.45	239	3261	1146	0.588	0.207	263	3336	1171	0.601	0.211
BC 3	Rock	15.1188	0.0	240	14528	5520	0.096	0.037	264	14970	5631	0.099	0.037
	Top	1.0000	0.45	241	2364	1836	0.430	0.334	265	2380	1844	0.433	0.335
	Mid	1.0011	0.45	242	2518	1403	0.457	0.255	266	2546	1420	0.462	0.258
	Btm	1.007	0.45	243	12654	940	2.285	0.170	267	13001	923	2.347	0.167
TW 1	Rock	15.0005	0.0	244	13394	4811	0.089	0.032	268	13388	4807	0.089	0.032
	Top	1.0116	0.45	245	4257	5083	0.765	0.914	269	4292	5181	0.771	0.931
	Mid	1.0177	0.45	246	3177	2505	0.568	0.448	270	3422	2698	0.611	0.482
	Btm	1.0084	0.45	247	2749	1249	0.496	0.225	271	3101	1406	0.559	0.254
TW 2	Rock	15.0273	0.0	248	14422	5134	0.096	0.034	272	14439	5208	0.096	0.035
	Top	0.9986	0.45	249	4077	4882	0.742	0.889	273	4087	4886	0.744	0.890
	Mid	1.0118	0.45	250	3603	2732	0.647	0.491	274	3826	2939	0.688	0.528
	Btm	1.0035	0.45	251	2883	1292	0.522	0.234	275	2884	1311	0.523	0.238
TW 3	Rock	15.0066	0.0	252	11170	4214	0.074	0.028	276	11375	4239	0.076	0.028
	Top	1.0037	0.45	253	50599	3930	9.166	0.712	277	54703	4262	9.909	0.772
	Mid	0.9994	0.45	254	3366	2674	0.612	0.487	278	3434	2751	0.625	0.501
	Btm	0.9986	0.45	255	3051	1421	0.555	0.259	279	3055	1445	0.556	0.263

Table 18. Acid extraction calculations to determine total mass of zinc and copper contained on the media layers (top, mid, btm) and covering pea gravel (rock).

Level	Density	Vol.	Mass	Biochar - Unfiltered									
	g/L	L	g	Zn					Cu				
				mg/g	stdev	95 CI	mg	±	mg/g	stdev	96 CI	mg	±
Rock	1581.1	0.362	572	0.089	0.005	0.014	51	7.8	0.032	0.004	0.009	18	5.3
Top	98	0.483	47	0.498	0.057	0.142	24	6.7	0.347	0.019	0.047	16	2.2
Mid	98	0.483	47	0.435	0.042	0.104	21	4.9	0.224	0.025	0.061	11	2.9
Btm	98	0.483	47	1.098	0.842	2.091	52	98.9	0.189	0.015	0.038	9	1.8
Level	Density	Vol.	Mass	Torrefied Wood - Unfiltered									
	g/L	L	g	Zn					Cu				
				mg/g	stdev	95 CI	mg	±	mg/g	stdev	97 CI	mg	±
Rock	1581.1	0.362	572	0.087	0.009	0.022	50	12.8	0.031	0.003	0.006	18	3.6
Top	172	0.483	83	0.754	0.011	0.102	63	8.5	0.838	0.090	0.223	70	18.5
Mid	172	0.483	83	0.609	0.033	0.081	51	6.7	0.475	0.019	0.048	39	4.0
Btm	172	0.483	83	0.524	0.024	0.061	44	5.0	0.239	0.014	0.035	20	2.9
Level	Density	Vol.	Mass	Biochar - Filtered									
	g/L	L	g	Zn					Cu				
				mg/g	stdev	95 CI	mg	±	mg/g	stdev	96 CI	mg	±
Rock	1581.1	0.362	572	0.092	0.005	0.01	52	8	0.032	0.004	0.01	19	5.0
Top	98	0.483	47	0.497	0.056	0.503	24	23.8	0.349	0.020	0.051	16	2.4
Mid	98	0.483	47	0.446	0.030	0.074	21	3.5	0.230	0.020	0.050	11	2.4
Btm	98	0.483	47	0.513	0.088	0.795	24	37.6	0.190	0.018	0.045	9	2.1
				Total mg Zn = 121 72					Total mg Cu = 55 11.9				
Level	Density	Vol.	Mass	Torrefied Wood - Filtered									
	g/L	L	g	Zn					Cu				
				mg/g	stdev	95 CI	mg	±	mg/g	stdev	97 CI	mg	±
Rock	1581.1	0.362	572	0.087	0.008	0.02	50	12.0	0.032	0.003	0.01	18	3.7
Top	172	0.483	83	0.758	0.014	0.122	63	10.2	0.864	0.067	0.168	72	13.9
Mid	172	0.483	83	0.641	0.033	0.083	53	6.9	0.504	0.019	0.047	42	3.9
Btm	172	0.483	83	0.546	0.017	0.041	45	3.4	0.251	0.011	0.026	21	2.2
				Total mg Zn = 211 32.4					Total mg Cu = 153 23.7				

Table 19. Total suspended solids data for laboratory column tests.

