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PERFORMANCE OF COMMERCIALY AVAILABLE SOIL AMENDMENTS
FOR ENHANCED REMOVAL OF COPPER IN BIORETENTION MEDIA

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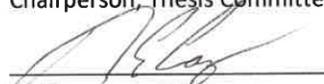
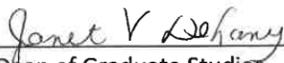
THESIS APPROVAL PAGE

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entitled Performance of Commercially Available Soil Amendments for Enhanced

Copper Removal in Bioretention Media

has been approved by the thesis committee as satisfactorily completing the thesis requirements for the degree Master of Science in Environmental Science

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Chapter 1: Contributions of Copper from Copper Roofing Materials into Stormwater

Characteristics and Usage of Copper Roofing Materials

Copper roofing continues to be a specialty roofing material utilized throughout the world due to the durability, aesthetic quality, and enhanced safety against fires (Bielmyer et al. 2012). The use of copper roofing materials provides a cost-effective substitute for traditional asphalt shingles, as little to no maintenance is required throughout the roofs' longer lifespan (Hedberg et al. 2014). Copper roofs are naturally resistant to algal growth and even traditional asphalt shingle roofing materials tend to incorporate copper granules or rods to aid in the prevention of algal growth (Charters et al., 2016). As copper roofing materials age through exposure to temperature, humidity, and precipitation in the atmosphere, they form a natural patina which is aesthetically desired.

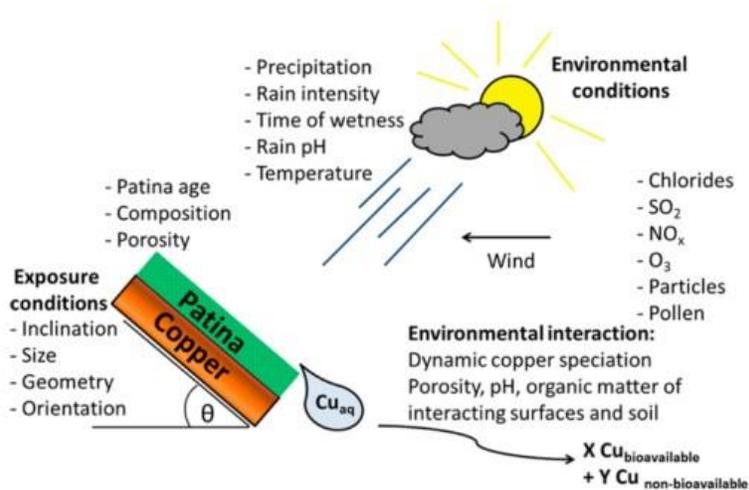


Figure 1. Depiction of the Environmental Conditions which affect the Release of Copper from Copper Roofing Materials. (Hedberg et al., 2014).

Figure 1 depicts the multitude of environmental conditions that dictates patina formation, oxidation, and dissolution in natural environments, including how copper

interacts with the environment once it has been released from copper roofing materials. These patinas vary depending on various environmental parameters, but generally; nutty brown colored patinas form with as Cu_2O as the main corrosion product, and blueish-green patinas form with Cu_2O inner layers covered by an outer layer of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ (Odnevall Wallinder et al., 2009). The formation of these patinas is caused by electrochemical processes and cause the potential release of copper as these patinas can be dissolved during precipitation events (Odnevall Wallinder et al., 2009). These patinas contain copper in a more leachable form allowing for release into the environment. Two distinct phenomena can occur in patinas on copper roofs in natural conditions: dissolution and oxidation. Dissolution likely occurs in storm events where naturally slightly acidic rainwater can dissolve these patinas and release copper into the runoff and into the environment (Odnevall Wallinder et al., 2009). Oxidation occurs when patinas slightly dissolve, then re-precipitated, usually as a more oxidized form. Both oxidation and dissolution play a large role in the release of copper into the environment, but dissolution is the primary means of copper release (Odnevall Wallinder et al., 2009).

Copper Release into Stormwater

Copper release into stormwater has garnered increasing attention over the past few years due the potential adverse effects on biota at low ppb concentrations. Copper has been identified as exceeding impairment concentrations in 844 waterways across the United States (Chang et al. 2016). The extent of copper roofing materials contribution to copper impairment in waterways is variable, however many areas, like the Pacific Northwest, are acting to limit the release of copper from all potential sources.

Regulations established in the state of Washington in 2010 sought to phase out and eventually prohibit the use of copper in automobile brake pads; as studies conducted in

Puget Sound found that brake pad wear accounted for about 15% (about 37 tons/year) of the total copper release into the Sound (Norton et al., 2011). The same study showed that roofing materials accounted for 11% (27 tons/year) of the copper loading to the Sound (Norton et al., 2011). Both copper roofs and traditional asphalt-shingle roofs can export high concentrations of copper during storm events. Bertling et al. (2006), demonstrated that both naturally and artificially patinated roofs have high variability in copper exports during storm events depending on: rain pH, dry and wet periods, wind speed and directions, intensity and timing of rain. The median copper export concentration was 3,200 $\mu\text{g/L}$ with a range of 850-18,000 $\mu\text{g/L}$. Another study portrayed similar results where a newly installed copper roof had copper exports ranging from 800-8,000 $\mu\text{g/L}$, and an older roof of similar composition had copper exports ranging from 800-4,000 $\mu\text{g/L}$ (Pennington and Brown 2016). In comparison, traditional asphalt-shingle roofs embedded with copper granules for algal growth resistance export on average 160 $\mu\text{g/L}$ during storm events (Velleux et al. 2012). Elevated copper concentrations in waterways from various sources, including roofing materials, are linked to a host of adverse effects on biota.

Effects of Copper from Stormwater

Over the past decade, heightened concerns about copper and other dissolved metals have been raised. Dissolved metals can cause a wide variety of sub-lethal and lethal effects at extremely low concentrations $\mu\text{g/L}$ (ppb) (Sanudo-Wilhelmy et al. 2002). The toxicities and effects of trace metals (e.g., copper, zinc, lead, cadmium, silver, and gold) vary drastically, so the effects of each individual metal must be fully understood in order to combat potentially harmful effects.

Of particular concern in the Pacific Northwest is the decline in salmonid populations. Salmonids are historically, economically, and socially important species and

their declining populations have regulators and conservationists concerned. Copper is of concern its ability to alter the sensory capacity and behavior of a wide variety of aquatic organisms including salmonid populations (Norton et al., 2011). Studies have demonstrated that low ppb copper concentrations adversely affect the sensory ability of salmonid populations, in particular, their olfactory neurophysiology responses (Baldwin et al. 2003; Erickson et al. 1996; Meyer and Adams 2010; Sandahl et al. 2004). These concerns have prompted regulators to phase out copper brake pads and additional regulations prohibiting other copper sources like copper roofing material will likely follow.

Aqueous Copper Toxicity

Mechanism of Toxicity

Copper can produce both sub-lethal and lethal effects in aquatic organisms at low ppb concentrations. The mechanism by which copper causes effects is through an interaction with the biotic ligand. For aquatic organisms, the biotic ligands for metal binding are various active ion uptake and transport pathways (Niyogi and Wood 2004). These active ion pathways have specific metal binding affinities ($\log K$) and capacities (B_{\max}) that can be quantified for metal-pathway interactions. In general, the active ion transporters have significantly higher binding affinities for trace metals (e.g., copper, cadmium, zinc, lead) than more environmentally abundant metals (calcium, magnesium, sodium, and potassium). As these active ion transporters bind trace metals, they become less available for essential ion transport processes. The inhibition of these processes are likely the cause of acute mortality at high metal concentrations, however even at low concentrations the inhibition of these processes can cause a range of sub-lethal effects (Baldwin et al. 2003). The binding affinities of metals to the gill surface provides a good

predictive analysis of the overall toxicity of the metal. As the binding affinity increases (log K increases), the copper 96-h LC₅₀ tends to decrease. So the higher the ability of a metal to bind to the gill surface, the lower the metal concentration needed to cause mortality (Niyogi and Wood 2004). For example, copper (Cu²⁺) the environmentally prevalent form, binds with the sodium (Na⁺) transporter causing sodium deficiencies in organisms (Niyogi and Wood 2004). Copper's binding affinity (7.4 - 8.0) is significantly higher for the sodium active transporter than sodium (2.3 - 3.2) itself. As a result, aquatic organisms exposed to copper tend to exhibit issues with sodium, potassium, and chloride deficiencies as these ion transporters no longer function properly (Niyogi and Wood 2004).

It has been well documented that olfactory functions within salmonid populations are essential for feeding, migration, and reproduction processes; including the successful navigation to natal streams for yearly spawns (Hasler and Wisby 1951). As the olfactory nervous system becomes impaired, salmonids can no longer actively avoid further copper exposure (Baldwin et al. 2003). Sandahl et al. showed that copper concentrations of 5 - 20 µg/L has a significant inhibitory effect on the olfactory response of juvenile Coho salmon (Sandahl et al. 2004). Baldwin et al. portray similar results where the olfactory nervous system of juvenile Coho salmon was substantially impaired from copper exposures from 1 - 20 µg/L, which "manifest itself on a time scale of minutes" and "may be weeks before the functional properties of the olfactory system recover" (Baldwin et al. 2003). Copper concentrations may not be the sole source of toxicity, but it becomes apparent that limiting the influx of copper to the environment is advisable. Spromberg et al. (2016) found that salmonid mortality from untreated urban runoff could not be successfully reproduced when exposing salmonids to similar copper concentrations that resembled the chemical composition of urban stormwater. This study suggests that the copper concentrations itself

may not be the sole source of toxicity, but rather a result of the whole effluent chemical composition itself (Spromberg et al. 2016).

Factors Affecting Copper Toxicity and Bioavailability

The toxicity of copper in aquatic systems can be drastically altered by other water quality parameters including: pH, hardness, and dissolved organic matter. The water quality of an aquatic system can greatly increase or decrease the ability of copper to bind to the gill surface and ultimately cause toxicological effects.

The pH of an aquatic system has a significant effect on the ability of copper to bind to an organisms' biotic ligand. In general, as the pH of a system increases (more basic), the toxicity of metals, like copper, tends to decrease. As the pH increases, ligands like carbonates, bicarbonates, sulfates, and hydroxides tend to be deprotonated and available for metal binding. These ligands when deprotonated tend to have higher binding affinities for metals compared to the biotic ligands. These ligands can form complexes with the metals, sequestering them into a less bioavailable forms that is significantly less toxic. These metal-ligand formations are relatively stable and do not readily leach back into solution, unless the pH decreases. If a lower amount of copper ions can bind with the biotic ligand than the overall bioavailability decreases as does the potential toxicological effects. Erickson et al. (1996) found that the copper 96-hr LC₅₀ copper toxicity for fathead minnows ranged from 0.1 μM (6.3 ppb) when the pH was 6.5 to nearly 2 μM (127 ppb) pH was increased to 9.

The hardness of an aquatic system can also affect the toxicity and bioavailability of copper to aquatic organisms. Hardness is defined as the summation of the equivalents of divalent cations, primarily calcium and magnesium concentrations in natural waters. These cations can compete for binding on the biotic ligand and limit the potential toxicological effects. These cations tend to have significantly lower binding affinities for the biotic ligand

compared to copper, but these cations also are present at higher concentrations aquatic systems. As hardness increases the overall toxicity of copper tends to decrease. Hardness can also alter the ligands available for binding metals as magnesium and calcium will readily bind to ligands like chloride, carbonate, and bicarbonate. However, copper also tends to have higher binding affinities for these ligands compared to these more abundant environmental cations. Overall, it is a dynamic equilibrium as metals and environmental cations compete for binding to dissolved ligands in solution and to the biotic ligand.

Erickson et al. (1996) observed that as hardness increased from 1 to 4 meq/L the 96-h LC₅₀ increased from 1.5 (95.2 ppb) to 3.75 (238 ppb) μ M copper.

The amount of dissolved organic matter (DOM) in an aquatic system is significant in the overall toxicity of copper to aquatic organisms. DOM usually consists of large organic acids, like fulvic and humic acids, made from the decomposition of plant materials. DOM limits the toxicological effects of metals by providing favorable binding sites for metal binding rather than the metal binding to the biotic ligand (Erickson et al. 1996; McIntyre et al. 2015; Trenouth and Gharabaghi 2015). These binding sites tend to be organic functional groups (e.g., hydroxyls, carboxyls, and carboxylates) that when deprotonated have high affinities for metal binding. The Cu-DOM complex tends to reduce bioavailability due to the complex not being able to cross the organisms' membrane due to large molecular size. As the dissolved organic carbon (DOC), a measure of DOM concentrations, increases from 0 - 5 mg/L, the 96-hr LC₅₀ for fathead minnows increased from about 1.5 (95 ppb) to 7 (445 ppb) μ M copper (Erickson et al. 1996). The DOM concentration tends to have the largest effect on the bioavailability of copper in an aquatic system. In any aquatic system, there is a dynamic equilibrium that must be fully understood

to predict the potential toxicological effects that toxicants like copper will have on organisms.

Quantifying Toxicity using the Biotic Ligand Model (BLM)

Determining the potential toxicity that metals may cause in an aquatic system may be extremely difficult due to the multitude of variables that impact bioavailability and overall toxicity. To combat and solve these issues, models have been developed to simulate how water quality parameters like pH, alkalinity, DOC, and major ions will affect the toxicity of copper, and other metals, in aquatic systems. The Biotic Ligand Model (BLM) was formulated to be a chemical equilibrium model that predicts potential toxicological effects of metals in solution, accounting for the known effects of water chemistry and the physiology of various test organisms (Paquin et al. 2002). The fundamental idea behind the BLM is that by analyzing the effects water chemistry has on metal binding to an organism and knowing the physiological response organisms have to metal concentrations in an aquatic environment, the model can provide quantitative results for the toxicity of copper exposure or provide regulatory endpoints for water bodies (Figure 2).

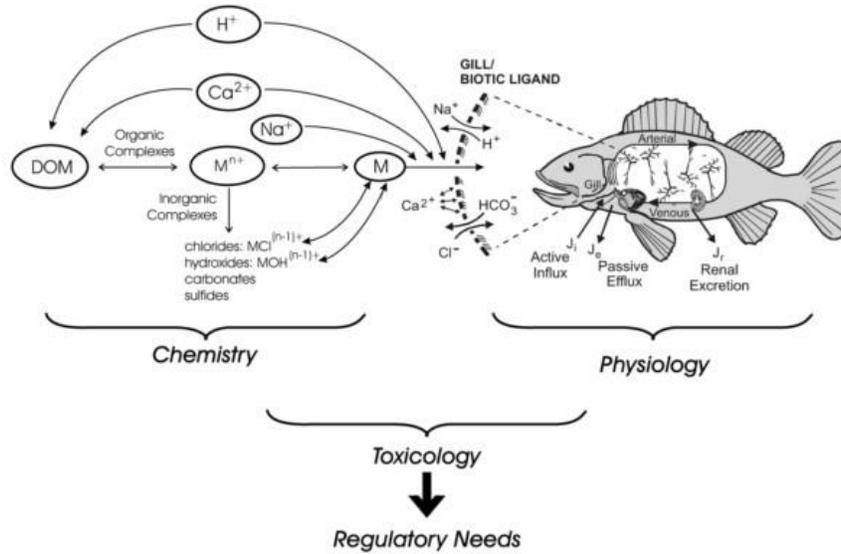


Figure 2. Schematic representation of the Biotic Ligand Model (BLM) showing the interfaces between water chemistry, organism physiology, and toxicology. (Paquin et al., 2002).

The BLM uses a mass balance equation to predict metal binding potential to the biotic ligand and eventually the overall toxicological effect a specific metal will have on an organism in an aquatic system:

$$[L_b^-]_T = [L_b^-] + [HL_b] + \sum_{i=1}^{NM_i} [M_iL_b^+]$$

"where $[L_b^-]_T$ is the total binding site density of the biotic ligand (e.g., nmol of available sites/g of tissue), $[HL_b]$ is the concentration of protonated sites, NM_i is the number of metal complexes $[M_iL_b^+]$ (e.g., CuL^+ CaL^+ , etc.) that form with the biotic ligand $[L_b^-]$ “ (Di Toro et al. 2001). The model then uses these calculations to provide toxicological predictions that can be utilized from a regulatory standpoint.

The BLM provides predictions for acute (criterion maximum concentration) and chronic (criterion continuous concentration) water quality criteria and lethal concentration to 50% of a population (LC_{50}) for specified water bodies with known water chemistry

parameters and various organisms (Niyogi and Wood 2004). In addition, the BLM can calculate the potential toxicity to an organism of a known copper exposure in an aquatic system with known water chemistry through the predicted final acute value (FAV). The predictive ability of the BLM allows for site-specific copper and other metal ion regulations, rather than general regulations for all water bodies. Due to the flexibility and adaptability of the model, it has been adopted by the Environmental Protection Agency (EPA) and is the current basis for water quality criteria for copper.