Event	Gal.	Liters	Torried Wood 1				Torried Wood 2				Torried Wood 3				Biochar 1				Biochar 2				Biochar 3			
			Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L	Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L	Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L	Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L	Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L	Tare Wt. (g)	Dry Wt. (g)	Solids (g)	mg/L
FF	4	15	-	-	-	-	-	-	-	-	-	-	-	-	1.4	1.425	0.025	12.35	1.418	1.451	0.033	16.6	1.416	1.447	0.031	15.45
1	8	30	1.394	1.396	0.001	0.75	1.401	1.402	0.001	0.75	1.393	1.395	0.002	1.1	1.406	1.408	0.002	0.75	1.403	1.406	0.002	1.25	1.414	1.416	0.003	1.4
2	12	45	1.406	1.409	0.002	1.2	1.402	1.404	0.002	1	1.404	1.406	0.002	0.9	1.416	1.419	0.002	1.25	1.405	1.409	0.005	2.4	1.404	1.406	0.002	0.8
3	16	60	1.401	1.402	0.001	0.6	1.399	1.401	0.002	0.8	1.401	1.402	0.002	0.8	1.407	1.41	0.003	1.45	1.409	1.411	0.002	1.05	1.4	1.401	0.001	0.6
4	20	76	1.396	1.397	5E-04	0.25	1.398	1.398	4E-04	0.2	1.396	1.41	0.014	7.15	1.398	1.399	0.002	0.85	1.398	1.399	9E-04	0.45	1.405	1.406	1E-03	0.5
5	24	91	1.395	1.396	0.001	0.65	1.399	1.4	0.001	0.55	1.394	1.395	0.002	0.85	1.391	1.392	8E-04	0.4	1.417	1.418	9E-04	0.45	1.425	1.425	5E-04	0.25
6	28	106	1.398	1.4	0.002	1.05	1.403	1.405	0.002	1.1	1.415	1.417	0.002	0.95	-	-	-	-	-	-	-	-	-	-	-	-
7	32	121	1.385	1.386	0.001	0.5	1.411	1.411	6E-04	0.3	1.415	1.416	9E-04	0.45	1.402	1.409	0.007	3.65	1.406	1.409	0.003	1.65	1.413	1.418	0.005	2.65
8	36	136	1.396	1.397	9E-04	0.45	1.409	1.409	8E-04	0.4	1.408	1.409	3E-04	0.15	1.405	1.402	-0	-1.25	1.388	1.388	3E-04	0.15	1.404	1.406	0.001	0.65
9	40	151	1.407	1.408	6E-04	0.3	1.396	1.396	1E-04	0.05	1.399	1.399	1E-04	0.05	1.414	1.415	6E-04	0.3	1.404	1.406	0.001	0.6	1.405	1.405	8E-04	0.4
10	44	166	1.394	1.395	9E-04	0.45	1.402	1.403	0.001	0.55	1.396	1.397	0.001	0.65	1.413	1.414	9E-04	0.45	1.42	1.421	0.001	0.6	1.401	1.402	9E-04	0.45
11	48	181	1.396	1.396	2E-04	0.1	1.379	1.381	0.002	0.85	1.396	1.398	0.001	0.65	1.411	1.411	6E-04	0.3	1.405	1.406	9E-04	0.45	1.397	1.398	7E-04	0.35
12	52	197	1.408	1.408	0	0	1.399	1.399	5E-04	0.25	1.406	1.406	1E-04	0.05	1.407	1.407	5E-04	0.25	1.402	1.402	1E-04	0.05	1.403	1.403	5E-04	0.25
13	56	212	1.395	1.395	0	0	1.395	1.395	0	0	1.413	1.413	0	0	1.401	1.402	8E-04	0.4	1.404	1.405	6E-04	0.3	1.394	1.395	7E-04	0.35
14	60	227	1.404	1.404	2E-04	0.1	1.391	1.391	1E-04	0.05	1.399	1.399	2E-04	0.1	1.407	1.408	8E-04	0.4	1.399	1.4	0.001	0.55	1.395	1.396	9E-04	0.45
15	64	242	-	-	-	-	-	-	-	-	-	-	-	-	1.401	1.402	7E-04	0.35	1.404	1.404	1E-04	0.05	1.408	1.408	3E-04	0.15
16	68	257	-	-	-	-	-	-	-	-	-	-	-	-	1.381	1.381	5E-04	0.25	1.401	1.402	5E-04	0.25	1.394	1.395	3E-04	0.15
17	72	272	-	-	-	-	-	-	-	-	-	-	-	-	1.404	1.404	4E-04	0.2	1.398	1.399	6E-04	0.3	1.408	1.408	2E-04	0.1
18	76	287	-	-	-	-	-	-	-	-	-	-	-	-	1.408	1.408	6E-04	0.3	1.408	1.408	4E-04	0.2	1.394	1.395	6E-04	0.3
19	80	302	-	-	-	-	-	-	-	-	-	-	-	-	1.407	1.408	5E-04	0.25	1.403	1.403	3E-04	0.15	1.401	1.401	2E-04	0.1
20	84	318	1.403	1.403	0	0	1.397	1.397	3E-04	0.15	1.406	1.407	6E-04	0.3	1.396	1.396	0	0	1.398	1.399	3E-04	0.15	1.41	1.41	1E-04	0.05
21	88	333	1.381	1.381	3E-04	0.15	1.399	1.401	0.001	0.7	1.409	1.409	6E-04	0.3	-	-	-	-	-	-	-	-	-	-	-	-
40	164	620	1.403	1.404	8E-04	0.4	-	-	-	-	-	-	-	-	1.399	1.4	6E-04	0.3	-	-	-	-	-	-	-	-

Table 20. Laboratory TSS calculations and associated graph.

Gal.	Liters	Torried Wood			Biochar		
		Ave.	Std. Dev.	95% CI	Ave.	Std. Dev.	95% CI
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
4	15	-	-	-	14.80	2.20	5.46
8	30	0.87	0.20	0.50	1.13	0.34	0.85
12	45	1.03	0.15	0.38	1.48	0.83	2.05
16	61	0.73	0.12	0.29	1.03	0.43	1.06
20	76	2.53	4.00	9.93	0.60	0.22	0.54
24	91	0.68	0.15	0.38	0.37	0.10	0.26
28	106	1.03	0.08	0.19	-	-	-
32	121	0.42	0.10	0.26	2.65	1.00	2.48
36	136	0.33	0.16	0.40	-0.15	0.98	2.45
40	151	0.13	0.14	0.36	0.43	0.15	0.38
44	167	0.55	0.10	0.25	0.50	0.09	0.22
48	182	0.53	0.39	0.96	0.37	0.08	0.19
52	197	0.10	0.13	0.33	0.18	0.12	0.29
56	212	0.00	0.00	0.00	0.35	0.05	0.12
60	227	0.08	0.03	0.07	0.47	0.08	0.19
64	242	-	-	-	0.18	0.15	0.38
68	257	-	-	-	0.22	0.06	0.14
72	273	-	-	-	0.20	0.10	0.25
76	288	-	-	-	0.27	0.06	0.14
80	303	-	-	-	0.17	0.08	0.19
84	318	0.15	0.15	0.37	0.07	0.08	0.19
88	333	0.38	0.28	0.71	-	-	-
164	621	0.40	-	-	0.30	-	-

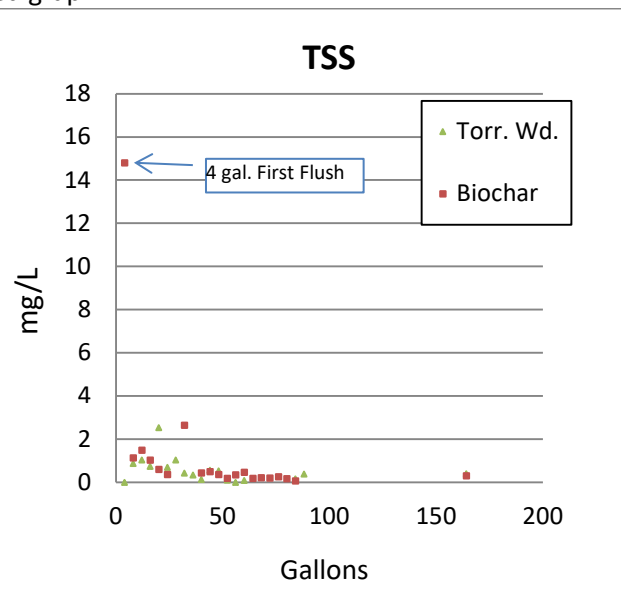


Table 21. Raw wood and pea gravel laboratory column data.

Gal.	L	Average Influent									Ave. Raw Wood									Ave. Pea Gravel								
		Zn			Cu			pH			Zn			Cu			pH			Zn			Cu			pH		
		(µg/L)	stdev	95 CI	(µg/L)	stdev	95 CI	-	stdev	95 CI	(µg/L)	stdev	95 CI	(µg/L)	stdev	95 CI	-	stdev	95 CI	(µg/L)	stdev	95 CI	(µg/L)	stdev	95 CI	-	stdev	95 CI
0.2	0.757	286	6.49	16	86	1.82	4.53	5.94	0.02	0.04	50.6	7.7	19.0	15.5	1.76	4.37	4.24	0.02	0.06	99.5	11.1	27.5	32.3	3.67	9.12	6.47	0.05	0.12
8	30.28	286			86			5.94			10.0	2.0	4.9	3.23	0.32	0.80	4.55	0.03	0.07	52.0	10.3	25.5	11.5	1.84	4.58	6.32	0.04	0.11
16	60.57	286			86			5.94			9.9	1.0	2.5	2.96	0.06	0.15	4.75	0.02	0.04	57.6	8.4	20.9	11.8	1.92	4.76	6.29	0.03	0.08
16.2	61.32	280	1.41	3.51	84	0.04	0.09	6.00	0.05	0.12	7.4	1.6	3.9	4.97	0.81	2.02	4.28	0.05	0.13	46.6	7.7	19.1	15.1	2.33	5.79	6.39	0.03	0.08
24	90.85	280			84			6.00			2.7	0.9	2.3	2.69	1.06	2.63	4.79	0.03	0.07	54.8	2.5	6.2	13.2	0.87	2.17	6.24	0.07	0.17
32	121.1	280			84			6.00			4.9	2.4	5.8	2.92	0.61	1.51	4.95	0.08	0.20	63.7	0.8	2.0	14.4	0.51	1.27	6.25	0.04	0.09
32.2	121.9	290	0.92	2.28	85	1.03	2.56	5.99	0.12	0.29	5.3	1.0	2.4	9.84	1.00	2.48	4.55	0.02	0.05	47.4	9.8	24.3	12.0	2.47	6.14	6.26	0.22	0.55
40	151.4	290			85			5.99			3.3	0.8	2.1	4.66	0.17	0.43	4.94	0.01	0.02	60.8	3.3	8.2	12.9	1.33	3.30	6.05	0.19	0.47
48	181.7	290			85			5.99			2.3	0.2	0.6	3.86	0.15	0.38	5.04	0.04	0.11	66.8	4.3	10.7	13.4	0.61	1.50	6.01	0.19	0.47
48.2	182.5	292	5.59	14	80	2.48	6.16	6.05	0.05	0.14	7.2	2.0	4.9	3.66	0.09	0.21	4.63	0.07	0.17	45.6	4.7	11.6	47.1	4.24	10.5	6.28	0.03	0.08
56	212	292			80			6.05			2.6	0.9	2.1	0.33	0.10	0.25	5.04	0.06	0.14	53.1	2.0	5.1	42.5	0.46	1.13	6.22	0.01	0.03
64	242.3	292			80			6.05			3.6	1.4	3.5	0.44	0.18	0.46	5.18	0.11	0.27	67.2	8.9	22.0	41.8	4.81	11.9	6.13	0.02	0.04
64.2	243	278	8.80	22	81	2.13	5.29	6.04	0.04	0.11	4.6	0.8	2.1	2.20	0.25	0.61	4.79	0.05	0.11	52.4	8.8	22.0	21.7	1.24	3.08	6.43	0.11	0.27
72	272.5	278			81			6.04			4.8	1.5	3.8	0.80	0.16	0.39	5.18	0.06	0.15	61.8	1.3	3.1	13.2	0.59	1.47	6.27	0.08	0.19
80	302.8	278			81			6.04			4.8	1.2	2.9	0.81	0.15	0.38	5.26	0.04	0.10	67.8	3.7	9.2	14.6	0.61	1.52	6.35	0.03	0.07
80.2	303.6	276	4.44	11	78	1.07	2.67	6.04	0.05	0.11	4.8	2.3	5.7	0.94	0.42	1.05	5.28	0.19	0.48	43.8	1.6	4.0	21.1	2.03	5.04	6.26	0.11	0.27
88	333.1	276			78			6.04			7.7	3.0	7.3	0.66	0.19	0.46	5.36	0.09	0.23	59.5	3.2	8.0	21.2	0.44	1.10	6.21	0.10	0.24
96	363.4	276			78			6.04			10.1	3.9	9.7	0.77	0.25	0.61	5.29	0.02	0.05	65.4	2.3	5.7	21.4	1.00	2.47	6.20	0.08	0.21
96.2	364.2	283	8.88	22	83	2.17	5.38	6.05	0.03	0.07	3.2	2.1	5.1	21.3	1.05	2.60	5.15	0.07	0.17	56.7	13.3	33.1	61.8	11.4	28.3	6.35	0.05	0.12
104	393.7	283			83			6.05			4.5	1.1	2.8	6.57	0.20	0.51	5.39	0.07	0.17	60.2	3.3	8.2	44.6	2.03	5.03	6.20	0.16	0.40
112	424	283			83			6.05			12.1	2.3	5.7	5.10	1.85	4.60	5.37	0.04	0.10	64.4	2.3	5.7	42.0	4.30	10.7	6.20	0.14	0.36