SCMs for Remediation of Copper Removal from Roofing Runoff

In the past few decades, the application and complexity of stormwater control measures has grown substantially. Initially, stormwater control measures were developed to protect against potential flooding; however, in recent years, stormwater control measures have focused on altering the quality of stormwater (Roy-Poirier et al. 2010). SCMs tend to adopt two main principles: low-cost development (LCD) and low-impact design (LID) (Dietz 2007). LID initiatives have been adopted as a mechanism to control and treat stormwater, while limiting the disturbance and reducing impact to "soils, vegetation, and aquatic system on site"(Dietz 2007). Another primary focus is to mitigate stormwater as close to the source as possible, rather than treating stormwater at wastewater treatment plants or the receiving waters themselves (Davis 2008). The primary mechanisms utilized by LID/LCD processes are increasing infiltration of stormwater and enhancing stormwater water quality by removing pollutants using adsorption, biological, and filtration processes (Ahiablame et al., 2012). There have been a multitude of structural designs implemented to institute the principles of LCD/LID into practice, including bioretention systems.

Bioretention systems are one of the primary structural designs used to adhere to the LCD/LID principles the majority of stormwater control practitioners are adopting (Figure 3). Bioretention systems tend to be relatively small areas that are depressed compared to the surrounding topography and that allow for infiltration and maximum contact time for stormwater. These areas are typically fitted with an underdrain in a permeable gravel layer that promotes water drainage to prevent flooding in the structure itself, filled with organic-rich highly permeable soil allow for infiltration and pollutant attenuation, and then planted with native, terrestrial vegetation to promote further pollutant removal and water retention (Roy-Poirier et al. 2010). These bioretention systems are designed to mimic natural environments, like micro-wetlands, in an attempt to process and treat stormwater from an urbanized area (Dietz 2007).

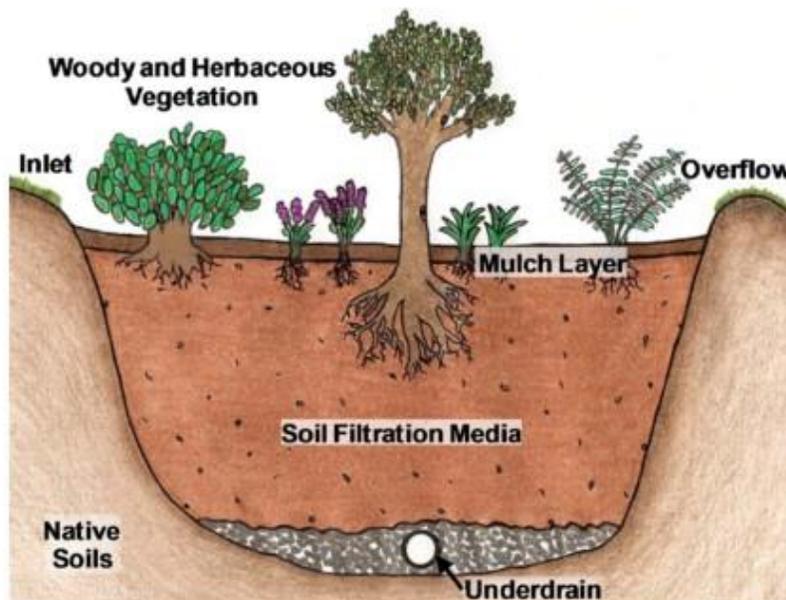


Figure 3. A cross-section view of a schematic representation of a typical bioretention system. Typical structural layout of a bioretention system would contain: a gravel-laden bottom with an underdrain, high permeability soil filtration media, and native vegetation planted throughout. (Roy-Poirier et al., 2010).

There has been substantial research performed on the effectiveness of bioretention systems for both maintaining natural hydrological processes, but also pollutant removal in

urbanized stormwater management settings. Davis et al. (2008) observed that bioretention systems, similar in design to Figure 3, were able to reduce peak stormwater flows from an asphalt parking lot from 44 - 63% with nearly 18% of storm events not producing outflow from the underdrain demonstrating that the entire storm content is captured within the bioretention structure. Other studies have conveyed similar results with peak flow reductions anywhere from 40 - 97% in bioretention systems where the length and magnitude of storm having a significant effect (Ahiablame et al., 2012}. Short, high magnitude events typical of summer thunderstorms tended to have lower reductions of peak flows; whereas, areas of long-low magnitude storms tended to have higher reductions in peak flows (Roy-Poirier et al. 2010). Bioretention systems also reduce the total suspended solids (TSS), nutrients (e.g, nitrogen and phosphorus), and trace metal concentrations (e.g., lead, zinc, copper), and organic contaminants like polyaromatic hydrocarbons (PAHs) (Dietz 2007; Kim, Seagren, and Davis 2000; Sun and Davis 2007; Zhang et al. 2013). Metal removal (from 30 - 99%) by bioretention structures is highly dependent on the media utilized within the bioretention structure itself. Zhang et al. (2009) demonstrated that the addition of fly ash to the media in bioretention structures can substantially increase the metal attenuation capability of the system.

All of these studies demonstrate that bioretention systems can greatly alter the stormwater dynamics in urban and suburban environments and bioretention systems can be utilized in specific situation to treat potentially polluted stormwater. Due to the efficiency and flexibility of bioretention system, they may be utilized to attenuate copper in stormwater runoff from copper roofing materials to reduce the bioavailability and toxicity of runoff from copper roofing materials.

Chapter 2: Attenuation of Copper in Soils and Commercially Available Soil Amendments

Mechanisms for Copper Attenuation in Soils and Soil Amendments

The composition of media in bioretention structures greatly influences the ability of the bioretention structures to attenuate contaminants like copper. The media within bioretention structures, usually a combination of various types of soils and amendments, can attenuate contaminants through a variety of mechanisms. All of these attenuation mechanisms decrease the overall toxicity of a contaminant by reducing the copper bioavailability either on a temporary or permanent basis (Figure 4). The addition of amendments to the media formulations within bioretention structures may decrease the toxicological effects of copper entering the environment by increasing the attenuation through adsorption, precipitation, and/or absorption.

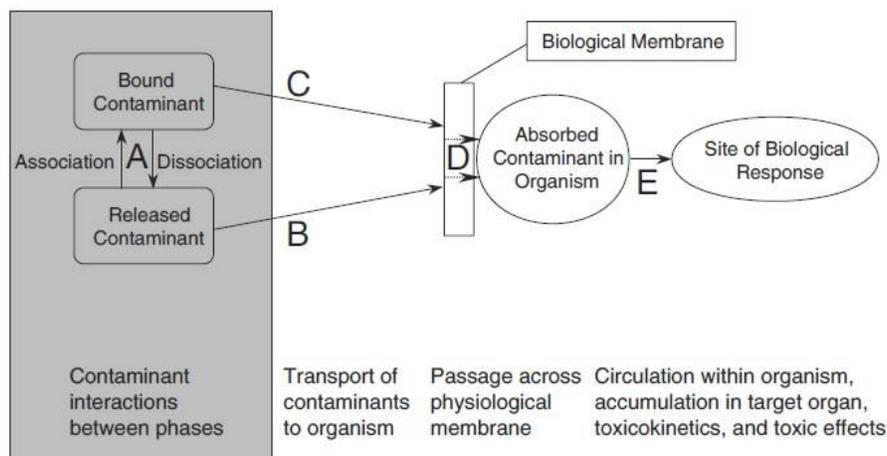


Figure 4. Schematic of Bioavailability of a Contaminant in Soils and Sediments. The attenuation of contaminants that occurs within the media of bioretention structures occurs in Grey highlighted portion of schematic. (National Research Council, 2003)

Adsorption

Contaminant adsorption to soil, sediment, and amendment surfaces is one mechanism to decrease the bioavailability of a contaminant. Adsorption is defined as, "the binding of an ion or small molecule to a surface at an isolated site - a two dimensional surface complex that can be electrostatic, chemical, or hydrophobic" (National Research Council 2003). Copper can adsorb to a surface through both chemical and electrostatic interactions governed by pH. Copper (Cu^{2+}) at most environmental conditions, can electrostatically bind with negatively charged surfaces of dissolved organic matter (DOM), aluminosilicate clays, and mineral oxides. These electrostatic bonds, called outer-sphere complexation, are weak and can be easily displaced by other ions. The exchangeability of ions on a surface is dictated by the ionic charge and ion size with binding strength increasing with decreasing ionic size and increasing charge (National Research Council 2003). Copper has one of the highest binding affinities based on ionic charge and ionic size compared to other transition metals, as stated by the Irving-Williams series (Sposito 2008). As a result, copper (Cu^{2+}) readily adsorbs to the surface of negatively charged substrates and is not readily exchanged with other metals unless present at substantially higher concentrations. Alkali and alkali earth metals compete for binding sites relatively poorly compared to transition metals; however, due to their higher concentrations, can out compete transition metals for binding sites. The ability of a soil to facilitate cation exchange is called the "cation exchange capacity" (CEC) and soils have variable values depending on functional groups, surface area, and molecular structure (Sposito 2008).

Another type of adsorption reaction involves a chemical interaction. Dissolved organic matter (DOM) contains functional groups that facilitate chemical adsorption including: carboxyls (RCOO^-), hydroxyl (RO^-), and carbonyl (RCO) (Sposito 2008). These functional groups can chemically bind (Cu^{2+}) greatly reducing bioavailability. Both electrostatic and chemical adsorption are highly reliant on pH (National Research Council 2003). Both electrostatic and chemical adsorption require negatively charged surfaces, as deprotonated functional groups or negatively charged surfaces. The pH affects the H^+ concentration with increasing H^+ ions as pH decreases (more acidic) and decreasing H^+ ions as pH increases (more basic). Under acidic conditions, the increased presence of H^+ ions prevents electrostatic binding by copper ions as the majority of negatively charged sites present for binding are occupied by H^+ ions. Also, under acidic conditions, functional groups like carboxyls and hydroxyls are protonated and neutrally charged and not available for Cu binding. Under basic conditions, there is a higher affinity for adsorption of copper ions either electrostatically or chemically (National Research Council 2003).

Precipitation and Complexation

Precipitation reactions occurring between contaminants and dissolved anions or ligands, present from soil dissolution are another mechanism by which bio-retention structures decrease the bioavailability of a contaminant. Precipitation reactions are more prevalent when contaminant concentrations are high, as seen copper roofing runoff. The most important precipitates that occur within soil solutions include: hydroxides, oxyhydroxides, carbonates, and sulfides (Evans 1989). The extent of precipitation is

dependent upon the solubility product and the activity of the constituent ions forming the precipitate in solution using the following equation:

$$K_{sp} = [Me^+]^A [L^-]^B$$

where [Me] is the concentration of metal in solution, [L] is the concentration of the ligand in solution, A is the molar coefficient of the metal, and B is the molar coefficient of the ligand. If the product of the activities of the constituent ions (L and Me) is greater than the K_{sp} for that compound, then a precipitate will form and if the product of the activities of the constituent ions (L and Me) activity is less than the K_{sp} for that compound, then a precipitate will not form. The formation of precipitates can reduce the metal bioavailability in solution, if they remain as precipitates.

Copper hydroxide ($Cu(OH)_2$) and copper sulfide (CuS) are the two primary precipitates that are likely to form in bioretention structures receiving copper roof runoff. The formation of copper hydroxide is mediated by the solubility product equation, where the product of $[Cu^{2+}]$ and $[OH^-]^2$ must be greater than the K_{sp} for $(Cu(OH)_2)$ for a precipitate to form. As a result, the formation of copper hydroxide is largely dependent on the pH conditions with higher pH conditions providing the needed concentration of hydroxide anions for precipitate formation (Evans 1989). The formation of copper sulfides is not entirely mediated by the solubility product equation, but also dependent on the partial pressure of sulfide gas in the soil (Evans 1989). The formation of hydrogen sulfide gas (H_2S) occurs only in anoxic conditions where bacteria reduce sulfate anions (SO_4^{2-}) into hydrogen sulfide gas (Evans 1989). This is likely to occur in bioretention structures, especially over longer time frames, as the soil becomes depleted in oxygen so anoxic conditions exist.

The complexation of copper ions by inorganic ligands can reduce the bioavailability of copper ions in soils (Santore et al. 2001). Copper readily forms a variety of inorganic complexes (sulfates, hydroxides, carbonates, chlorides, and bicarbonates) in solution depending on the pH and concentration of these inorganic ligands in the surrounding environment. Copper can form aqueous complexes with all of which are less bioavailable than the free copper ion (Niyogi and Wood 2004). Soil amendments leach these inorganic ligands into solution at heightened concentrations promoting complexation and decreasing copper's bioavailability. Precipitation and complexation mechanisms are not quantified during this study, but should provide additional copper attenuation in bioretention media.

Physical Absorption

Absorption is defined as "the uptake of a species within another materials, similar to how a sponge soaks up water" (National Research Council 2003). The process of physical absorption occurs over a longer time frame where metal ions become incorporated into the lattice structure of soils reducing their bioavailability. There are two main mechanisms of absorption processes occurring within soils, intraparticle surface diffusion and occlusion. Intraparticle surface diffusion can be described as the process by which amorphous minerals absorb metal ions through rapid adsorption to the surface and slow adsorption along micropores (Figure 5). There are three primary hydrous amorphous oxides which undergo intraparticle surface diffusion: iron, aluminum and manganese (Axe and Trivedi 2002). All of these hydrous amorphous oxides exist as metastable minerals, meaning that these minerals are at a higher energy state than the stable state but must overcome an activation energy barrier to achieve stability. This process of achieving

stability can occur slowly over long time periods (most environmental applications) or with sudden changes in temperature and pressure (Axe and Trivedi 2002). During the metastability phase, these hydrous amorphous oxides can readily adsorb metals which then become incorporated into the crystalline structure (Axe and Trivedi 2002). Some studies have shown that these "aging" processes through surface diffusion into hydrous amorphous oxides may account for 40-60% of metal retention in soils over an extended time frame, and the metal retention increases as age increases (Axe and Trivedi 2002; Scheckel et al. 2000).

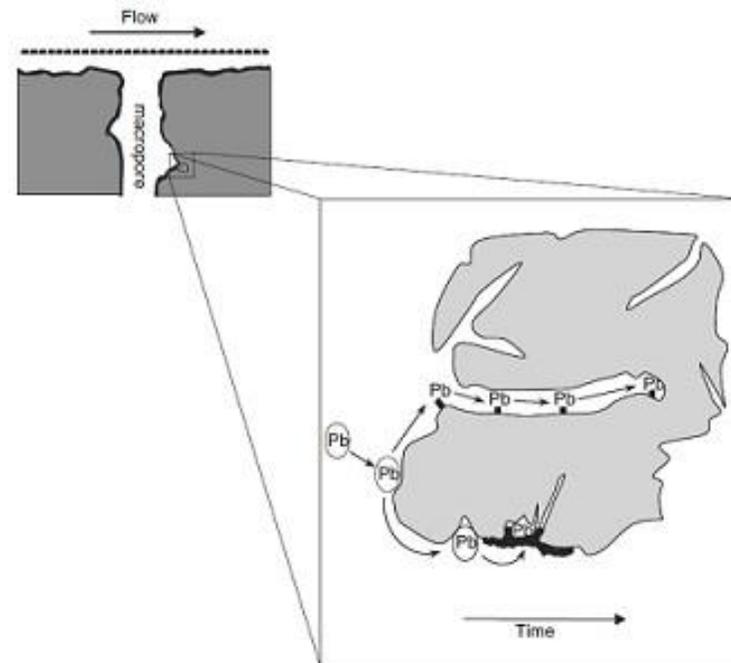


Figure 5. Depiction of physical absorption process over time using lead as an example. The upper pathway demonstrates the migration of metal ions and intra-particle surface diffusion. The lower pathway demonstrates occlusion (National Research Council, 2003)

Occlusion is another mechanism of absorption that can occur within soil (National Research Council 2003). The process of occlusion occurs when metal ion migrate into micropores of soils through surface adsorption over time. As these metals migrate, other

minerals and organic matter can precipitate onto the surface of these micropores, sequestering the metals within these micropores (Figure 5). The process of occlusion is not as prominent as intraparticle surface diffusion, and more difficult to model and predict, but occlusion still can play a role in metal attenuating and sequestration.