112.2	424.7	281	0.67	1.67	80	0.03	0.08	6.13	0.05	0.12	10.1	3.5	8.7	8.72	2.73	6.78	5.08	0.12	0.30	51.8	9.4	23.2	42.5	4.05	10.1	6.39	0.05	0.12
120	454.2	281			80			6.13			7.4	2.2	5.4	0.79	0.15	0.36	5.35	0.07	0.18	53.9	1.9	4.7	30.4	2.33	5.78	6.35	0.10	0.25
128	484.5	281			80			6.13			9.8	4.2	10.5	1.28	0.91	2.27	5.47	0.12	0.31	63.1	3.7	9.2	30.1	2.39	5.95	6.32	0.12	0.30
128.2	485.3	287	3.41	8.48	83	1.70	4.21	6.09	0.05	0.12	10.0	4.2	10.4	7.79	1.71	4.24	5.10	0.06	0.15	53.2	2.8	6.8	19.6	1.14	2.82	6.33	0.05	0.13
136	514.8	287			83			6.09			11.6	0.7	1.8	2.53	0.15	0.37	5.25	0.10	0.24	65.3	2.2	5.6	16.5	0.99	2.47	6.23	0.07	0.18
144	545.1	287			83			6.09			18.4	4.4	10.9	2.69	0.41	1.02	5.33	0.04	0.10	74.3	1.1	2.8	18.1	0.43	1.07	6.23	0.06	0.14
144.2	545.9	261	11	28	82	3.25	8.07	6.08	0.04	0.09	13.1	5.3	13.2	19.7	3.59	8.92	5.12	0.07	0.18	57.1	10.8	26.8	18.9	2.73	6.79	6.43	0.03	0.09
152.0	575.4	261			82			6.08			13.4	3.2	8.0	5.01	0.40	0.99	5.35	0.05	0.13	68.2	7.9	19.7	14.7	1.94	4.83	6.22	0.03	0.06
160.0	605.7	261			82			6.08			18.3	3.5	8.8	5.30	0.81	2.00	5.38	0.08	0.21	63.4	3.0	7.5	12.5	0.81	2.02	6.17	0.05	0.11
160.2	606.4	269	6.35	16	80	1.56	3.86	6.30	0.09	0.21	19.6	7.8	19.3	17.0	0.89	2.20	5.16	0.13	0.34	50.5	6.0	14.8	12.2	2.21	5.50	6.26	0.07	0.16
168.0	635.9	269			80			6.30			17.3	4.6	11.4	3.83	0.41	1.03	5.39	0.04	0.09	72.8	0.9	2.3	15.4	0.29	0.72	6.33	0.03	0.07
176.0	666.2	269			80			6.30			20.7	4.9	12.1	3.59	0.49	1.21	5.56	0.21	0.52	68.7	4.8	11.9	13.7	0.92	2.29	6.31	0.08	0.19
176.2	667	268	1.51	3.76	78	0.53	1.32	6.20	0.04	0.09	16.0	3.3	8.3	7.68	1.97	4.90	5.20	0.13	0.31	53.3	5.0	12.4	12.6	1.28	3.19	6.44	0.05	0.13
184.0	696.5	268			78						19.7	5.6	13.8	1.31	0.27	0.67	5.38	0.03	0.08	67.0	3.2	8.1	13.5	0.78	1.94	6.15	0.09	0.22
192.0	726.8	268			78						22.3	4.6	11.5	1.53	0.26	0.64	5.45	0.04	0.11	74.9	0.8	2.0	15.0	0.30	0.74	6.16	0.03	0.07
192.2	727.6	288	9.00	22	80	0.49	1.22	6.25	0.26	0.65	22.9	4.0	36.3	4.27	1.06	2.62	5.47	0.10	0.24	55.0	3.8	9.3	13.2	0.80	2.00	6.32	0.03	0.08
200.0	757.1	288			80						14.3	7.0	17.3	0.69	0.16	0.41	5.44	0.13	0.32	65.7	3.0	7.4	13.3	1.01	2.52	6.31	0.11	0.26
208.0	787.4	288			80						12.5	2.1	5.3	0.43	0.02	0.05	5.50	0.02	0.05	75.7	5.4	13.4	14.8	1.29	3.21	6.30	0.09	0.23
208.2	788.1	273	6.41	16	78	1.47	3.64	6.32	0.20	0.50	17.4	4.9	12.2	1.62	0.44	1.09	5.34	0.04	0.11	64.1	5.1	12.6	17.4	3.01	7.47	6.41	0.06	0.14
216.0	817.6	273			78						29.0	4.2	10.5	1.10	0.16	0.39	5.46	0.05	0.12	76.6	6.4	15.9	14.9	1.10	2.73	6.29	0.11	0.27
224.0	847.9	273			78						29.2	5.5	13.8	0.92	0.14	0.36	5.45	0.04	0.11	84.9	4.4	11.0	17.0	0.79	1.95	6.27	0.09	0.22
224.2	848.7	270	1.97	4.89	77	0.68	1.70	6.16	0.03	0.07	31.5	2.5	6.3	1.96	1.13	2.81	5.19	0.06	0.16	57.6	6.1	15.2	12.5	1.66	4.12	6.32	0.04	0.10
232.0	878.2	270			77						14.2	5.3	13.1	0.50	0.18	0.44	5.44	0.09	0.22	72.8	3.4	8.4	13.1	1.11	2.			

Table 21. Raw wood and pea gravel laboratory column tests - continued.

Gal.	L	Average Influent									Ave. Raw Wood									Ave. Pea Gravel								
		Zn			Cu			pH			Zn			Cu			pH			Zn			Cu			pH		
		(µg/L)	stdev	95 Cl	(µg/L)	stdev	95 Cl	-	stdev	95 Cl	(µg/L)	stdev	95 Cl	(µg/L)	stdev	95 Cl	-	stdev	95 Cl	(µg/L)	stdev	95 Cl	(µg/L)	stdev	95 Cl	-	stdev	95 Cl
272.2	1030	275	5.48	14	66	1.20	2.99	6.24	0.03	0.07	38.0	7.7	19.1	1.65	0.55	1.36	5.34	0.14	0.35	55.8	7.8	19.4	14.5	1.78	4.42	6.31	0.03	0.08
280.0	1060	275			66						39.4	6.1	15.1	1.17	0.18	0.45	5.46	0.06	0.15	69.0	3.1	7.7	13.4	0.70	1.75	6.20	0.14	0.34
288.0	1090	275			66						40.4	12.7	31.6	1.05	0.33	0.81	5.41	0.14	0.35	74.3	5.4	13.5	14.1	1.29	3.21	6.16	0.13	0.33
288.2	1091	277	6.79	17	80	3.06	7.60	6.20	0.05	0.14	37.2	8.2	20.5	20.9	1.24	3.09	5.33	0.09	0.21	54.8	12.1	30.1	31.6	6.96	17.3	6.36	0.05	0.12
296.0	1120	277			80						38.2	9.3	23.1	5.85	1.06	2.64	5.45	0.02	0.05	66.9	10.6	26.2	27.8	5.46	13.6	6.20	0.03	0.06
304.0	1151	277			80						34.6	11.3	28.1	4.54	0.94	2.33	5.52	0.04	0.11	69.2	3.4	8.5	25.6	1.74	4.32	6.24	0.02	0.05
304.2	1152	282	3.77	9.37	80	0.54	1.33	6.17	0.07	0.18	52.2	5.3	13.1	26.3	1.48	3.69	5.36	0.09	0.23	59.3	0.5	1.2	13.7	0.53	1.32	6.30	0.03	0.08
312.0	1181	282			80						41.8	16.0	39.7	7.65	1.33	3.31	5.58	0.04	0.09	68.1	6.1	15.0	14.2	1.16	2.88	6.23	0.03	0.07
320.0	1211	282			80						54.1	17.4	43.2	6.84	1.72	4.28	5.65	0.08	0.21	81.8	4.9	12.2	18.3	0.76	1.88	6.30	0.04	0.10
320.2	1212	250	3.76	9.34	63	0.26	0.64	6.39	0.16	0.39	45.7	4.8	11.9	5.94	1.23	3.07	5.46	0.05	0.13	65.0	8.5	21.1	12.0	5.77	14.3	6.33	0.05	0.13
328.0	1242	250			63						39.9	8.5	21.1	1.18	0.15	0.38	5.48	0.07	0.18	75.7	7.4	18.5	17.2	2.60	6.45	6.15	0.01	0.03
336.0	1272	250			63						51.4	0.2	0.5	1.44	0.18	0.46	5.48	0.19	0.46	76.7	8.7	21.6	16.9	2.73	6.78	6.19	0.03	0.08
336.2	1273	243	1.54	3.83	80	0.19	0.48	6.13	0.09	0.21	40.4	10.5	26.1	12.8	2.19	5.44	5.50	0.02	0.05	66.5	7.5	18.7	17.8	4.25	10.5	6.19	0.08	0.19
344.0	1302	243			80						42.7	15.4	38.2	2.91	1.05	2.60	5.70	0.07	0.16	74.2	8.7	21.6	14.9	1.77	4.39	6.17	0.04	0.10
352.0	1332	243			80						49.6	13.2	32.7	2.53	0.66	1.64	5.63	0.09	0.22	76.1	6.0	14.9	14.8	1.38	3.42	6.23	0.14	0.34
352.2	1333	244	1.30	3.24	76	2.41	5.99	6.19	0.05	0.12	53.4	5.8	14.5	5.45	1.63	4.04	5.52	0.03	0.08	63.9	9.0	22.3	16.4	2.53	6.28	6.16	0.02	0.04
360.0	1363	244			76						57.0	12.4	30.9	1.34	0.29	0.71	5.66	0.06	0.14	79.8	6.6	16.3	17.1	2.08	5.16	6.06	0.06	0.15
368.0	1393	244			76						71.0	10.9	27.1	1.62	0.33	0.82	5.63	0.03	0.07	81.1	1.7	4.2	17.1	0.72	1.80	6.23	0.06	0.14
368.2	1394	250	7.42	18	72	1.00	2.49	6.13	0.07	0.17	64.8	11.6	28.9	4.18	0.59	5.26	5.53	0.05	0.12	61.7	1.9	4.7	12.0	1.05	2.60	6.20	0.03	0.07
376.0	1423	250			72						67.1	9.4	23.3	1.70	0.53	1.31	5.68	0.04	0.10	80.1	3.0	7.5	16.1	1.01	2.50	6.11	0.05	0.12
384.0	1454	250			72						68.2	12.2	30.4	1.65	0.43	1.06	5.68	0.07	0.17	80.2	5.2	13.0	15.9	2.45	6.08	6.22	0.04	0.10
384.2	1454	250	4.09	10	66	1.05	2.60	6.22	0.08	0.20	92.5	15.3	37.9	8.16	4.62	11.5	5.50	0.17	0.41	70.6	11.1	27.5	57.1	4.74	11.8	6.28	0.13	0.31
392.0	1484	250			66						74.3	8.2	20.3	1.73	0.43	1.06	5.63	0.05	0.11	76.7	4.3	10.6	55.9	3.74	9.29	6.40	0.05	0.12
400.0	1514	250			66						74.3	11.3	28.0	1.62	0.37	0.92	5.66	0.04	0.09	75.0	4.7	11.6	50.4	0.20	0.49	6.42	0.11	0.28
400.2	1515	259	11	26	77	0.73	1.81	6.23	0.11	0.28	96.3	4.2	10.4	3.35	0.60	1.48	5.55	0.15	0.36	58.4	4.3	10.6	28.8	8.93	22.2	6.30	0.09	0.21
408.0	1544	259			77						85.8	5.0	12.5	1.93	0.58	1.45	5.67	0.06	0.14	81.2	6.0	14.8	30.7	7.02	17.4	6.45	0.03	0.07
416.0	1575	259			77						62.1	7.7	19.2	1.18	0.11	0.27	5.76	0.12	0.31	78.2	4.1	10.2	27.3	6.17	15.3	6.47	0.06	0.14
416.2	1575	251	1.46	3.62	68	3.57	8.87	6.11	0.03	0.08	81.3	3.9	9.6	1.66	0.23	0.56	5.60	0.04	0.11	71.6	3.2	7.9	33.3	1.08	2.67	6.41	0.03	0.08
424.0	1605	251			68						84.3	1.7	4.3	1.62	0.17	0.43	5.71	0.02	0.05	83.3	3.1	7.8	34.6	0.74	1.84	6.39	0.09	0.21
432.0	1635	251			68						88.8	5.8	14.5	1.52	0.09	0.21	5.77	0.03	0.08	92.0	4.7	11.6	36.3	1.96	4.86	6.38	0.07	0.16

Table 22. Raw wood and pea gravel (rock) composite sample metal concentration (µg/L) data.