Commercially Available Soil Amendments

Altering the media within bioretention structures through the use of soil amendments has been shown to increase metal attenuation from various sources. Due to the planned application of these control methods, soil amendments selected were commercially available at a relatively low-cost. In theory, the soil amendments would be added to the bioretention media to achieve copper runoff concentrations consistently $< 14 \mu\text{g L}^{-1}$. This would allow for the adoption of these bioretention structures at feasible costs while still decreasing the amount of copper entering the environment. Biochar, zeolite, and greensand were selected due to high cation exchange capacity and availability at a low cost across the United States.

Biochar

Biochar has recently become one of the most researched and favored soil amendments utilized for various agriculture, commercial, and remediation purposes. Biochar is a form of black carbon which can be synthesized by the slow/fast pyrolysis and gasification of biomass (Uchimiya, Klasson, et al. 2011). The pyrolysis temperature and gasification process greatly alters the properties of the resulting biochar, but virtually all biochars readily attenuate pollutants, such as trace metals (Uchimiya, Klasson, et al. 2011). In general, biochar has a high pH value, high cation exchange capacity (CEC), an

overall microporous structure, and numerous active functional sites for pollutant binding (Jiang et al. 2012; Zhang et al. 2013).

There are four main mechanisms by which biochar attenuates trace metals and reduce their bioavailability: cation release, functional group complexation, physical adsorption, and surface precipitation (Zhang et al. 2013). Biochar promotes trace metal exchange with Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and other cations and inner-sphere complexation with the humic and mineral oxide derivatives present in the structure of biochar (Zhang et al. 2013). Also, biochar contains numerous functional groups including carboxylic acids and hydroxides which when deprotonated can readily complex metals (Zhang et al. 2013). Finally, the microporous structure of biochar provides the ability to physically absorb metals and the phosphate and carbonate groups can provide sites for salt formation with trace metals (Zhang et al. 2013).

Biochar studies have shown that soils amendments with biochar tend to have a higher ability to attenuate copper compared to the soil alone. Norfolk and San Joaquin soil amended with biochar showed increased copper attenuation (Uchimiya, Wartelle, et al. 2011). Additionally, biochars synthesized under various pyrolysis temperatures and can affect this attenuation ability. Zhang et al. showed similar results, where the removal of trace metals like cadmium and copper was between 79.6 - 90% (Zhang et al. 2013). These studies suggest that biochar can potentially increase the performance and efficiency of copper removal from stormwater.

Zeolite

Zeolite is available in both natural and synthetic forms. Zeolites are alkaline, microporous aluminosilicate minerals with a three-dimensional framework and an overall

negative charge that can readily be neutralized through the introduction of exchangeable cations (Shi et al. 2009). Zeolites contain a tetrahedral framework of silicate $[\text{SiO}_4]^{-4}$ and aluminosilicate $[\text{AlO}_4]^{-5}$ which when substituted, impart the overall negative charge and allows for cation exchange (Mozgawa and Bajda 2006). Zeolites are applicable for trace metal attenuation due to increasing soil pH, microporous structure, and high CEC.

Zeolites utilize three mechanisms to attenuate trace metals: increasing soil pH, precipitation of metals, and cation exchange. Zeolites readily leach anions into solution that can precipitate trace metals. Also, zeolites increase the soil pH by exchanging H^+ ions from the bulk soil solution onto the zeolite surface resulting in a lower concentration of H^+ in the bulk soil solution increasing cation exchange and copper attenuation (Shi et al. 2009). Finally, the substitution of silicon and aluminum in the aluminosilicate tetrahedrons provides a high CEC, especially when the micropores are large enough to allow for passage of trace metals. Zeolite can have up to 5 meq/g of CEC (Shi et al. 2009).

Studies have demonstrated zeolite's ability for trace metal attenuation (Ma et al. 2006; Reddy, Xie, and Dastgheibi 2014b; Shi et al. 2009; Wang et al. 2016). Reddy et al (2014) showed that zeolite as a filter material for removal of trace metals from urban stormwater runoff was able to attenuate 97.9 - 99% of copper. There was not an evident decrease in attenuation percentage when copper concentrations in the runoff increased. Other studies portray similar results for zeolite's ability to attenuate trace metals and demonstrate why zeolite could be utilized as a soil amendment to increase copper attenuating from copper roofing material.

Greensand

Greensand is mostly comprised of glauconite; a clay mineral occurring naturally across the East Coast of the United States $((K,Na)(Fe^{3+}Al,Mg)_2(Si,Al)_4O_{10}(OH)_2)$ (Heckman and Tedrow 2004). Glauconite is utilized as a soil amendment to promote water retention, increase potassium and magnesium concentrations, and loosen clay-based soils. Glauconite, unlike many other clay minerals, exists as sand-sized particles, which results in a larger surface area for cation exchange (Heckman and Tedrow 2004). These micropores allow for heightened water-holding capacity, as well as, high CEC due to increased surface area for cation exchange (Heckman and Tedrow 2004). Research has shown that greensand can readily attenuate a wide variety of trace metals (cadmium, lead, copper, zinc) and other pollutants (Heckman and Tedrow 2004).

Greensand facilitates trace metal attenuation using similar mechanisms as both zeolite and biochar. The glauconite contains functional groups with high binding affinities for metals (Franus and Bandura 2014). The microporous structure of greensand contains sites allowing for the physical adsorption of trace metals. Finally, greensand facilitates an increase in soil and solution pH which prompts the precipitation of metal-hydroxides in solution (Franus and Bandura 2014). Franus et al. demonstrated that the sorption capacity of glauconite for metals ranges from 9.12 mg/g for lead to 2.96 mg/g for copper. These values are within the range of other natural media materials and justify the use of greensand as a potential soil amendment for enhanced copper removal in bioretention system (Hao et al., 1987; Smith et al. 1996). Greensand has been demonstrated to readily attenuate trace metals, allowing greensand to be an ideal candidate for use as a soil amendment for copper removal from copper roofing runoff.

Soil Amendment Selection

The three soil amendments described are ideal candidates for inclusion in this study due to high affinities for attenuating of trace metals, and commercial availability at low costs to maintain the LCD and LID directives. These soil amendments' abilities to attenuate metals vary depending on environmental conditions including: ionic strength of solution, pH of soil and solution, initial concentration of metal, characteristics of overlaying or mixed soil, and initial characteristics of the soil amendment (Franus and Bandura 2014; Shi et al. 2009; Zhang et al. 2013). These unknowns coupled with soil amendments not previously being tested under conditions where the initial metal concentration regularly exceeds $1,087 \mu\text{g L}^{-1}$ (LaBarre et al. 2016) and as high as $7,000 \mu\text{g L}^{-1}$ (Pennington and Brown 2016) prompted further research. This thesis will evaluate how each of these soil amendments perform under the specific conditions which would be present from copper roofing runoff, in an attempt to determine which amendment would be best utilized in a field setting.

Hypotheses and Goals

The inclusion of these soil amendments is likely to increase the copper attenuation in bioretention structures, but it must be determined which amendment best attenuates copper while remaining as only a small fraction of the overall bioretention media formulation. The overall goal of this thesis is to determine which amendment(s) most efficiently attenuates copper in a laboratory environment designed to simulate copper roofing runoff, then institute that amendment in a previously established field copper roof environment to determine if the chosen amendment can attenuate copper to achieve

effluent concentrations consistently $<14 \mu\text{g L}^{-1}$. To achieve these goals and effectively evaluate the hypothesis, the following questions must be answered:

1. Which soil amendment most effectively attenuates copper from synthetic stormwater designed to mimic copper roof runoff?
2. Does the soil amendment function most effectively as an admixture or as an underlaying layer?
3. Does the volume ratio of soil amendment effect the copper attenuation?
4. How does the soil amendment perform in a field environment?
5. Can this soil amendment consistently achieve effluent copper concentrations $<14 \mu\text{g L}^{-1}$?
6. Can this soil amendment be incorporated into bioretention structures while maintaining LID and LCD designs?

Questions 1, 2, and 3 were answered through a series of laboratory column studies to determine how effectively the chosen soil amendments could attenuate copper in a controlled environment (Chapter 3). The laboratory column studies were designed to address the effectiveness of the amendment in general, but also, the most effective design use of these amendments whether mixed throughout the bioretention media or as a separate layer underneath. After these laboratory column studies were completed, a chosen soil amendment was incorporated into a pre-established copper roofing field study, in order to address and answer questions 4, 5, and 6 (Chapter 4). The field study will determine how efficiently and effectively the chosen soil amendment formulation will perform in a bioretention field study both compared to control and results from a previous field study. The overall goal of both the laboratory and field studies will be to

determine if a soil amendment when added to bioretention media will consistently decrease copper concentration in copper roofing runoff below the potential effluent maximum of $< 14 \mu\text{g L}^{-1}$.

Chapter 3: Evaluating Soil Amendments for Cu Removal in Bioretention Media

Introduction

To evaluate the three selected soil amendments: biochar, greensand, and zeolite, on their ability to attenuate copper column studies were performed starting in October 2015 and concluding in December of 2016. There were three distinct studies performed: a pilot study, an extended duration study, and a half media volume column study. A pilot study conducted in early October 2015 began the investigation into the applicability of various commercially available soil amendments to attenuate copper from stormwater run-off. The column study are designed to determine the efficiency of each soil amendment at attenuating copper from synthetic stormwater to simulate copper roofing runoff. Multiple soil amendments were tested over a short duration exposure to synthetic stormwater spiked with copper. The Extended Duration Studies were a more in-depth evaluation of each soil amendment and formulation type (admixture vs. under-layer) to determine which amendment-formulations were most effective at not only attenuating copper, but also, reducing the potential toxicity of copper remaining in column effluents. Finally, the Half Media Selected Column Study was performed to further elucidate the most effective amendment formulation when exposed to more strenuous conditions compared to the Extended Duration Column Studies. The Half Media Selected Column Study was conducted to provide further support and allow for the definitive ability to choose a single soil amendment and treatment type for use in the field. The organization and methodology utilized throughout these three column studies provided evidence for the selection of a single amendment formulation for incorporation into a field study. Additionally, the media components were characterized to provide a better understanding

of the factors that can affect the medias' ability to attenuate copper in a bioretention setting. The characterization of the media and soil amendments consisted of five components: particle size distribution, cation exchange capacity (CEC), total organic carbon (TOC) content, leachable copper content, and pH.

In this chapter, the analytical methods utilized for the laboratory column studies will be discussed at length, as similar methods were used for all three column studies. The Methods and Results for the media characterization and each of the three column follow. Finally, the results from each aspect of the laboratory evaluation will be discussed, in context of, the potential ability of the amendment formulation to attenuate copper from copper roofing runoff. The discussion will be focused on how and why the selected soil amendment formulation was chosen for use in the field study.

Materials and Methods

Analytical Methods

The analytical methods for the quantification of both copper and major ion concentrations in column effluents remained consistent throughout all three column studies. For each column study, the effluents were collected and transferred into 50 mL centrifuge tubes for later analysis. For Inductively Coupled Plasma Mass Spectrometer (ICP-MS) analysis of copper concentrations the following procedure was conducted for all analyses utilizing a Thermo Elemental VG PQ Excell ICP-MS with an ASX-520 HS Auto-sampler. For each sample, 10 mL was transferred to a 50 mL centrifuge tube and 300 μ L of 7 N HNO₃ was added, then the sample was agitated on a shaker table for 5 minutes. Each sample was then filtered using a 0.45 μ m syringe filter into a separate 25 mL centrifuge tube and then a 5 mL aliquot of the filtrate was collected using a 5 mL

pipette. Finally, 50 μL of 100 ppb In solution in 2% HNO_3 was added to each sample to serve as a 1 ppb In internal standard for ICP-MS analysis. For every ten samples, a duplicate was analyzed along with the samples for QA/QC; additionally, a standard reference material (SRM) 2709a (San Joaquin Soil; NIST) was analyzed as a check standard at least twice every run during all ICP-MS analyses to ensure proper calibration and accuracy. The calibration for each ICP-MS analysis consisted of a two tiered calibration. The calibrations standards were the following concentrations: 1 ppb, 5 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb, 200 ppb, and 400 ppb with each standard being made in 2 % HNO_3 with 1 ppb In internal standard. Since the concentrations of the synthetic stormwater were significantly higher compared to the column effluents, and since column effluents were routinely below 20 ppb, two separate calibration curves were utilized for the synthetic stormwaters and column effluents. The low copper concentration calibration curve excluded the 200 and 400 ppb standards, while the high copper concentration standards excluded the 1 and 5 ppb standards. The low copper concentration calibration curve was utilized to calculate the copper concentration in the column effluents, while the high copper concentration calibration curve was used to calculate the copper concentration in the synthetic stormwaters. Each ICP-MS analysis was checked for QA/QC using the In internal standard concentration, duplicate unknowns, and SRM; if any of these were not within reasonable limits (1 ± 0.2 ppb In, <10% difference in duplicates, and > 80% recovery for Cu in SRM) then analysis was determined to be unacceptable and new sub-sample was prepared and analyzed.

For all Ion Chromatography (IC) analysis, a Dionex ICS-500 Ion Chromatograph equipped with DIONEX Autosampler was utilized. Each sample and standard was filtered into a plastic vial using a 0.45 µm syringe filter. A separate calibration curve was used for cations and anions consisting of the following concentrations: 1, 5, 10, 50, 100 and 200 ppm (cations) 1, 5, 10, 25, and 50 ppm (anions). For all IC analyses, a duplicate sample was conducted for every ten samples and a check standard for both cations and anions was included in every IC analysis set. The results were analyzed for QA/QC using the duplicate and check standard for every IC run with an acceptable range of < 10% difference in duplicates and >80% recovery in check standard concentrations for all cations and anions.

Characterization of Media

The particle size distribution analysis was performed for the standard bioretention media and soil amendments. This was done utilizing USA Standard soil sieves and ASTM D421 methodology. USA Standard soil sieves numbers 3/8, 4, 10, 40, 100, and 200 were placed onto a W.S. Tyler Ro-Tap Sieve Shaker and 1000 g, 500 g, or 250 g of media was added to the top of the sieve stack depending upon the density of the media. For example, 250 g of biochar was used rather than 500 g or 100 g due to the extremely low density of biochar compared to the standard media and other soil amendments. The sieves were allowed to shake for 5 minutes, and the contents within each sieve were measured. This process was repeated at least three times for each media and soil amendment and the percentage of particles by weight in each sieve was calculated and averaged for each. The averages for each were plotted on a particle size distribution plot.

Cation exchange capacity analysis was performed for the standard bioretention media and soil amendments following the simple barium chloride extraction procedure outlined in (Hendershot and Duquette 1985). Approximately 5.00 g of the media and soil amendments were added to a centrifuge tube, washed, and shaken overnight with a 0.100 M BaCl₂ solution. The solution was centrifuged and the mass of the supernatant was measured and collected. Each sample was then washed with a 0.500 M MgCl₂ solution, shaken for two hours, centrifuged, and then the supernatant mass was measured and collected. This process was repeated for a total of four MgCl₂ washes. The supernatant samples from each wash were analyzed with ion chromatography (IC) to determine the extent of barium exchange onto the media, and then the ability of magnesium to exchange with the barium during the MgCl₂ washes. This process was repeated in at least triplicates for the standard bioretention media and soil amendments and then the cation exchange capacity was calculated for each in cmol (+) charge/kg of soil and plotted with standard error bars.

The total organic carbon (TOC) content on the standard bioretention media and soil amendments was analyzed using a Shimadzu TOC-VCHP Analyzer. This was done in triplicate for the media and each soil amendment and SRM 8704 (Buffalo River Sediment; NIST) was used as a check standard. The total organic carbon content was plotted for the media and soil amendments with standard error bars.

The pH of the standard bioretention media and soil amendments were analyzed using Scientific Engineering Response and Analytical Services (SERAS) standard operation procedure 1844: Soil pH determination. Prior to measurement, each soil or amendment was sieved using an ASTM no. 10 sieve and air dried overnight. After each

soil or amendment prepared, approximately 10 g of each was measured into a beaker and approximately 10 mL (10 g equivalent) of 0.01 M CaCl₂ were added to each beaker. The mixture was placed onto a shaker table at 750 RPM for an hour and allowed to settle for an hour. The mixture after settling was analyzed using Thermo Scientific Orion 8102BNUWP Ross Ultra Combination Probe with a two point calibration utilizing Low Ionic Strength (LIS) buffers of known pH of 4.10 and 6.97. The slope of the calibration was 97.9 which falls well into the acceptable range. Each mixture was analyzed separately with the probe being rinsed and cleaned thoroughly after each sample. Each soil and amendment was measured in triplicate and the results were averaged.