#	gal.	L	Composite Samples																	
			RW 1			RW 2			RW 3			Rock 1			Rock 2			Rock 3		
			#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu	#	Zn	Cu
1	8	30.28	22	22.04	7.047	24	18.97	7.438	26	24.52	7.7	110	64.13	15.36	112	54.14	12.55	114	56.53	12.73
2	24	90.85	49	7.596	6.767	51	5.043	4.871	53	7.307	2.757	137	53.72	13.25	139	48.52	12.08	141	49.95	12.25
3	40	151.4	76	5.815	7.505	78	3.895	6.12	80	6.375	6.123	164	57.6	12.38	166	55.8	11.46	168	55.49	11.58
4	56	212	109	7.345	2.163	111	5.032	1.594	113	5.708	1.45	191	64.04	45.6	193	50.26	40.39	195	56.5	40.9
5	72	272.5	136	4.905	1.667	138	3.649	2.911	140	6.264	1.425	218	60.23	13.19	220	64	11.25	222	62.17	12.77
6	88	333.1	163	6.648	0.929	165	6.049	0.651	167	15.28	1.801	245	60.85	21.27	247	61.42	21.08	249	62.16	21.01
7	104	393.7	190	10.85	9.529	192	8.057	9.217	194	8.781	8.398	23	61.36	51.07	25	52.41	42.11	27	57.13	39.06
8	120	454.2	217	13.93	1.979	219	12.56	1.587	221	14.63	2.494	50	58.6	31.12	52	54.52	28.64	54	58.78	26.25
9	136	514.8	244	14.21	3.955	246	13.2	3.608	248	19	3.919	77	64.64	15.14	79	63.21	15.08	81	63.14	16.22
10	152	575.4	22	18.9	10.13	24	15.16	6.054	26	19.94	7.137	104	69.17	14.62	106	55.51	11.31	108	63.5	13.49
11	168	635.9	49	21.85	5.82	51	28.73	5.917	53	15.94	4.947	131	71.74	13.84	133	61.74	12.5	135	63.61	13.36
12	184	696.5	76	17.98	2.668	78	32.07	2.484	80	19.49	2.457	158	67.82	13.5	160	59.24	11.68	162	63.86	12.58
13	200	757.1	103	21.83	1.962	105	16.19	1.534	107	16.41	1.404	185	71.08	12.96	187	63.3	11.78	189	66.98	12.71
14	216	817.6	130	35.89	1.369	132	24.78	1.413	134	24.26	1.031	212	81.97	16.87	214	76.3	14.71	216	71.05	13.85
15	232	878.2	157	27.4	1.472	159	32.52	1.57	161	20.51	0.873	239	69.21	12.23	241	65.71	11.08	243	77.21	12.77
16	248	938.8	184	30.34	1.821	186	26.56	1.432	188	30.19	1.461	266	68.61	40.57	268	67.17	35.67	270	68.76	35.15
17	264	999.3	211	40.3	2.004	213	34.7	1.441	215	30.04	1.223	293	84.04	49.07	295	76.51	46.24	297	68.58	39.54
18	280	1060	238	34.24	1.534	240	41.23	1.463	242	36.53	1.139	23	70.44	13.02	25	64.23	12.07	27	67.45	12.91
19	296	1120	265	40.37	7.978	267	38.54	7.494	269	35.26	5.654	50	79.63	33.89	52	58.61	24.64	54	59.7	22.36
20	312	1181	292	47.33	10.97	294	46.09	10.46	296	40.56	8.154	77	76.34	16.74	79	69.26	14.28	81	68.56	15.08
21	328	1242	22	41.13	2.189	24	39.67	2.047	26	41.45	2.125	104	85.17	18.68	106	75.48	16.99	108	65.02	13.36
22	344	1302	49	56.79	6.2	51	44	3.545	53	43.48	3.343	131	75.83	14.59	133	73.5	14.6	135	67.77	12.89
23	360	1363	76	56.37	2.368	78	57.19	2.401	80	54.67	2.087	158	84.92	18.26	160	73.4	14.85	162	75.64	15.96
24	376	1423	103	68.8	2.681	105	63.91	2.481	107	56.16	1.873	185	75.82	14.3	187	74.34	14.93	189	80.26	16.91
25	392	1484	130	105.1	3.146	132	74.21	2.63	134	64.02	2.08	202	70.04	53.06	203	73.14	47.66	204	256.7	92.97
26	408	1544	157	87.49	2.779	159	87	2.26	161	75.09	1.428	217	68.68	36.74	218	274.7	88.48	219	75.91	34.84
27	424	1605	184	70.56	2.158	186	81.25	1.848	188	79.29	1.877	229	84.17	35.7	230	76.56	33.64	231	87.01	33.87

7.3 - Field Data

The data in Table 23 represent influent and effluent copper and zinc concentrations for the pilot scale field column containing biochar.

Table 23. Influent and effluent constituent concentration data for the pilot column.

Date	Sampler	Solids (mg/L)						%VSS	Filtered Sample					pH	Total Metals (ppb)			T.M. Blanks (ppb)					
		Vol.	Tare	Dried	Muff	TSS	VSS		Sample	Zn	Ave. Zn	Cu	Ave. Cu		Sample	Zn	Cu	Sample	Zn	Cu			
		(mL)	(g)	(g)	(g)	(mg/L)	(mg/L)		(%)	#	(ppb)	(ppb)	(ppb)		#	(ppb)	(ppb)	#	(ppb)	(ppb)			
August 14	Influent (I1) (Samples 1-12)	80	1.395	1.404	1.399	110	60	45%	1	114.5	122.7	20.7	22.0	-	13	244.9	44.3	17	11.1	2.0			
									2	130.9		23.3											
									3	-		-											
	Influent (I2) (Samples 13-24)	500	1.385	1.471	1.435	172	70	59%	4	109.3	108.5	12.8	12.3	6.43	14	295.0	45.7						
									5	106.0		12.2											
									6	110.1		11.9											
	Effluent (E3) (Samples 1-12)	80	1.398	1.406	1.403	97	37	62%	7	114.5	110.0	22.0	21.6	6.21	15	218.2	73.6	18	6.7	1.6			
									8	106.7		21.5											
									9	108.7		21.3											
	Effluent (E4) (Samples 13-24)	80	1.398	1.405	1.403	79	26	67%	10	87.5	87.9	15.3	15.4	6.34	16	149.4	26.7						
									11	86.9		14.9											
									12	89.4		16.0											
August 29	Influent (I1) (Samples 1-12)	80	1.395	1.408	1.401	164	79	52%	1	58.5	59.5	8.1	8.0	6.79	13	195.6	31.0	17	5.9	0.5			
									2	60.5		8.0											
									3	56.2		7.3											
	Influent (I2) (Samples 13-24)	80	1.408	1.411	1.41	36	9	76%	4	29.1	32.3	5.7	4.3	6.79	14	67.2	11.5						
									5	26.0		3.5											
									6	41.6		3.6											
	Effluent (E3) (Samples 1-12)	80	1.416	1.419	1.418	34	19	44%	7	18.7	18.7	10.2	10.1	7.31	15	47.7	17.0	18	2.8	0.5			
									8	18.7		10.2											
									9	18.7		9.9											
	Effluent (E4) (Samples 13-24)	80	1.394	1.395	1.395	11	5	56%	10	10.7	10.7	6.2	6.3	7.33	16	24.1	8.5						
									11	10.6		6.5											
									12	10.8		6.2											
October 10	Influent (I1) (Samples 1-6)	80	1.385	1.41	1.406	312	49	84%	1	31.4	45.1	3.0	3.0	6.66	7	143.2	37.7	9	15.0	4.3			
									2	58.8		3.0											
									3	31.2		3.0											
	Effluent (I2) (Samples 1-6)	80	1.412	1.422	1.419	130	46	64%	4	13.4	28.1	2.6	2.6	6.65	8	78.1	15.3						
									5	25.6		2.6											
									6	45.4		2.7											

Table 24. Sludge sample volatile fraction data table.

Solids tests					
Tare wt	Dry wt.	Mass	Muff wt.	Inert	% Volatile
(g)	(g)	(g)	(g)	(g)	(%)
86.3033	93.6872	7.38	91.2458	4.94	33.1%
88.9258	96.0668	7.14	93.6553	4.73	33.8%
66.5243	73.7703	7.25	71.3500	4.83	33.4%
* per EPA 1684 section 11					

Table 25. Sludge sample total extractable metals data table.

Total Metals Extraction											Blank		
Dry & Ground	HNO3	HCL	Diluted	Sample	Zn	Zn	Ave. Zn	Cu	Cu	Ave. Cu	Sample	Zn	Cu
(g)	(mL)	(mL)	(mL)	#	(µg/L)	(mg/kg)	(mg/kg)	(µg/L)	(mg/kg)	(mg/kg)	#	(µg/L)	(µg/L)
1.0010	4	10	100	19	7644.2	763.7	731.2	1120.0	111.9	106.5	22	11.2	1.3
1.0020				20	6577.4	656.4		872.9	87.1				
1.0023				21	7752.0	773.4		1209.1	120.6				
*per EPA 200.7 section 11.3													

The data in Table 26 through Table 34 are influent and effluent copper and zinc concentrations for the pilot scale field column containing raw wood crumbles. Twenty four discrete influent and effluent samples were used to develop three composite samples for each stormwater runoff event. Comp1, comp2 and comp3 were produced by mixing discrete sample bottles 1-8, 9-16, and 17-24, respectively.

Table 26. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 1/17/2016 runoff event.

1/17/2016					
	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	10.4	0.5	3.7	0.5	64%
Comp2	7.5	0.1	3.5	1.0	53%
Comp3	7.2	0.7	7.2	0.7	0%
Sol Cu (µg/L)					
Comp1	2.7	1.6	2.3	0.1	15%
Comp2	1.8	0.1	1.7	0.1	6%
Comp3	1.4	0.1	1.5	0.1	-7%
Total Zn (µg/L)					
Comp1	93.5	5.2	32.7	15.1	65%
Comp2	72.6	8.8	42.7	7.2	41%
Comp3	77.5	13.2	50.2	45.4	35%
Sol Zn (µg/L)					
Comp1	53.3	6.0	17.9	1.9	66%
Comp2	35.0	4.1	21.0	5.7	40%
Comp3	31.8	0.3	16.8	0.7	47%
TSS (mg/L)					
Comp1	48.5	1.5	12.3	17.4	75%
Comp2	32.3	2.9	9.9	0.9	69%
Comp3	30.9	2.1	12.7	10.0	59%
VSS (mg/L)					
Comp1	20.0		9.0		55%
Comp2	14.3		6.6		54%
Comp3	11.9		5.3		55%

Table 27. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 1/23/2016 runoff event.

1/23/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	10.9	4.0	4.3	0.1	61%
Comp2	7.7	0.4	3.8	0.3	51%
Comp3	5.7	0.9	3.4	0.2	40%
Sol Cu (µg/L)					
Comp1	3.6	0.1	3.7	0.1	-3%
Comp2	3.0	0.1	2.3	0.1	23%
Comp3	2.4	0.1	2.0	0.1	17%
Total Zn (µg/L)					
Comp1	114.2	9.9	39.2	6.0	66%
Comp2	93.1	17.2	37.6	8.3	60%
Comp3	65.4	28.9	30.1	0.7	54%
Sol Zn (µg/L)					
Comp1	76.0	2.6	36.1	1.8	53%
Comp2	54.9	0.5	28.1	1.3	49%
Comp3	38.7	1.9	21.5	2.0	44%
TSS (mg/L)					
Comp1	41.3	9.0	9.9	1.5	76%
Comp2	27.3	1.5	8.1	2.6	70%
Comp3	16.9	4.1	8.4	3.6	50%
VSS (mg/L)					
Comp1	12.8		6.5		49%
Comp2	8.5		4.0		53%
Comp3	7.6		4.4		42%

Table 28. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 1/27/2016 runoff event.

1/27/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	20.8	0.2	7.9	0.2	62%
Comp2	16.2	1.0	5.7	0.2	65%
Comp3	13.4	1.3	4.8	0.7	64%
Sol Cu (µg/L)					
Comp1	3.5	0.1	3.0	0.2	14%
Comp2	2.7	0.1	2.4	0.1	11%
Comp3	2.3	0.0	1.9	0.0	17%
Total Zn (µg/L)					
Comp1	215.4	13.3	75.8	3.3	65%
Comp2	160.9	8.0	49.7	7.4	69%
Comp3	130	7.5	39	2.2	70%
Sol Zn (µg/L)					
Comp1	76.0	4.2	40.8	6.0	46%
Comp2	54.9	6.7	32.4	4.4	41%
Comp3	38.7	5.8	22.2	2.5	43%
TSS (mg/L)					
Comp1	75.5	2.3	20.5	2.9	73%
Comp2	61.5	2.3	14.4	1.1	77%
Comp3	50.5	0.6	13.1	2.6	74%
VSS (mg/L)					
Comp1	31.9		9.1		71%
Comp2	24.0		7.1		70%
Comp3	22.4		6.0		73%

Table 29. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 2/17/2016 runoff event.

2/17/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	10.3	1.0	4.1	0.1	60%
Comp2	7.4	0.4	3.2	0.3	57%
Comp3	5.2	0.5	2.3	0.0	56%
Sol Cu (µg/L)					
Comp1	1.7	0.1	1.5	0.2	12%
Comp2	1.4	0.2	1.3	0.0	7%
Comp3	1.2	0.1	1.1	0.1	8%
Total Zn (µg/L)					
Comp1	114	9.5	53.5	3.6	53%
Comp2	88.9	18.0	52.6	10.7	41%
Comp3	70.5	18.9	36.6	6.5	48%
Sol Zn (µg/L)					
Comp1	54.5	4.1	27.2	3.6	50%
Comp2	41.5	2.0	21.1	1.4	49%
Comp3	35.4	10.5	19.4	5.3	45%
TSS (mg/L)					
Comp1	46.9	2.5	12.5	2.5	73%
Comp2	30.0	1.0	7.3	2.1	76%
Comp3	20.1	0.6	5.6	0.6	72%
VSS (mg/L)					
Comp1	19.9		4.7		76%
Comp2	12.7		3.5		72%
Comp3	8.9		2.7		70%

Table 30. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 2/28/2016 runoff event.