The final aspect of media characterization performed on the column media was analyzing the leachable copper content of the media components. Leachable copper was determined through the use of acid digestion and ICP-MS analysis. Approximately 0.200 g of each media component, in triplicate, was digested with 7N HNO₃ in individual Teflon bombs at 120 C. After heating overnight, the contents were then uncapped and dried until all of the 7N HNO₃ had completely evaporated. To each Teflon bomb, 20 mL of Internal Standard Solution (ISS), containing Indium at 1 ppb as an internal standard, and acidified to 2% HNO₃. Solids was allowed to go back into solution upon heating for 2 hours at 120 C, then the contents of each Teflon bomb were transferred into a pre-weighed 50 mL centrifuge tube, and each Teflon bomb was rinsed with 3 washes of ISS. The total mass of ISS and media sample was measured to calculate the dilution factor of the solid sample. Finally, the samples were filtered into 15 mL centrifuges tubes using a 0.45 μm filter and analyzed on ICP-MS as previously described.

Pilot Study

Nine combinations of bioretention media and amendment were evaluated as a single column without replication. A control column containing only the standard bioretention media and a 250 mL underlying sand layer provided a baseline for copper attenuation. Columns were designed using 30 cm tall, 7.6 cm diameter PVC pipes equipped with an end-cap where a 1.25 cm diameter hole was drilled to allow for effluent water to drain. The bottom layer of all treatment columns were a geotextile fabric and 150 mL sand layer to prevent loss of media. Above the base layer, each column was filled with standard bioretention media, and soil amendments that varied for each column. The top layer of each column was a 40 mL sand layer to aid in water dispersion throughout the entire column (Figure 6). A standard bioretention media was created according to Prince Georges County Bioretention Manual: 50% sieved and washed sand, 25% sieved leaf compost, and 25% sieved topsoil by weight (Prince George's County 2002). The three soil amendments: biochar, zeolite, and greensand were added to each column as either mixed or layered columns (Figure 6).

The biochar was purchased from The Biochar Company which specializes in providing biochar for garden and agricultural outlets. The Soil Reef™ Pure Biochar was utilized for this study, and is marketed as a soil enhancement amendment that is made through the pyrolysis of wood and forest residues. The greensand was purchased from Epsoma which manufactures and sells a multitude of agricultural goods designed for soil enhancement. The greensand used for this study was Epsoma's Organic Greensand created from natural glauconite $((K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2)$ that is primarily composed of iron-potassium silicate and able to bind sandy soil, increase moisture

retention, and provide potash to soils. Finally, the zeolite was purchased from The Seed Supply Company which provides a variety of soil amendments and seeds to agricultural-based customers. The zeolite utilized for this study was the Raw Supply Granular Clinoptilolite zeolite $((\text{Na,K,Ca})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36} * 12 \text{H}_2\text{O})$ which is marketed as a naturally occurring material comprised of aluminosilicate cage-like structures that can bind positively charged cations, retain soil moisture, and provide essential plant nutrients.

As layered columns, the biochar, zeolite and greensand were measured by volume and added as a layer underneath the standard bioretention media separated by geotextile fabric to prevent mixing between the soil amendment and the bioretention media. As mixed columns, the soil amendments were added by volume to the bioretention media, thoroughly mixed, and then added to the column (Figure 6). The volume of bioretention media added decreased as higher volumes of soil amendments were added in order to maintain consistent column bed volumes throughout. Biochar was evaluated at varying volumes for both layered and mixed treatments ranging from 100-300 mL while zeolite and greensand were evaluated only at 100 mL volumes for both layered and mixed treatments in this pilot study (Table 1). Each combination was evaluated as a single column without replication, and a control containing only the standard bioretention media and a 250 mL underlying sand layer, rather than 150 mL underlying sand layer, provided a baseline for copper attenuation.

Synthetic stormwater was pumped into each column using an Ismatech BVP Process ISM 404 peristaltic pump. Each synthetic stormwater was spiked with copper to simulate stormwater runoff from a copper roofing structure. Synthetic stormwater was created in 20 L Nalgene containers containing the components listed in Table 2. Each

column was placed on a ring stand and a collection bottle was placed underneath. The peristaltic pump was utilized to deliver the copper spiked synthetic stormwater onto the top of each column, then allowing for gravitational advection through the column. An initial wash phase was conducted which consisted of pumping deionized water from the peristaltic pump onto the surface of each column and allowing each column to completely drain. This initial wash phase consisted of a 7.5 hour (5 bed volumes) total wash with deionized water at 30-40 mL/min flow rate. The wash phase allowed the columns to settle and provide more uniform bed volumes and removed sediments which could potentially clog the column during the experimental period. The wash period also allowed for stabilization of ion exports from each column prior to exposure to copper spiked synthetic stormwater. After the wash period, bed volumes were calculated for each column from the bottom geotextile fabric to the top layer of sand. The bed volumes for the columns ranged from 680-780 cm³.

After the wash period and bed volumes were calculated, flow rates were calculated for the peristaltic pump to provide 2 L of synthetic stormwater to each column at a rate of 1.639 mL/min (6 in/hr). A flow rate values given by other studies including 2.734 mL/min (10.01 in/hr) conducted by the New Jersey Department of Environmental Protection (New Jersey Stormwater Best Management Practices Manual 1999) and 0.4288 mL/min (1.57 in/hr) conducted by the University of Maryland (Kim et al., 2000). The columns were subjected to five distinct and separate additions of 1000 µg L⁻¹ copper spiked synthetic stormwater. Each addition was conducted on consecutive days with approximately 2.4 bed volumes of synthetic stormwater added to each column. The effluents were collected for each addition, weighed to provide a total mass of effluent

collected, and a 40 mL subsample was collected in centrifuge tubes. Additionally, a 40 mL subsample of all copper spiked synthetic stormwaters were collected for ICP-MS analysis following the methods stated above.

Extended Duration Column Studies

The methodology was consistent between the pilot study and the extended duration studies with a few minor adjustments. One modification was each amendment was tested as four treatment types: a 100 mL and 300 mL admixture and a 100 mL and 300 mL underlayer with duplicates for each column including the control column. As a result, each extended duration amendment study consisted of ten columns with each amendment tested separately as a different study. The copper spiked stormwater concentration was raised to 4000 $\mu\text{g L}^{-1}$ Cu to further stress the columns while maintaining copper concentrations that have been seen in field environments (Karlén et al. 2002; LaBarre et al. 2016; Pennington and Brown 2016). Prior to additions of copper spiked synthetic stormwater, a wash period was conducted and bed volumes were calculated for each column as in the pilot study. Each addition was conducted on mostly consecutive days with approximately 2.2 bed volumes of synthetic stormwater added to each column. The effluents were collected for each addition, weighed to provide a total mass of synthetic stormwater added, and a 40 mL subsample was collected to be analyzed for copper concentration. The samples from every third addition and all synthetic stormwaters were analyzed for copper concentrations using ICP-MS.

Another aspect of the extended duration column experiments that differed from the pilot study was that column effluents and synthetic stormwaters were analyzed for major cations and anions. This analysis provided further insight into the overall

performance of the columns with columns that exported higher cation concentrations being more favorable to increase competition for binding sites with copper in effluents. The overall purpose of utilizing ion chromatographic analysis, in addition to ICP-MS analysis, is to provide further differentiation as to which amendment and treatment type will best promote copper attenuation and decrease copper toxicity in copper roofing effluents in a field environment.

Half Media Selected Column Study

The methodology was consistent with the previous column studies with some alterations. For column selection, the highest performing treatment type from each of the Extended Duration Column Studies was used for this study which included: Biochar 300 mL underlayer, Greensand 300 mL admixture, and Zeolite 300 mL admixture. Each column was duplicated and in addition, two control column containing all Bioretention Standard Media (BSM) as in previous studies, were used for a total eight test columns. Each column only contained half of the total media as in previous studies (Table 3) this change was made to allow for a quicker determination of breakthrough by reducing the total bed volume of the column.

At the beginning of the experiment the concentration of copper in the synthetic stormwater was increased to approximately 20,000 $\mu\text{g/L}$, above typical concentrations seen in field (Karlén et al. 2002; LaBarre et al. 2016; Pennington and Brown 2016). The copper concentration remained 20,000 $\mu\text{g/L}$ for the first 20 stormwater additions, but was increased to 100,000 $\mu\text{g/L}$ for the final 5 additions because breakthrough had not been seen in the columns after the 20th addition. Each addition was conducted on mostly consecutive days with approximately 3.5 bed volumes of copper spiked synthetic

stormwater added to each column at the same flow rate. The effluents were collected for each addition, weighed to provide a total mass of synthetic stormwater added, and a 40 mL subsample was collected. The samples from every other addition and all synthetic stormwaters were analyzed by ICP-MS. After the alteration of copper concentrations to 100,000 $\mu\text{g/L}$ after the 20th stormwater addition, all column effluents from all synthetic stormwater additions were analyzed using ICP-MS. This change was made to accommodate the ability to determine the moment at which breakthrough occurred in each column. This study was the final effort to provide evidence to choose a single amendment/treatment type and the alterations for this study were made to promote a quicker and more distinct differentiation between columns.

Results

Pilot Study

Each soil amendment/treatment performance during the five additions were normalized to the performance of the control to provide a baseline for copper attenuation and determine which soil amendments/treatments were most effective in copper attenuation (Figure 7). Control column copper export ranged from 34-84 $\mu\text{g L}^{-1}$ Cu during the five additions, and no column achieved copper exports $<14 \mu\text{g L}^{-1}$ for any addition throughout the pilot study. Throughout the five additions, all biochar amendments in the mixed treatments failed to attenuate copper more effectively than control. Also, the mixed treatments for both zeolite and greensand performed better than their layered counterparts, but both greensand and zeolite amendments consistently performed better than the control and better than the biochar layer treatments. The biochar layer treatments consistently performed better than the control, but the difference

between the 200 to 300 mL layers was minimal. This pilot study highlighted that the addition of these amendments showed increased copper attenuation compared to control, but did not convey that any particular amendment or treatment type as substantially more effective than any other.

Two main changes in further studies to achieve more definitive results included: duplicates for each column are required to provide replication of data for statistical analysis and a longer experimental period to provide more data on how each column performed as bed loads of copper spiked synthetic stormwater increase. This pilot study did support the idea that these amendments have potential to attenuate copper more efficiently than conventional bioretention media, but further, more extensive studies are required for each amendment and treatment type to determine which is most effective.

Characterization of Media

The characterization of the media components was performed as comparison for the specifications of bioretention media outlined in the Stormwater Management Manual for Western Washington (SWMMWW). The SWMMWW have specified design criteria that "custom" bioretention soil mixes must meet to be incorporated in a bioretention design. The requirements listed in the SWMMWW and the results from the characterization of media can be found in Table 4.

The media utilized for the laboratory column studies did not completely comply with the specification listed in the SWMMWW manual, but it must be noted that the characterization results are not completely representative of admixture and underlayer amended formulations. In general, the BSM and soil amendments were significantly below the acid extractable copper limit of 750 mg Cu/kg of dry soil listed in the

SWMMWW with the BSM containing the highest copper content but still being a factor of 10 below the threshold at 35- 60 mg Cu/kg of dry soil. Also, the BSM and soil amendments were all within the range of soil pH listed in the SWMMWW demonstrating that the BSM and soil amendments are adequate buffers. Additionally, the BSM and soil amendments all contained a smaller percentage of fine-grained particles (smaller than #200 Sieve) than the SWMMWW listed, with all containing between 0.25 and 1.25% fines by weight compared to the 2-5% denoted in the SWMMWW. The % fines can greatly influence infiltration rate in bioretention system which ultimately alters residence time and potentially the ability of bioretention systems to attenuate pollutants. Also, the % fines can influence the total suspended sediment in the effluents of bioretention systems which can alter the potential toxicity of various pollutants in effluent waters including copper. The BSM and soil amendments all had substantially lower cation exchange capacities than the SWMMWW recommends for bioretention media, but in the SWMMWW it notes that CEC measurements are not necessary if all other criteria are met as, "soil mixes meeting above specification do not have to be tested for CEC. They will readily meet the minimum CEC." This note highlights that the barium chloride extractions utilized to measure CEC may underestimate the CEC capability of the BSM and soil amendments tested. None of the media tested were above 4 meq/100 g dry soil, and the SWMMWW requires at least 5 meq/100 d dry soil. Finally, the % organic matter was lower than requirement for all the media tested except for biochar. The % organic matter is not completely representative for the soil amendments as greensand and zeolite chemically contain very little carbon and likely little to no organic matter, while biochar is made from the pyrolysis and gasification of biomass so the % organic matter is high.

The characterization of the media demonstrated that the BSM and soil amendments are adequate for bioretention systems with some issues apparent, that may be accounted for and corrected when the amendments are utilized as admixtures or underlayers. It is important to note that these characterizations do not completely predict the ability of BSM or soil amendments to attenuate copper in a bioretention system, but these characteristics can help explain results seen in the laboratory and field experiments.

Extended Duration Column Studies

The columns in the Extended Duration Column Studies were analyzed for copper attenuation by determining the copper exports from each column over bed volumes of copper spiked synthetic stormwater additions. The most effective treatment type from each amendment study was depicted in Figure 8. All columns, including control, consistently exported copper concentrations $< 14 \mu\text{g L}^{-1}$ over a substantial period of bed volume additions. Additionally, all columns experienced heightened copper exports during the first few additions, but all columns reached equilibrium copper exports after about 20 bed volumes of stormwater. In general, all amended columns outperformed the control columns, but after increasing bed volume additions, Greensand admixture (GM300) began to export similar and higher concentrations compared to control columns. Biochar underlayer (BL300) and zeolite underlayer (ZL300) consistently outperformed control and GM300 columns. ZL300 columns consistently exported lower copper concentrations than all other columns. Also, BL300 and ZL300 columns showed substantially lower variability between columns, with much lower standard error (generally $< \pm 1$ ppb) compared to both control and GM300 columns where standard error tended to $> \pm 2$ ppb. The Extended Duration Column Studies demonstrated that

these amended columns could facilitate copper exports lower than $<10 \mu\text{g L}^{-1}$ but there was little variation between each column amendment-treatment type.

The column exports were also analyzed for cation concentrations (sodium, magnesium, calcium, and potassium). The cation concentrations of the column effluents can alter the toxicity of the stormwater to aquatic biota, so this analysis can be useful in understanding how each amendment-treatment type may affect the toxicity of the effluents. Figure 9 portrays the results from the cation analysis of the effluents from the most effective treatment type from each amendment study (BL300, GM300 and ZL300). Additionally, Figure 9 conveys the cation concentration of the synthetic stormwater itself to provide a baseline of cation concentrations. Figure 9 shows that each column experienced higher cation concentrations during the first few bed volume additions, but reaching a stable equilibrium of cation export after about 20 bed volumes. Also, all columns exported consistently higher cation concentrations compared to the cation content of the synthetic stormwater. The BL300 consistently exported lower concentrations of cations than all other columns while the GM300 also tended to export lower cation concentrations than the control columns. ZL300 was the only column which consistently exported higher cation concentrations than the control column, exporting on average 5x higher cation concentrations than the synthetic stormwater contained. The cation analysis showed use of a soil amendments tend to increase cation concentrations which will likely reduce the toxicity of copper in the effluents.

Finally, the cation exchange capacity of the columns was compared to the total copper loading of each column during the extended duration column experiment. This was done through a series of calculations: first, the theoretical cation exchange capacity

of each column was calculated using the CEC measurements and by knowing total weight of media used in each column, and second, the total copper loading was calculated from the summation of copper loading through each column for all additions. The result is shown in Figure 10 portray the theoretical CEC of each column compared to the average copper loading experience by each column during the Extended Duration Column Studies. In general, the amended columns showed a higher theoretical column CEC compared to the control columns, with GM300 having a substantially higher CEC compared to all other column. Notably, the ZL300 columns had the lowest of all amended columns, but still comparable to the control columns. Also, all columns demonstrated much higher CEC than was accounted for by the copper loading during the Extended Duration Column Studies, with only about one half of the total CEC occupied by copper cations.

Half Media Selected Column Study

The final laboratory column study conducted was an attempt to provide evidence and validation for the selection of a single amendment-treatment type for use in the copper roof runoff field study. The soil amendment-treatment combinations, Biochar 300 mL underlayer (BL300), Greensand 300 mL admixture (GM300), and zeolite 300 mL admixture (ZL300), were exposed to higher concentrations (approximately 20,000 ppb for the first 20 stormwater additions and 100,000 ppb for the final additions) of copper spiked synthetic stormwater, in order to, reach breakthrough in the columns.

Breakthrough in the column studies can be describes as the point at which the cation exchange capacity of the media has been fulfilled by the influx of copper ions resulting in the export of elevated copper concentrations compared to a previous equilibrium state. In

contrast to the Extended Duration column Study figures, Figure 11 shows the cumulative copper export loading over cumulative bed volumes on a logarithmic scale. In addition, the inset in Figure 11 is a magnification of the final four additions to each column to fully portray how each column experienced breakthrough and how breakthrough affected the loading export of copper.

This study further validated the results from the Extended Duration Column Study that these columns can export $<14 \mu\text{g L}^{-1}$ on a consistent basis with all columns, including control, exporting $<14 \mu\text{g L}^{-1}$ consistently through over 80 bed volumes of copper spiked synthetic stormwater through the columns. Additionally, as seen in the Extended Duration Column Studies, all amended columns outperformed the control columns throughout the study demonstrating that soil amendments can attribute higher copper retention when utilized as soil amendments in bioretention studies (Inset Figure 11). These additions occur after breakthrough has occurred in each column; however, the extent of breakthrough was different for each amendment-treatment type. All the columns experienced breakthrough around the 90th bed volume, with the control columns exporting substantially higher copper concentrations than each amended column. On average the control columns exported about $1,400 \mu\text{g L}^{-1}$ BL300 columns exported about $900 \mu\text{g L}^{-1}$, GM300 exported $1,200 \mu\text{g L}^{-1}$, and ZL300 exported $300 \mu\text{g L}^{-1}$ during the breakthrough period. ZL300 exported substantially lower copper concentrations compared to other columns and was more consistent in the export concentrations during the final few additions when the copper concentration in the stormwater was increased. The Half Media Column Study, corroborated results from the Extended Duration Column Study, that consistently exported lower copper concentrations throughout the entire study,

and experienced a less abrupt breakthrough compared to all other columns, including control.

Discussion

These laboratory column studies were designed to evaluate the effectiveness of commercially available soil amendments for incorporation into bioretention system. These soil amendments were tested under similar conditions as would be seen in the field, and coupled with the chemical and physical characterization of the amendments, these studies can provide a reliable and accurate portrayal of their applicability as amendments to bioretention media for enhanced metal attenuation, especially copper. This discussion will be centered on determining how each chemical/physical characteristic affects the amendments metal attenuation ability and how each study ultimately allowed for the choosing of a single amendment-treatment combination for use in the field study.

Attenuation of Cu from Spiked Synthetic Stormwater

One of the most important aspect of any bioretention system is the ability to attenuate pollutants from influent waters and reduce the concentration of these pollutants in effluent waters. For this study, the primary aspect of concern for these soil amendments was their ability to attenuate copper from synthetic stormwater. Previous studies have demonstrated the ability of biochar, greensand, and zeolite to attenuate metals, including copper, and these column studies had similar results (Franus and Bandura 2014; Lim et al. 2015; Reddy et al., 2014; Uchimiya et al. 2011). In general, the amended columns and control columns could consistently reduce copper concentrations by > 90 % to a concentration <10 $\mu\text{g L}^{-1}$.

One key aspect that must be addressed is the disparity between copper concentrations in effluents seen in a previous study using bioretention systems (LaBarre et al. 2016), compared to those seen from laboratory column effluents. The previous field study noted that copper effluents from bioretention planter boxes and swale averaged 66 and 28 $\mu\text{g L}^{-1}$, respectively from an average influent copper concentration of 1,068 $\mu\text{g L}^{-1}$ (LaBarre et al. 2016). In comparison, these column studies demonstrated that all amended and control bioretention column could consistently export $<14 \mu\text{g L}^{-1}$ from an initial concentration much higher than 1,068 $\mu\text{g L}^{-1}$. The variation in results can likely be attributed to a few key factors that were different in the laboratory study compared to the field study. One primary difference is the laboratory column study was the ability to diffuse the incoming synthetic stormwater across the entire area of the column and allow all the media within the column to be utilized for copper attenuation. It is extremely likely that in the field bioretention boxes channeling within the media occurred over the course of the study and only a small fraction of the media was being accessed for copper attenuation, resulting in the higher copper exports on a consistent basis. Of similar note, the retention time of stormwater within the columns was likely higher compared to field bioretention boxes due to this factor. A longer retention time would allow for more complexation, precipitation, and binding of copper ions to the media and amendment within the column, and could attribute to the consistently lower copper exports. These factors can account for the substantially lower copper exports seen in the laboratory column studies compared to the previous field study, especially considering the enhanced copper attenuation in the control columns that had similar media formulation to the bioretention boxes.

Both the Extended Duration and Half Media Selected Column studies focused primarily on the ability for the media-amendment formulations to attenuate copper from synthetic stormwater. The Extended Duration Column Studies demonstrated that standard bioretention media and media-amendment formulations can substantially decrease copper concentrations in effluents (Figure 9). Throughout the Extended Duration Column Studies, the copper concentration in effluents remained below $14 \mu\text{g L}^{-1}$ and no instances of breakthrough were seen. To validate these results, the cumulative copper loading during these studies was compared to the total calculated cation exchange capacity of each column (Figure 10). Figure 10 demonstrates that the copper loading did not exceed the total cation exchange capacity of the columns, and as a result, the low copper concentrations seen throughout the studies in the effluent water are probable as the media can still readily attenuate the influent copper ions. In addition there are multiple other attenuation mechanisms occurring within the columns rather than strict cation exchange including: complexation, precipitation, and physical adsorption. These other mechanisms are difficult to quantify especially during the course of the columns study itself; however, these mechanism undoubtedly account for some portion of attenuation and demonstrate how the cation exchange capacity may not fully estimate the copper attenuation ability of a media-amendment formulation column. Despite no breakthrough occurring in the best performing media-amendment formulation, slight variability could be seen between each column. The inability to differentiate between performance of control and media-amendment formulations during the Extended Duration Column study led to the conducting on the Half Media Selected Column Study.

The Half Media Selected Column Study primarily focused on the ability of the media-amendment formulation within the columns to attenuate copper from synthetic spiked stormwater. The results aligned well with the previous study, but as copper loading increased and media volume decreased breakthrough occurred within the columns. The important aspect of the Half Media Selected Column study was how and when breakthrough occurred within each column. The copper loading exports remained rather consistent with the previous study until the copper concentration in the synthetic spiked stormwater was increased to approximately $100,000 \mu\text{g L}^{-1}$ for the final few additions. All amended columns consistently had lower cumulative copper loading compared to the control columns, and that ZL300 outperformed all other columns; all similar results to the Extended Duration Column Study (Figure 11). The occurrences of breakthrough does provide insight into each columns' ability to not only resist breakthrough, but attenuate extremely high copper concentration in stormwater. response to the addition of higher copper concentration spiked stormwater. As bed volumes of the elevated copper synthetic stormwater increased, all amended columns began to outperform the control columns and ZL300 had substantially lower cumulative loading compared to all other columns.

Water Chemistry of Column Effluents

The water chemistry of column effluents is extremely important in determining how the media-amendment formulations can mitigate copper toxicity. The water chemistry of the effluents for each column could also be used as evidence for the choosing of an amendment, especially since the media-amendment formulations chosen for the Half Media Selected Column Study all performed relatively consistently. An

analysis of the water chemistry for the column effluents can help predict the copper toxicity in the effluents and differentiate the performance of each media-amendment formulation.

During the Extended Duration Column Study, the pH and the cation concentrations of the effluents was consistently analyzed to obtain further knowledge about the ability of the media-amendment columns to reduce copper toxicity in the column effluents. The major cation concentration in the columns' effluents are portrayed as total cation exports (meq/L) which accounts for the disparity in charge between the cations and allowing for direct comparison between the columns. The major cation concentration is important due to their ability compete for binding with copper, and other metal ions, to the biotic ligand. If the copper cation cannot bind to the biotic ligand, then no toxicological effect will occur, greatly reducing the toxicity of copper in the solution. As a result, the higher the cation concentrations, the lower the potential toxicity of copper in effluents assuming that the copper concentrations remain constant. Since the copper concentrations between the various media-amendment columns were similar, the major cation concentrations can provide a good portrayal of the difference in copper toxicity in the effluents of each column. The analysis demonstrated all columns exported higher cation concentrations than could be attributed to the synthetic stormwater. Also, ZL300 significantly outperformed all other columns at exporting higher cation concentrations. In comparison, GM300 and BL300 consistently exported about half of the total cations as milliequivalents per liter compared to ZL300 and control columns which may limit the ability of these columns to reduce the potential toxicity of copper in the effluents.

The ability of bioretention structures to alter the pH of effluents can also help reduce the toxicity of metals. During the Extended Duration Column Study, the pH of the effluents and copper spiked synthetic stormwater was consistently monitored to determine how the media-amendment formulations altered the pH in the column effluents. Throughout the Extended Duration Column Study, the copper spiked synthetic stormwater averaged a pH of 6.3, slightly above the pH of normal rainwater, but relatively close to the 5.5-6.0 pH of rainwater across the United States (Odnevall Wallinder et al., 2009). Preferably, the media-amendment columns would increase the pH of column effluents to help reduce the toxic potential of copper. At higher pHs, organic ligands, like carbonates and bicarbonates become deprotonated, allowing these ligands to bind copper ions in solution and prevent them from binding to the biotic ligands in organisms. Throughout the Extended Duration Column Study, all columns increased the pH in the effluents with averages of: 7.3 for control columns, 7.5 for BL300 columns, 7.7 for GM300 columns, and 7.6 for ZL300 columns. These results show that all soil amendments promoted higher buffering capacities in the columns, producing higher pH in the effluents compared to the original copper spiked stormwater and average control column effluents. All amended columns had relatively consistent effluent pHs about 1 full pH unit above the influent pH, which will reduce the toxicological potential of copper ions in the columns' effluents.

Conclusions: Choosing a Soil Amendment

The two key questions that needed to be addressed to choose a media-amendment formulation are: Which column reduces the copper concentrations most effectively and consistently? And which column most effectively reduces the potential toxicity of copper in effluents? ZL300 treatment was the most successful treatment both in terms of copper attenuation and reduction of potential toxicological effects of released copper. ZL300 consistently outperformed all other treatments including the average control columns in copper attenuation. Additionally, ZL300 had the lowest and most consistent breakthrough during the Half Media Selected Column Study where all other columns exported higher copper concentrations once breakthrough occurred. BL300 consistently outperforms the average control columns in copper attenuation, but does not compete well with either the average control columns or ZL300 columns in cation export. ZL300 columns consistently exported higher cation concentrations compared to all columns including the average control column, while BL300 columns consistently exported consistently lower cation concentrations than the average control columns. Based on these three factors, the best treatment type for copper attenuation and reduction of copper toxicity appears to be ZL300, which was chosen to be utilized in the copper roof field study.

Figures and Tables

Table 1. Column Media and Amendment Formulations for Pilot Study.

Column	Media Mass (g)	Amendment Volume (mL)
control	900	0
Biochar Mix 100	900	100
Biochar Mix 200	800	200
Biochar Mix 300	700	300
Biochar Layer 100	900	100
Biochar Layer 200	800	200
Biochar Layer 300	700	300
Greensand Mix 100	900	100
Greensand Layer 100	900	100
Zeolite Mix 100	900	100
Zeolite Layer 100	900	100

Table 2. Copper Spiked Synthetic Stormwater Formulation for Pilot Study. All components remain consistent throughout all column studies, except Copper (Cu) concentrations which are alters as specified for each study.

Chemical Name	Conc. Stock Solution (mg/L)	Volume Used (mL)	Syn. Stormwater Conc. (mg/L)
CaSO ₄	2,036	50	5.09
MgCl	2,000	20	2.00
KCl	1,900	20	1.90
NaNO ₃	1,900	20	1.90
NaHCO ₃	5,500	20	5.50
Cu	1,000	40	2.00
H ₂ O	Deionized	19,830	N/A

Table 3. Column Media and Amendment Formulations for Half Media Selected Column Study.

Column	Media Mass (g)	Amendment Volume (mL)
Control	450	0
Biochar Layer 300	350	150
Greensand Mix 300	350	150
Zeolite Layer 300	350	150

Table 4. SWMMWW (Stormwater Management Manual of Western Washington) requirements for "custom" bioretention media along with the results from the characterization of the media and soil amendments utilized in the laboratory column studies. CEC is expressed as the standard error range of CEC (n=4) for each amendment/soil type in meq/100 g dry soil, % Organic Matter is expressed as average % Organic Matter by weight (n=4) for each amendment/soil type, % Fines is expressed as the average percentage smaller (n=4) than #200 Sieve by weight for each soil/amendment type, and acid extractable copper is expressed as average (n=3) mg Cu/ kg of dry soil for each soil/amendment type.

Soil/Amendment	Soil pH	CEC	% Organic Matter	% Fines	Acid Extractable Cu
SWMMWW	5.5 - 7.0	> 5	5-8	2-5	750
BSM	7.36	1.8-2.3	0.3	1.22	35-60
Biochar	7.18	3.0-3.45	35	0.94	26-29
Greensand	6.49	2.0-2.35	0.025	0.27	5-6
Zeolite	7.64	1.75-2.45	0.001	0.24	5-7

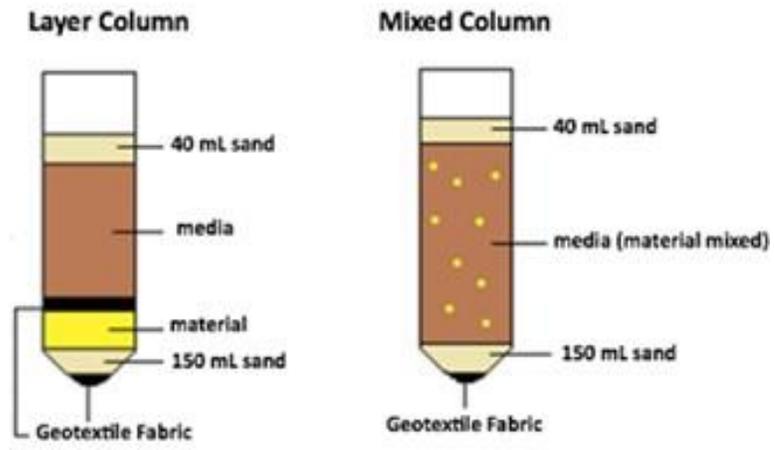


Figure 6. Depiction of Layered and admixture Columns for all Column Studies.

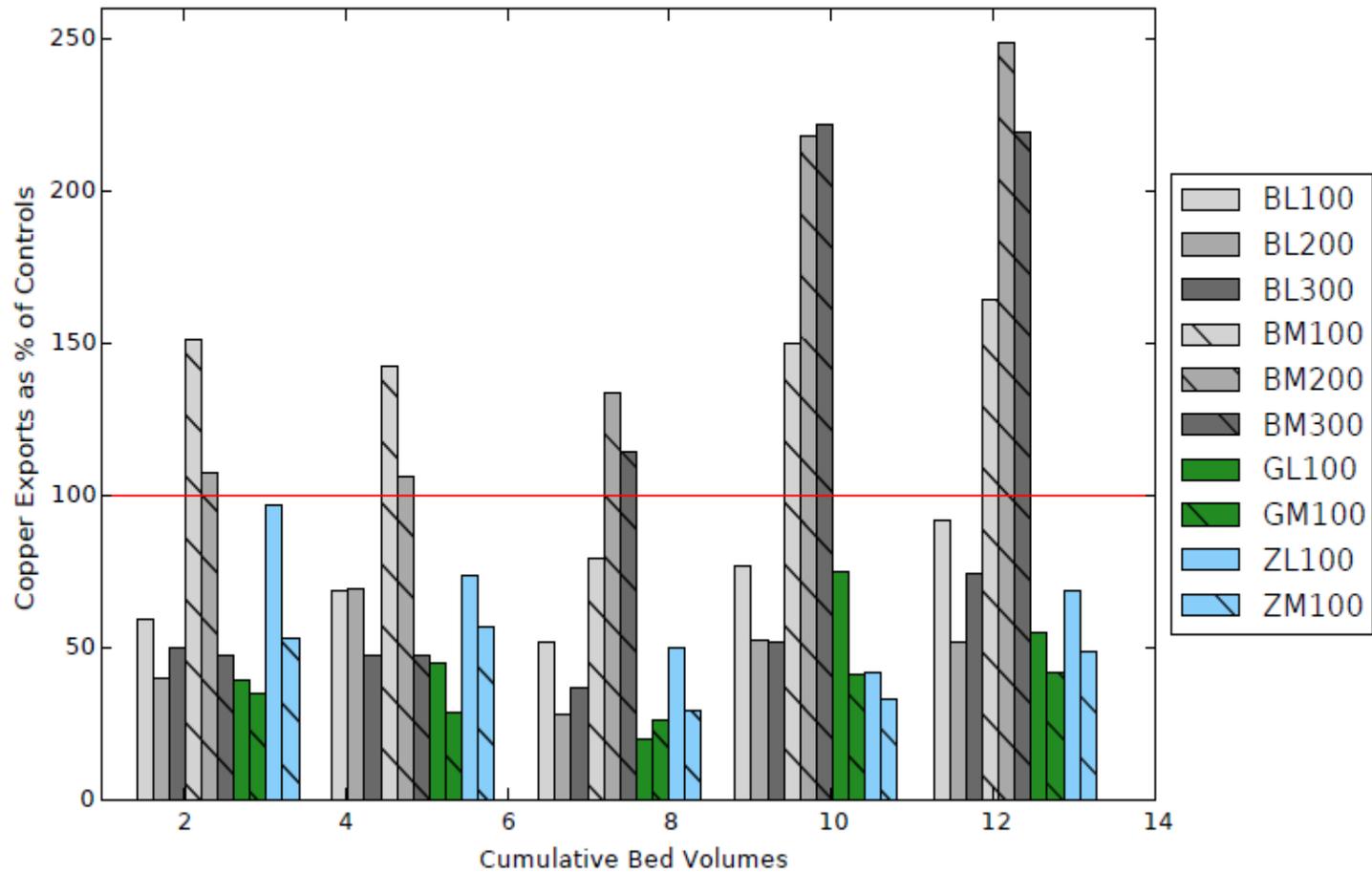


Figure 7. Copper concentration after addition of Cu spiked synthetic rain water from the Pilot Column Study expressed as % of control export, with red line depicted 100 % of control. Biochar underlayer 100-300 (BL100, BL200, and BL300), biochar admixture 100-300 (BM100, BM200, BM300), greensand admixture 100 (GM100), greensand underlayer (GL100), zeolite admixture 100 (ZL100) and zeolite underlayer 100 (ZL100). In general, most amendment and treatment formulations attenuate copper more effectively than control columns noted by the bars well below the red line of 100 % of control. The pilot study demonstrated that all three amendments can attenuate copper and further investigation is needed to differentiate which amendment and treatment type will be best applied in a field study.