2/28/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	10	0.8	4.4	0.1	56%
Comp2	6.3	1.1	4.6	0.4	27%
Comp3	7.1	1.0	2.6	2.1	63%
Sol Cu (µg/L)					
Comp1	2.2	0.2	2.1	0.1	5%
Comp2	2.1	0.0	1.9	0.1	10%
Comp3	1.0	0.1	1.1	0.1	-10%
Total Zn (µg/L)					
Comp1	78.6	0.7	40.4	15.0	49%
Comp2	78.2	0.5	48.3	21.3	38%
Comp3	78.7	6.5	36.4	13.7	54%
Sol Zn (µg/L)					
Comp1	33.0	8.9	27.2	3.8	18%
Comp2	34.0	2.4	21.1	5.3	38%
Comp3	39.7	3.3	19.4	1.5	51%
TSS (mg/L)					
Comp1	47.7	5.0	10.9	1.5	77%
Comp2	22.7	3.8	13.6	1.1	40%
Comp3	43.1	1.1	6.0	3.6	86%
VSS (mg/L)					
Comp1	18.1		4.5		75%
Comp2	9.5		5.1		46%
Comp3	15.9		2.4		85%

Table 31. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 3/13/2016 runoff event.

3/13/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	7.6	0.7	4.0	0.3	47%
Comp2	5.8	0.6	4.1	0.1	29%
Comp3	6.0	0.3	4.4	0.2	27%
Sol Cu (µg/L)					
Comp1	2.0	0.1	2.2	0.2	-10%
Comp2	2.3	0.2	2.3	0.1	0%
Comp3	2.4	0.2	2.3	0.0	4%
Total Zn (µg/L)					
Comp1	59.2	1.6	35.6	4.6	40%
Comp2	45.7	6.5	33.3	4.4	27%
Comp3	49.4	2.7	36.2	6.0	27%
Sol Zn (µg/L)					
Comp1	27.9	1.9	24.9	5.3	11%
Comp2	29.1	3.0	25.0	6.2	14%
Comp3	32.0	5.2	25.7	7.0	20%
TSS (mg/L)					
Comp1	39.2	4.3	9.7	2.5	75%
Comp2	22.1	3.2	10.1	3.0	54%
Comp3	22.3	4.1	10.4	2.3	53%
VSS (mg/L)					
Comp1	13.6		3.1		77%
Comp2	9.1		4.5		51%
Comp3	10.1		2.5		75%

Table 32. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 3/21/2016 runoff event.

3/21/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	16.5	2.3	9.2	4.6	44%
Comp2	12.4	0.7	5.8	1.3	53%
Comp3	8.5	0.3	5	4.1	41%
Sol Cu (µg/L)					
Comp1	4.4	0.5	4.6	1.4	-5%
Comp2	3.2	0.7	3.1	0.1	3%
Comp3	2.1	0.2	2.2	0.1	-5%
Total Zn (µg/L)					
Comp1	151.2	13.5	80.2	9.1	47%
Comp2	119.6	12.8	53.9	9.5	55%
Comp3	82.4	0.8	37.6	10.1	54%
Sol Zn (µg/L)					
Comp1	72.6	0.4	54.1	5.4	25%
Comp2	57.6	10.6	38.8	5.3	33%
Comp3	47.1	2.3	29.4	5.7	38%
TSS (mg/L)					
Comp1	64.9	1.5	18.3	1.1	72%
Comp2	50.9	3.0	13.1	5.1	74%
Comp3	36.0	3.0	8.0	4.3	78%
VSS (mg/L)					
Comp1	33.6		9.5		72%
Comp2	24.7		6.1		75%
Comp3	16.9		4.4		74%

Table 33. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 4/12/2016 runoff event.

4/12/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	52.3	1.0	39.8	0.8	24%
Comp2	43.3	1.3	35.3	0.7	18%
Comp3	34.2	1.2	28.8	0.7	16%
Sol Cu (µg/L)					
Comp1	14.2	1.6	20.4	6.2	-44%
Comp2	18.6	2.4	23.6	0.8	-27%
Comp3	18.2	0.3	20.9	2.3	-15%
Total Zn (µg/L)					
Comp1	329.6	7.7	230.9	0.6	30%
Comp2	271.1	11.8	199.2	8.7	27%
Comp3	194.2	8.0	145.4	6.4	25%
Sol Zn (µg/L)					
Comp1	134.8		150.8	21.9	-12%
Comp2	160.8	7.5	136.8	4.8	15%
Comp3	122.3	8.1	100.6	10.6	18%
TSS (mg/L)					
Comp1	219.3	17.4	84.0	9.9	62%
Comp2	118.0	0.0	48.0	17.9	59%
Comp3	86.0	14.9	35.3	5.7	59%
VSS (mg/L)					
Comp1	163.3		66.0		60%
Comp2	86.0		36.0		58%
Comp3	65.3		31.3		52%

Table 34. Influent and effluent concentrations for the field column containing raw wood crumbles. Samples collected during the 4/24/2016 runoff event.

4/24/2016	Influent	95% CI	Effluent	95% CI	%removal
Total Cu (µg/L)					
Comp1	22.6	8.0	10.2	1.3	55%
Comp2	12.0	0.7	7.9	0.1	34%
Comp3	9.3	0.6	5.4	0.3	42%
Sol Cu (µg/L)					
Comp1	6.2	0.3	7.2	0.2	-16%
Comp2	6.6	4.3	5.4	0.2	18%
Comp3	3.9	0.3	3.7	0.1	5%
Total Zn (µg/L)					
Comp1	99.1	7.2	59.4	6.2	40%
Comp2	83.6	9.0	47.5	2.1	43%
Comp3	63.6	6.5	40.3	10.3	37%
Sol Zn (µg/L)					
Comp1	51.2	2.6	46.1	6.9	10%
Comp2	46.0	3.5	35.2	4.5	23%
Comp3	38.6	3.4	26.6	4.5	31%
TSS (mg/L)					
Comp1	54.8	2.0	13.3	6.9	76%
Comp2	42.4	5.5	12.4	5.9	71%
Comp3	34.0	1.7	8.0	3.6	76%
VSS (mg/L)					
Comp1	28.0		9.5		66%
Comp2	18.7		6.1		67%
Comp3	17.1		4.4		74%

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