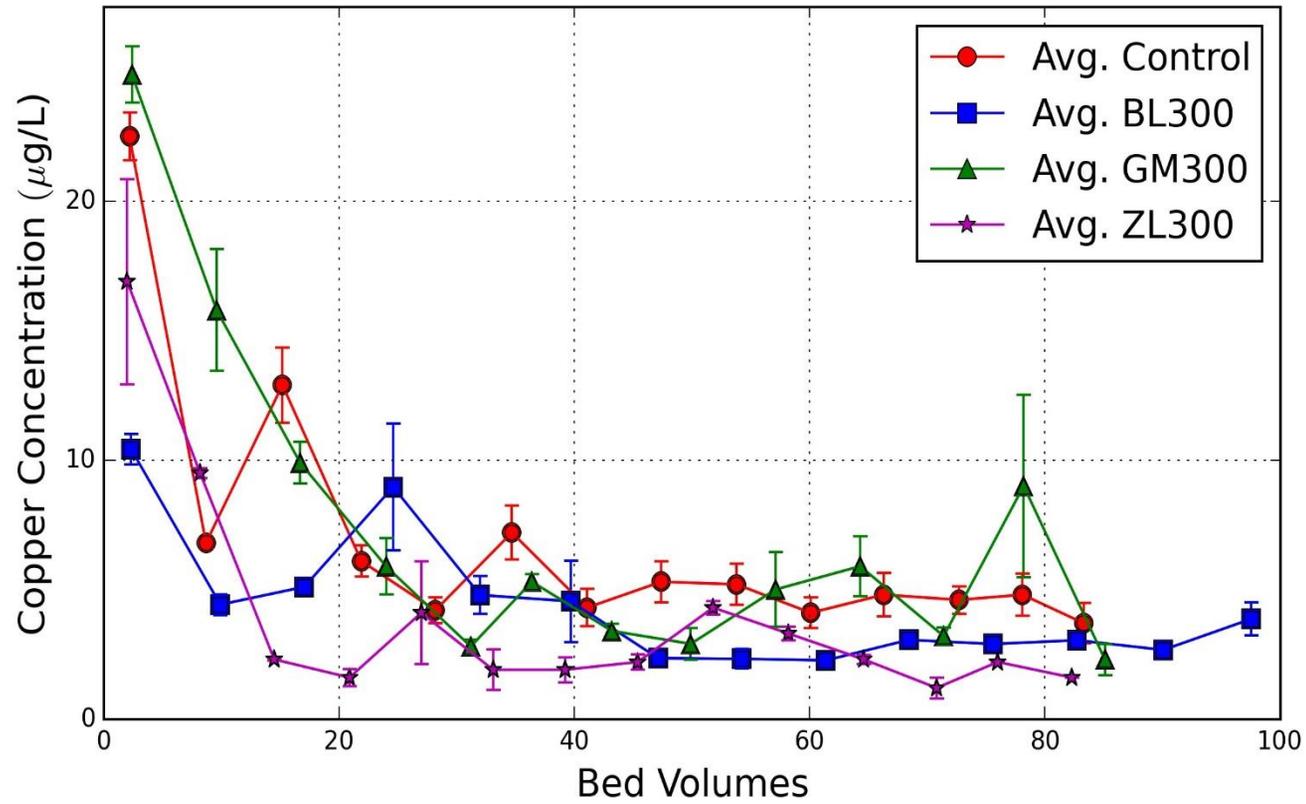


Figure 8. Copper concentration after addition of Cu spiked synthetic rain water for the Extended Duration Column Study with standard error bars for each averaged column. The top performing columns from each Extended Duration Column study are depicted: biochar underlayer 300 (BL300), greensand admixture 300 (GM300) and zeolite underlayer 300 (ZL300), as well as, the average of all control columns from the Extended Duration Column studies. All columns, including the average control columns, could consistently export Cu concentrations lower than 10 µg/L from initial Cu spiked synthetic stormwater containing 4,000 µg/L.

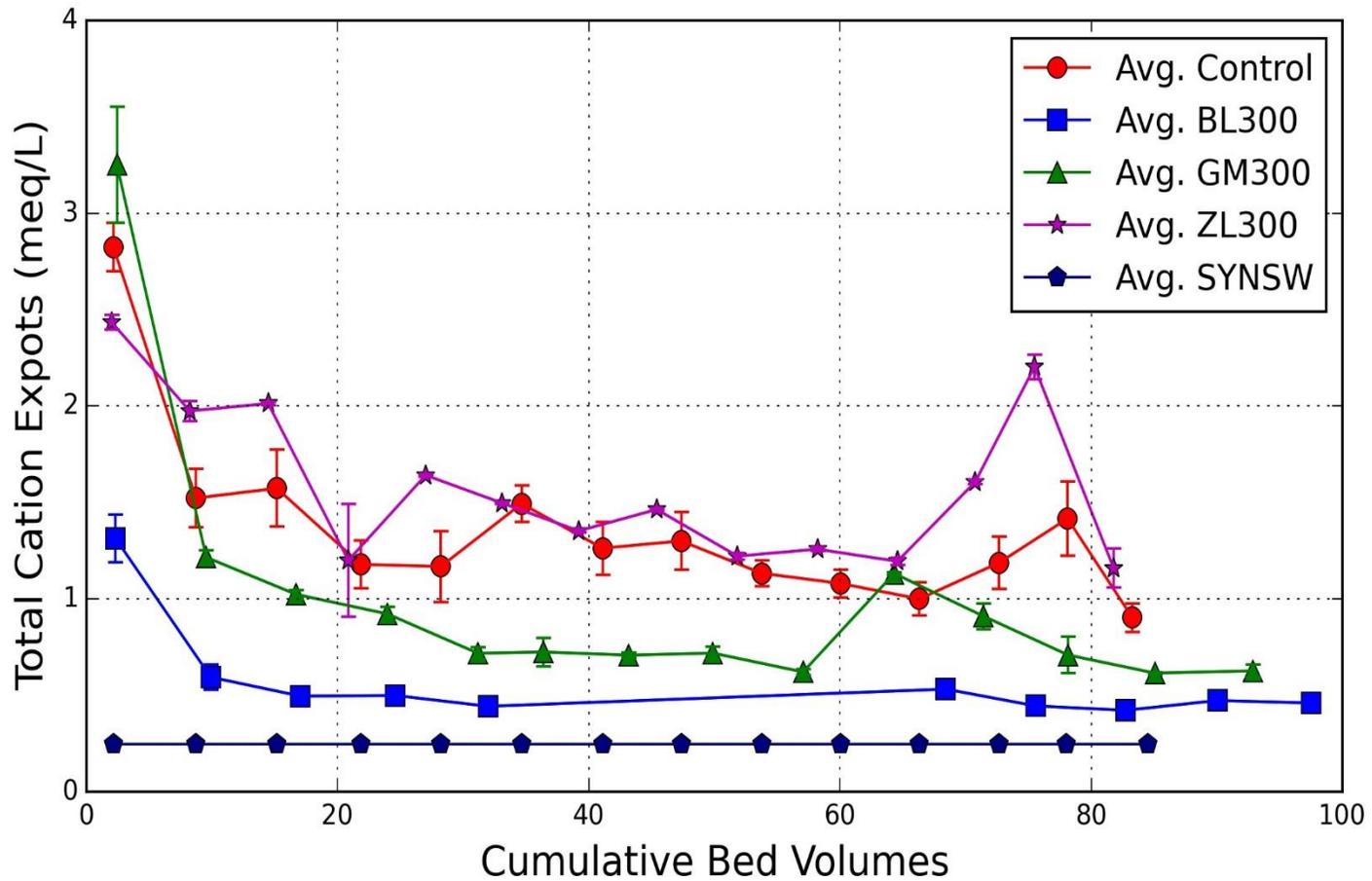


Figure 9. Total cation concentration throughout bed volumes additions of Cu spiked synthetic rain water with standard error bars for each average column. The top performing columns from each Extended Duration Column study are depicted: biochar underlayer 300 (BL300), greensand admixture 300 (GM300) and zeolite underlayer 300 (ZL300), as well as, the average of all control columns from the Extended Duration Column studies. Additionally, the total cation concentration in the synthetic stormwater is expressed to show how the columns affect the cation concentration. The total cation concentration is expressed in milliequivalence per liter and includes: sodium, magnesium, calcium, and potassium. All columns exported higher cation concentrations than was introduced via synthetic stormwater.

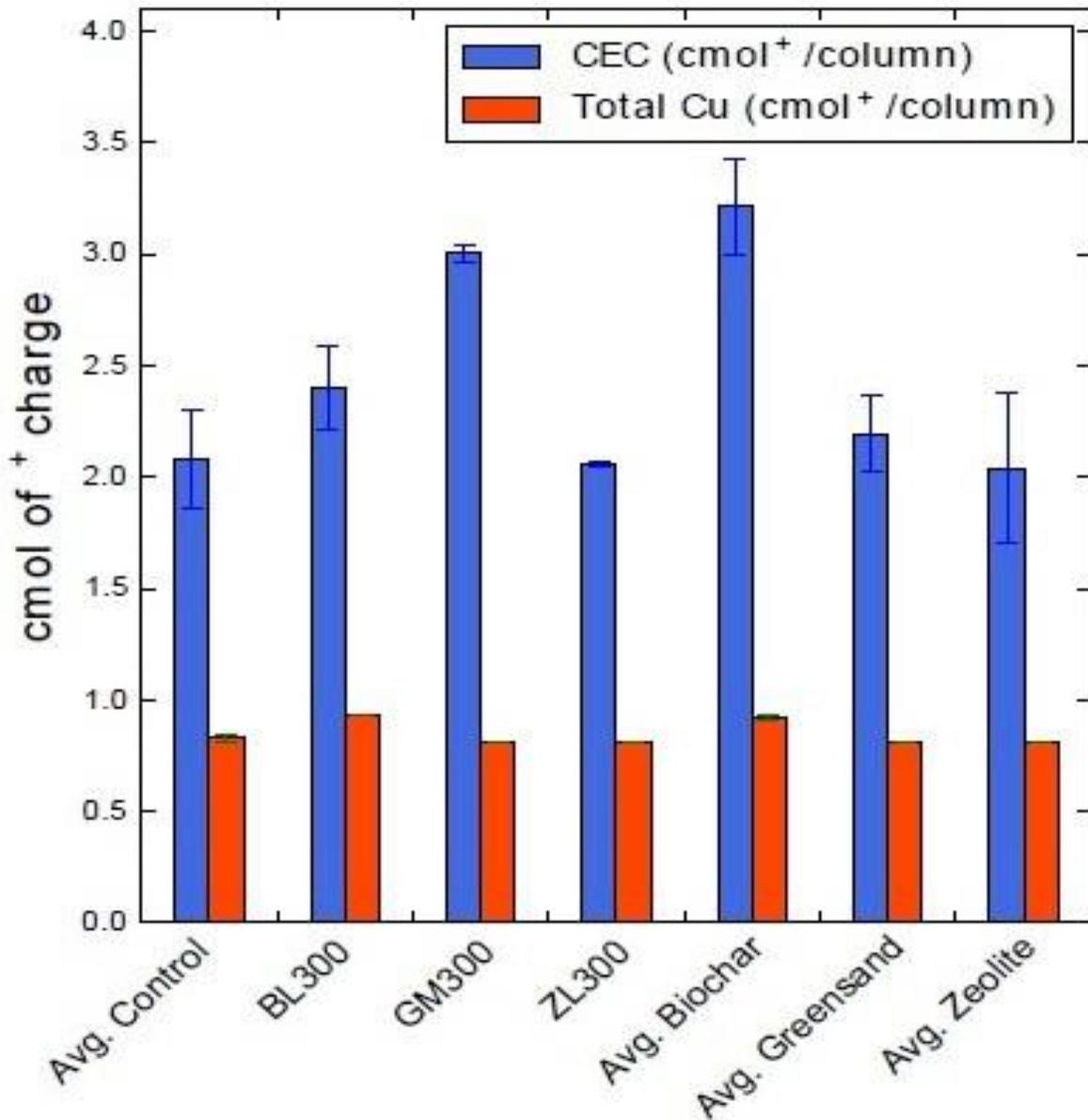


Figure 10. Cation exchange capacity (CEC) for each amended column and amendment expressed in (cmol⁺/column) with standard error bars from the Extended Duration Column Study. The average total Cu loading from the Extended Duration Column experiments for each column also expressed in (cmol⁺/column). The top performing columns from each Extended Duration Column study are depicted: biochar underlayer 300 (BL300), greensand admixture 300 (GM300) and zeolite underlayer 300 (ZL300), as well as, the average of all control columns from the Extended Duration Column studies. Overall, every column experienced about one-half of their CEC in cmol⁺ of Cu loading during the Extended Duration Column experiments which helps validate the low Cu (< 10 μg/L) seen in column exports throughout.

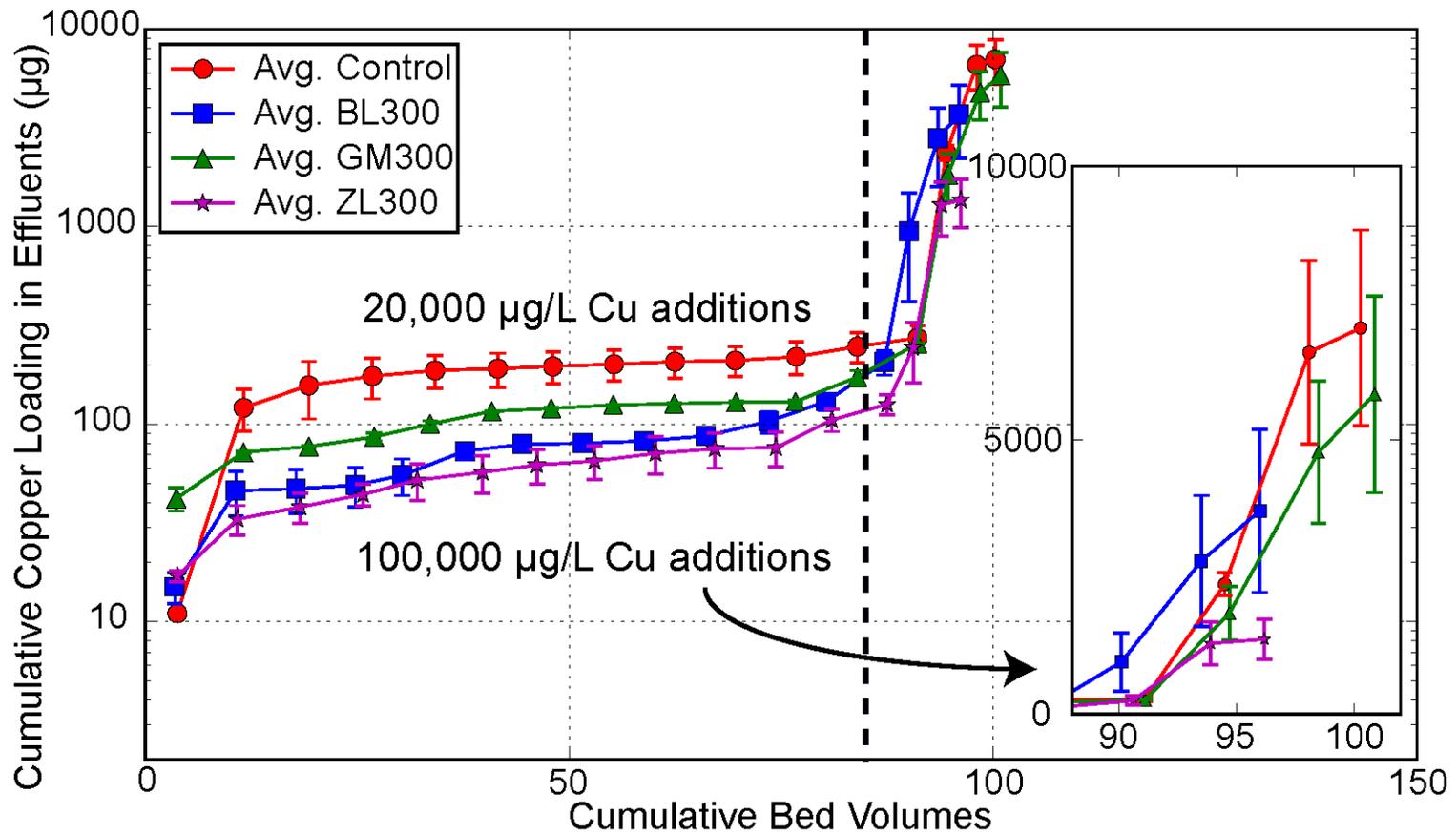


Figure 11. Cumulative Cu loading throughout bed volume additions of Cu spiked synthetic rain water with standard error bars for each averaged column for the Half Media Selected Column Studies on a logarithmic scale. The inset depicts the final additions where the Cu spiked synthetic stormwater concentrations was increased from 20,000 µg/L to 100,000 µg/L. The top performing columns from each Extended Duration Column study are depicted: biochar underlayer 300 (BL300), greensand admixture 300 (GM300) and zeolite underlayer 300 (ZL300) along with control columns. All amended columns outperformed the control columns throughout both the initial portions where copper concentrations were 20,000 µg/L and during the final additions when copper concentrations were increased to 100,000 µg/L.

Chapter 4: Zeolite as Soil Amendment to Bioretention Media in Planter Boxes as SCM for Copper Roof Runoff

Introduction

The laboratory column studies were designed to provide experimentally derived validation for the choice of a commercialize available soil amendment to incorporate into a field study utilizing bioretention planter boxes as a stormwater control measure for limiting copper effluents from a copper roofed picnic shelter. The columns studies demonstrated that the use of a zeolite layer underneath standard bioretention media in a 1:3 ratio can substantially increase copper attenuation in the planter boxes and also reduce the potential toxicity of copper concentrations remaining in the planter box effluents. The field study was designed to determine if the results seen in the laboratory column studies can be replicated in a real world setting. In order to evaluate the potential application of the bioretention planter boxes to comply with potential regulations focused on limiting copper exports from sources, like copper roofs. Previous research conducted at Towson University evaluated the effectiveness of two different SCMs at abating copper from copper roofing runoff during storm events. The use of bioretention SCMs were successful in sequestering trace metals from highway runoff; however, no studies had previously determined the applicability of these retention structures to the high copper concentrations emitted by copper roofing materials during storm events. This study determined bioretention SCMs could be applied to copper roofing effluents to decrease copper concentrations entering the environment during storm events. The bioretention structures utilized in the field study were designed in correspondence with the Stormwater Management Manual for Western Washington (SWMMWW). These design specifications were used due to the Pacific Northwest region, including the state of Washington, being an area of primary concern for

limiting copper effluents from entering waterways with copper roofing being one of many sources of copper to the environment (LaBarre et al. 2016).

Briefly, a newly constructed copper roof picnic shelter was subjected to storm events which were treated by two different SCMs in replicate. The SCMs included, swales and above-ground planter boxes. The copper roof was segmented into four distinct and equal sections with PVC gutters directing runoff into each of the four SCMs. The runoff was sampled prior to entering each of the swales and planter boxes, and then sampled again as effluents from the swales and planter boxes. This sampling scheme demonstrated how both the swales and planter boxes attenuated copper from copper roof runoff in similar conditions. In addition, two reference roofing plots were constructed; one containing asphalt shingles to provide copper concentrations of a typical roofing material and one containing acrylic plastic sheeting to provide background for atmospheric deposition of copper. For a more in-depth discussion of the materials and methods for the previous research please reference (LaBarre et al. 2016, 2017).

The overall goal of the previous research was to determine the efficacy of two SCM designs for their ability to attenuate copper at elevated concentration from copper roofing runoff. This study demonstrated promising results for the use of SCMs to attenuate copper even at elevated concentrations experienced from copper roofing runoff. Both SCMs greatly reduced the copper concentrations compared to the concentrations exhibited prior to being subjected to each SCM. The median copper concentration for all inlet sites throughout the field study was $1087 \mu\text{g L}^{-1}$, while the median copper concentrations for the planter boxes and swales effluents were 66 and $28 \mu\text{g L}^{-1}$ respectively (LaBarre et al. 2016). These results demonstrated that both planter boxes and swales as SCMs could decrease the copper concentrations by almost two orders of magnitude. The previous study

portrayed promising results; however, both SCMs evaluated failed to achieve copper effluents concentrations consistently lower than the $14 \mu\text{g L}^{-1}$ level desired by regulators in the Pacific Northwest. This field study attempted to determine if the application of the zeolite underlayer in bioretention planter boxes could also demonstrate that bioretention planter boxes equipped with this media formulation could outperform previous planter box effluents seen in LaBarre et al. and consistently export copper concentration lower than the regulatory desired $14 \mu\text{g L}^{-1}$.

Materials and Methods

Analytical Methods

For all stormwater samples the following analytical methods were conducted in order to quantify the water chemistry of copper roof effluents, bioretention planter box effluents, and control roof effluents; particularly, the copper concentrations, pH, major ions (cations and anions), alkalinity, and non-particulate organic carbon (NPOC). These analytical methods were performed to quantify the copper concentrations and potential toxicity of copper in the roof effluents and bioretention planter box effluents to determine the overall performance of the bioretention planter boxes both with and without the zeolite underlayer.

Copper concentrations were quantified utilizing a Thermo Elemental VG PQ Excell ICP-MS with an ASX-520 HS Auto-sampler. For each sample two different preparation techniques were performed: filtered-acidified (FA) and acidified-filtered (AF). In the FA technique utilized the following procedure, each sample was filtered into a 25 mL centrifuge tube using a $0.45 \mu\text{m}$ syringe filter. A 5 mL aliquot of the filtrate was collected using a 5 mL pipette and the remainder was discarded. The filtrate was acidified to 2% HNO_3 through the addition of $150 \mu\text{L}$ of 7 N HNO_3 . Finally, $50 \mu\text{L}$ of 100 ppb In solution

in 2% HNO₃ was added to each sample to serve as a 1 ppb In internal standard for ICP-MS analysis. The FA analysis provided an estimate of the dissolved copper concentration in the sample. For AF technique, 10 mL of each sample was transferred to a 50 mL centrifuge tube and 300 µL of 7 N HNO₃ was added, then the sample was agitated on a shaker table for at least 5 minutes. Each sample was filtered using a 0.45 µm syringe filter into a separate 25 mL centrifuge tube and then a 5 mL aliquot of the filtrate was collected using a 5 mL pipette. Finally, 50 µL of 100 ppb In solution in 2% HNO₃ was added to each sample to serve as a 1 ppb In internal standard for ICP-MS analysis. The AF technique provides quantification of the total copper concentration in the sample, including any particulate copper. For every ten samples, a duplicate was analyzed along with the samples for QA/QC; additionally, a standard reference material (SRM) 2709a (San Joaquin Soil; NIST) was analyzed as a check standard at least twice during all ICP-MS analyses to ensure proper calibration and accuracy. The calibration for each ICP-MS analysis consisted of a two-tiered calibration. The calibrations standards were the following concentrations: 5, 10, 25, 50, 100, 200, and 400 ppb with each standard being made in 2% HNO₃ with 1 ppb In internal standard. Each ICP-MS analysis was checked for QA/QC using the In internal standard concentration, duplicate unknowns, and SRM; if any of these were not within reasonable limits (1 ± 0.2 ppb In, <10% difference in duplicates, and >80% recovery for Cu in SRM) then analysis was determined to be unacceptable and samples were re-prepped and re-run.

For all Ion Chromatography (IC) analysis, a Dionex ICS-500 Ion Chromatograph equipped with Dionex Autosampler was utilized. Each sample and standard was filtered into a plastic vial using a 0.45 µm syringe filter. A separate calibration curve was used for cations and anions consisting of the following concentrations: 1, 5, 10, 50, 100 and 200

ppm (cations) 1, 5, 10, 25, and 50 ppm (anions). For all IC analyses, a duplicate sample was conducted for every ten samples and a check standard for both cations and anions was included in every IC analysis set. The results were analyzed for QA/QC using the duplicate and check standard for every IC run with an acceptable range of <10% difference in duplicates and >80% recovery in check standard concentrations for all cations and anions.

The pH of all samples were analyzed using a Thermo Scientific Orion 8102BNUWP Ross Ultra Combination Probe with a two point calibration utilizing Low Ionic Strength (LIS) buffers with known pH of 4.10 and 6.97. The slope of the calibration must exceed 90.0 or the probe was rinsed, the internal buffer was replaced, and re-calibrated until the slope was >90.0. Each sample was analyzed separately with the probe being rinsed and cleaned thoroughly after each sample. A duplicate was performed for each storm set and if the percent difference was >10%, then the probe was re-calibrated and the pH analyzed for all samples again. The alkalinity of all samples were analyzed using the same Thermo Scientific Orion 8102BNUWP Ross Ultra Combination Probe with a two point calibration and the following procedure: Approximately 25 mL of each sample was poured into a plastic 50 mL beaker and a small magnetic stir bar was added to beaker. The sample was placed onto a stir plate and two drops of bromocresol green-methyl red indicator was added to the sample and was allowed to thoroughly mix, turning the sample a light blue color. The pH probe was placed into the sample and allowed to equilibrate. A titration was then performed using 0.02 N H₂SO₄ to determine the alkalinity, as CaCO₃, in each sample. A 0.02 N H₂SO₄ solution was added drop-wise until the color of the sample turned a faint pink (around pH 4.5), this was verified for each sample via the pH probe. The amount of 0.02 N H₂SO₄ added via the titration was determined and the alkalinity was calculated using the following equation: Alkalinity (mg/L CaCO₃) = 40 * (mL of 0.02 N

H₂SO₄ added). A duplicate was performed for each storm set and if the percent difference was > 10% then the analyses were performed again.

Finally, the non-particulate organic carbon concentration in each sample was quantified utilizing a Shimadzu TOC-V CSH total organic carbon analyzer equipped with ASI-V autosampler. Approximately 30 mL of each sample was vacuum filtered using a 55 mm Whatman no. 2 filter paper into a Buchner funnel. The filtrate was transferred into a labeled glass vial, being sure to provide some space in the vial to allow for acid addition during NPOC analysis. A duplicate was analyzed for every storm set along with a 20 mg/L C check standard for QA/QC. Calibration standards were created for each analysis via a serial dilution of a 200 mg/L C standard at the following concentrations: 1, 5, 10, 25, 50, and 100 mg/L C. Each sample was analyzed for NPOC and QA/QC was performed where the calibration curve r-value had to exceed 95.0, the duplicate had to be within 10% difference, and the check standard recovery had to be >90%.

Site Design and Equipment

A 3 x 6 meter picnic shelter was constructed in the Glen Woods on the campus of Towson University in the summer of 2012. The picnic shelter was constructed using 16 ounce standing seam copper and the roof was divided into four sections each about 4.64 m² in area with a pitch of 4:12. In addition to the picnic shelter, two reference structures were built within five meters of the picnic shelter. Both of the reference structures were 1.22 x 2.44 meter with a 4:12 pitch, one containing asphalt shingles for comparison to common housing roofing material, and one with Plexiglas to provide background copper concentrations from atmospheric deposition in the area (Figure 12). All of these structures were built within a clearing in the Glen Woods to allow for precipitation to reach the structures without interference and built on a moderate slope to allow for drainage. This

copper roofed picnic shelter was utilized in the previous field study (LaBarre et al. 2016) and with a few adjustments was utilized again for the field study portion of this thesis.

Bioretention Planter Boxes

Two bioretention planter boxes were still in function after the previous field study, and two additional planter boxes were built to accommodate the other two downspouts which had previously drained into the underground bioretention swale which are no longer in use. The two additional planter boxes were built in January of 2017 using same specifications as the previously built planter boxes. Each planter boxes was 0.9 m x 0.9 m, made of composite wood material, with a plywood floorboard. Into each bioretention planter box, an impermeable plastic liner was carefully draped throughout the inside of the box and seated with metal tacks against the top of each box. The liner was important in protecting against the leaking of water and media during storm events and was treated with caution. Additionally, each planter box contained a 5 cm perforated PVC sub-drain that spanned the entire bottom of the box (0.9 m) and exited the box through one end via a 5 cm hole. The perforated sub-drain was covered with geotextile fabric to limit media from entering the sub-drain while allowing water to exit during storm events into the sub-drain. The impermeable liner was carefully sealed around the PVC sub-drain so that all water during storm events had to leave the planter box via the sub-drain and minimize any possible leaks within each box. The bioretention planter boxes that were established for the previous field study were excavated in February 2017 with the vegetative cover in each box carefully removed for later splitting and transplanting into the new planter boxes.

The two new planter boxes were transported to the Glen Woods in March 2017, placed into their respective locations, leveled so that each box slightly sloped towards the end of the box at which the PVC sub-drain exited the box, and then all four boxes were

filled with new bioretention media (Figure 13). The four bioretention planter boxes, two contained control media, and other two contained the zeolite underlayer. Each planter box first filled with approximately ~ 10 cm of aggregate no. 55 limestone which completely covered the PVC sub-drain. Approximately ~ 15 cm of pea-gravel was placed on top of the limestone and leveled out throughout the entire planter box. For the zeolite planter boxes: a layer of geotextile fabric was placed on top of the pea-gravel prior to the addition of zeolite to combat any migration of zeolite into the pea-gravel layer. Approximately ~ 15 cm of natural Raw Supply Granular Clinoptilolite zeolite $((\text{Na,K,Ca})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36} * 12 \text{H}_2\text{O})$ was placed into the planter box and then approximately ~ 30 cm of Maryland State Highway Administration (SHA) Bioretention Standard Media (BSM) 920.01.05 was carefully added above the zeolite underlayer. The vegetation from the prior planter boxes were separated equally into four portions and replanted into each box into the BSM layer with the BSM being covered by a small layer of hardwood mulch to aid in water dispersion and protective cover for the vegetation. For the SHA BSM planter boxes: a layer of geotextile fabric was placed above the pea gravel followed by approximately ~ 45 cm of SHA BSM 920.01.05 was added above the pea-gravel layer, then the vegetation from the previous boxes were transplanted and finished with a small layer of dark hardwood mulch (Figure 13). It is important to note that the standard bioretention media (SHA BSM 920.01.05) is the same media the Maryland State Highway Administration utilizes when constructing bioretention projects across the state, and this media is formulated and verified to meet the requirement for those applications.

From each of the four quarters of copper roof separate downspouts were constructed so that flow-weighted sampling could occur during storm events. After initial sampling, the effluent water was directed onto the top-center of each bioretention planter

box. The effluent water percolated through the media within each bioretention planter box and exited each box through an outlet pipe which delivered the water to another sampling box where flow-weighted sampling occurred (Figure 14).

The initial filling of media components occurred in late March, a leak was detected in Planter Box 3 (one of the planter boxes containing the zeolite underlayer). As a result, the planter box was completely excavated being sure to keep the media separated into distinct layers. The planter box was relined, resealed, and refilled following the exact same sampling procedure and order as before. This process took place in early May after it became evident that the leak could not be sealed without full excavation and relining. An important consideration is after refilling Planter Box 3 the media components were less settled compared to the other planter boxes which were subjected to prior rainfall events which allowed the media to settle and potentially flush finer material within the media.

Sampling Equipment

Sampling boxes were constructed where composite samples were collected during storm events on a flow-weighted basis. Stormwater samples were automatically collected after a specified volume of water had passed through the sampling box. Each sampling boxes contained of an automatic sampler (WS720; Xylem Corporation; College Station, TX) and a tipping bucket flow gauge (6506h; Unidata Pty Ltd; O'Connor, Western Australia) (Figure 15). The tipping buckets in each sampling box measured the flow rate and triggered flow-weighted sampling based on specified presets on a counter box relay where sampling specifications are adjusted (number of tips for each automatic sample). The counter box relay allows for sampling manipulation for each storm event with high volume storms events; the counter can be increased so that sampling occurs less frequently and the entire storm event can be sampled, and with low volume storm events, the counter

can be decreased so that sufficient sampling will occur to allow for characterization. The counter box relay was monitored by HOBOWare Pendant event data logger (UA-003-64, Onset Computer Corp; Bourne, MA) that recorded each time a sampling event was triggered. Events were downloaded after each storm event. In addition, a tipping bucket rain gauge (model 674, Teledyne ISCO; Lincoln, NE) attached to the Plexiglass control structure monitored overall rainfall for each storm event.

The sampling boxes were placed at the inlets prior to the bioretention planter boxes (PI) and at the outlets of each bioretention planter box (PO) as shown in (Figure 14) and at the inlet of the Plexiglass control structure to monitor copper concentrations from atmospheric deposition during storm events. Above all planter box inlet sampling boxes was a PVC pipe containing a small mesh filter that removed larger debris from the stormwater prior to the water entering the sampling boxes. Sampling boxes were canted towards a corner to allow stormwater to pool and be available for sampling via the automatic sampler once prompted by the flow-weighted sampling and counter box relay (Figure 15). Additionally, these sampling boxes contained a small pin-sized hole in the corner where pooling occurred which allowed any residual water to drain after each storm event to prevent water, algae, and bacterial growth within the sampling boxes. Composite samples from all inlets and outlets were collected into 3 L High Density Polyethylene (HDPE) containers for each storm event via the automatic sampler. Each container was which were equipped with a float trigger to abort sampling once the container was full.

Media Characterization

Media in the field study was characterized using the exact same methods and materials used during the Column Studies. The MD SHA BSM and Zeolite was

characterized for: particle size distribution, cation exchange capacity (CEC), total organic carbon (TOC), leachable copper, and pH.

Storm Sampling

Storm sampling took place between May and October 2017 after the site had been completely renovated, redesigned, and reconfigured. Storms were selected throughout the sampling period in an attempt to diversify the type of storms (i.e. summer thunderstorms compared to longer duration, lower intensity rainfall events); however, the majority of the storms were of similar precipitation dynamics due to climate in central Maryland during the sampling period. For each storm event the following steps were taken prior to the storm to ensure that each sampling box would operate properly. First, all HOBOWare Pendant loggers were deployed using the HOBOWare software which would count the number of occurrences of a specified number of rain gauges tips and note the time at which this occurred. Subsequently, the automatic sampler pumped a sample from each sampling box. Also, all gutters, downspouts, and tubing were checked for clogs and other debris to prevent any issues during the storm event which would prevent or alter the stormwater flow into and out of the sampling boxes. Finally, the counter box relay on each sampling box was set to a specified number of tip (i.e. 20) that would trigger a sample to be taken via the automatic sampler. This number was chosen based on the anticipated rainfall amount so that the anticipated volume and entire duration of a storm could be sampled without filling the 3 L Polyethylene containers.

After each storm event, sub-samples of from all bioretention planter box inlets (PI), bioretention planter box outlet (PO), and the Plexiglass control structure (C1) composite samples were transferred into labeled 1-L Polyethylene containers. All data loggers were collected and analyzed with the HOBOWare software for flow-weight analysis. All storm

samples were labeled using the methodology (yymmdd) and the location of the sample. Samples were transferred to the lab and analyzed for: pH, alkalinity, NPOC, major cations and anions (IC), and copper concentrations (ICP-MS) following the methodology described previously. Finally, the water chemistry of all samples were analyzed utilizing the Biotic Ligand Model (BLM) to determine the speciation and potential toxicity of copper within the storm samples, particularly for Cu *Daphnia magna* LC₅₀ in each storm sample. pH, DOC (as measured by NPOC), Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻, and alkalinity were entered as measured from the analytical analysis and a 20 C and 10% value were used for temperature and humic acid, respectively. If any cation or anion value was reported as below LOQ, then a value of 1.0 mg/L was entered into the model for that parameter.

Results

Media Characterization

The characterization of the media components, SHA BSM and zeolite was performed as comparison for the specifications of bioretention media outlines in the Stormwater Management Manual for Western Washington (SWMMWW). The SWMMWW have specified design criteria that "custom" bioretention soil mixes must meet to be incorporated in a bioretention design. Since, there are no distinct requirements for amended bioretention designs, these requirements were compared to the media used in this field study.

The results from the characterization demonstrated that SHA BSM and zeolite do not completely meet all the requirements outlines in the SWMMWW; however, the media contains characteristic of potentiality successful bioretention media (Table 5). The soil pH of both the SHA BSM and zeolite alone were higher than the recommended pH range of 5.5 - 7.0 at 6.99 and 7.64, respectively. This demonstrated that both the SHA BSM itself

and BSM with a zeolite underlayer would likely adequately buffer potentially acidic rainfall runoff from the copper roof during storm events. Additionally, both SHA and zeolite had substantially lower acid extractable copper concentrations compared to the SWMMWW requirement of less than 750 mg Cu/ kg of soil with 16 and 6 mg Cu/ kg of soil, respectively. The low concentration of copper within the media itself inhibits the media from being a potential source of copper and conveys the ability of the media to attenuate copper when utilized as treatment for copper roof runoff. The SWMMWW requires that bioretention media contain 2-5% fine material by weight that is smaller than a #200 sieve; both SHA BSM and zeolite had much lower percentages of fines by weight. Finer material can provide added surface area for surface attenuation of metals, like copper, but these fines can also clog drains and prevent planter boxes from operating successfully and effect residence time of water within the planter boxes, so the lower percentages of fines in the media utilized in the field study may have a beneficial impact by lowering the potential for clogging. The SHA BSM and zeolite had substantially lower cation exchange capacities than the SWMMWW calls for bioretention media, but in the SWMMWW it notes that CEC measurements are not necessary if all other criteria are met as, "soil mixes meeting above specification do not have to be tested for CEC. They will readily meet the minimum CEC." Additionally, the MD SHA does not have a requirement for CEC of bioretention media so it is understandable that the CEC of the media may be low if not formulated specifically to have a higher CEC. Finally, the percent organic matter (OM) was lower than required value for both SHA BSM and zeolite with 1.23 and 0.02% respectively. The percent organic matter is not completely representative for zeolite as zeolite chemically contains very little carbon and likely little to no organic matter except

from atmospheric and laboratory exposure; however, MD SHA requires 1.5% OM for bioretention media which was close to the value found this characterization.

Storm Sampling

Storm sampling took place between late May and early October 2017 with a total of ten distinct and separate storms being sampled. Storm types ranged from short duration summer thunderstorms to longer-lived lower volume storm events more characteristic of fall cold fronts in central Maryland. All but two of the storms resulted in the collection of samples from all inlets and outlets with one storm (170714) where only Planter Inlets 1 and 2 and Planter Outlets 1 and 2 successfully sampled the storm due to battery failure in the other sampling boxes. Another storm (170829) where Planter Outlet 2 did not collect a sample due to pump tubing failure. As a result, across the storm sampling period and the ten storms that were sampled; there were 10 samples collected from both Planter Inlet and Outlet 1, 9 samples collected from Planter Inlet and Outlet 2, and 9 samples collected from Planter Inlets and Outlets 3 and 4. Since each bioretention planter box was duplicated (i.e. both Planter Boxes 1 and 3 contained the zeolite underlayer), there was a total of 37 Inlet samples, 19 zeolite underlayer Planter Box outlets, and 18 SHA BSM Planter Box outlets samples collected.

Water Chemistry Analysis

Both zeolite and BSM planter boxes substantially increased the alkalinity of the effluents compared to inlet values (log-scale) with zeolite outlets averaging a higher alkalinity compared to BSM outlets (Figure 16 and Table6). The average alkalinity of inlet values was 8.05 mg/L CaCO₃ while the averages for both zeolite and BSM planter box outlets being over ten times higher with averages of 156 and 144 mg/L CaCO₃ respectively. Also, zeolite and BSM planter boxes increased the average NPOC within

effluents compared to inlet values; however, BSM outlets averaged higher NPOC concentration corresponding to the low % C of zeolite. The average NPOC for inlets was 4.3 mg/L C with both planter boxes increasing the NPOC in effluents by a factor of 4 with an average of 16.5 mg/L C for zeolite planter boxes and 17.9 mg/L C for BSM planter boxes. Both planter boxes increased the pH of effluents compared to inlet values with zeolite planter boxes averaging a higher pH for effluents compared to BSM planter boxes with an inlet average of 6.36 and zeolite planter box effluents averaging a pH of 7.88 and BSM planter box effluents a pH of 7.72. The total cation and anion concentrations were calculated for each stormwater sample rather than expressing the concentration of each individual cation and anion to simplify results while still investigating the overall effects that each planter box had on altering the water chemistry of the stormwater passing through the bioretention system (Figure 17 and Table 7). Zeolite and BSM planter boxes both greatly increased the total anion and cation concentrations compared to inlet values (log-scale) with zeolite planter boxes averaging both higher anion and cation values. The average inlet total cation concentration was 0.29 meq/L compared to Zeolite planter boxes (mean=3.91 meq/L, n=19) and SHA BSM planter boxes (mean=3.14 meq/L, n=18) with no significant difference using a one-way ANOVA between the planter box effluents (p=0.243). The total cation concentration in the zeolite planter box effluents was altered by the sodium concentration which was substantially higher for all storms compared to inlet and BSM planter box effluent, while SHA BSM planter box effluents tended to be slightly higher in calcium, magnesium and potassium concentrations compared to zeolite planter box effluents. The average inlet total anion concentration was 0.19 meq/L compared to zeolite and SHA BSM planter box effluents that had total anion concentration averages of 1.51 and 0.40 meq/L, respectively. Total anion concentrations were significantly greater,

using a one-way ANOVA, in zeolite planter boxes (n=19) effluent compared to BSM planter box effluents (n=18, p=0.002). The total anion concentration in the zeolite planter box outlets was substantially altered by the sulfate concentration which were always much higher in zeolite planter box effluents compared to SHA BSM.

Copper Attenuation and Load Reduction

Copper loading and load reductions percentages were calculated utilizing the copper concentrations and total flow data from the flow-weighted data loggers. Zeolite and BSM planter boxes both greatly reduced the copper concentration in effluents compared to inlet average of 934 $\mu\text{g/L}$ demonstrating the ability of both planter boxes to attenuate copper (Figure 18 and Table 8). Zeolite planter boxes had lower copper concentrations in effluents (mean= 17.7 $\mu\text{g/L}$, n=19), which were significantly lower than the SHA BSM planter box concentration (mean=29.2 $\mu\text{g/L}$, n=17, p-value=0.028). The copper loading and load reduction percentage was calculated for all storm events where samples were collected from a corresponding Inlet and Outlet pairings, except for the 170729 storm where flow data was deemed unreliable due to clogging of multiple gutters with leaf litter and other debris that was not addressed prior to the storm event. Copper load reduction percentage was higher for zeolite planter boxes (97.5%) compared to BSM planter boxes (93.4%) demonstrating the ability of the zeolite planter boxes to attenuate additional copper in stormwater compared to planter boxes containing standard bioretention media.

Biotic Ligand Modeling Outcomes

The Biotic Ligand Model (BLM) was utilized to determine how each planter box altered the water chemistry of the stormwater by analyzing changes in potential toxicity of copper in each stormwater sample. The BLM utilizes all the water chemistry parameters previously discussed to determine the potential lethal concentration to 50 % of *Daphnia*

magna population for Inlets (I), zeolite planter boxes effluents (Z), and BSM planter box effluents (B). The BLM analysis conveyed that both zeolite and BSM planter boxes drastically alter the potential toxicity of copper to *Daphnia magna* with Cu LC₅₀ of averages of 488.5 µg/L and 339.0 µg/L, respectively (Figure 19). The planter boxes on average increased the LC₅₀ by almost a factor of 50 (log-scale) compared to the average inlet value of 8.2 µg/L. Additionally, zeolite planter boxes averaged higher LC₅₀ values compared to BSM planter boxes demonstrating that zeolite planter boxes altered the water chemistry of effluents in a manner which better protects aquatic biota from the potential toxicological effects of copper.

Another analysis performed by the BLM was the calculation of Toxic Units (TU). TUs are calculated to provide a simplistic, easily-understandable value to convey overall toxicity of a toxicant or toxicant mixture. The TU value was calculated by dividing the dissolved copper concentrations (µg/L) by the Final Acute Value (µg/L) (FAV) provided by the US EPA Water Quality Criteria modeling using the BLM. The FAV is defined as the concentration of a chemical corresponding to a cumulative probability of 0.05 from acute toxicity tests for a defined genera where a TU < 1 would be protective, and TU > 1 would not be protective. This analysis demonstrated that for all storm events the bioretention planter boxes decreased the TUs compared to inlet values, with zeolite underlayer planter boxes consistently having lower associated TUs compared to SHA BSM planter boxes (Figure 20).

Discussion

Copper Attenuation and Load Reduction

SCMs and bioretention structures have been shown repeatedly to attenuate metals in stormwater at relatively high percentages and greatly reduce the loading of metals due to

the influx of stormwater (Davis et al. 2003; LaBarre et al. 2016; LeFevre et al. 2015; Trowsdale and Simcock 2011; Wang et al. 2016). In a previous field study, bioretention planter boxes reduced influent copper concentrations to an average planter box effluent of 66 $\mu\text{g/L}$, a reduction of approximately 94% (LaBarre et al. 2016). Additionally, these bioretention planter boxes reduced the copper loading by an average of approximately 91%. In comparison, this field study conveyed slightly different results, with both zeolite and SHA BSM planter boxes performing more efficiently compared to the LaBarre et al. (2016) planter boxes. On average, the SHA BSM planter boxes exported copper concentrations of 30 $\mu\text{g/L}$ with a load reduction ranging from 90-99%, consistent and slightly better than the range of the previous study. The zeolite planter boxes, on average, had copper concentrations of 11 $\mu\text{g/L}$ in effluents with a load reduction ranging from 95-99%. These results show that zeolite planter boxes tended to outperform SHA BSM and LaBarre et al. (2016) planter boxes both in terms of copper concentration in effluents and total copper load reduction from copper roof runoff (Figure 18). The first storm event sampled, 170605, did have higher effluent copper concentrations from the SHA BSM planter boxes compared to all other storms, and the only storm where effluent copper concentrations exceeded 100 $\mu\text{g/L}$. While this storm appears as an outlier, there may have been some phenomena occurring which can explain these difference. The primary difference seen during this storm events was the total cation concentration in planter box effluents were 1.80 meq/L compared to the SHA BSM planter box average from all storms events of 3.14 meq/L. It appears that during this storm event there was less cation exchange occurring resulting in lower cation concentration in effluents and higher copper concentrations. This is likely to occur at a lower pH; however, the rainfall pH was similar to all other storm events and the zeolite planter box copper effluents were similar for this

storm as all other storm events. While this storm event did have elevated copper effluents from the SHA BSM planter boxes, a full understanding of the phenomena occurring has not been formulated.

There are a multitude of factors which influence the ability of these bioretention planter boxes to attenuate copper, but this study was centered on simply investigating whether the addition of zeolite as an underlayer would increase copper attenuation and reduce the potential toxicity of copper in stormwater runoff. It appears as though the zeolite underlayer (mean= 17.7 $\mu\text{g Cu/L}$, n=19) did significantly reduce the copper concentrations in planter box effluents and promote a larger load reduction compared BSM planter boxes (mean=29.2 $\mu\text{g Cu/L}$, n=17, p-value=0.028). The main mechanism by which the zeolite planter boxes increased attenuation was likely through surface adsorption or cation exchange.

Previous studies, like LaBarre et al. (2016), demonstrated that the ability of these bioretention planter boxes to attenuate Cu was dependent on the precipitation dynamics including total rainfall volume and intensity. While it is extremely likely that these factors are of importance, this study did not look into these effects on copper attenuation or load reduction. The storm sampling period for this study was relatively short, May to October, and the majority of the storm sampled were afternoon thunderstorms which in the Maryland region are characteristically short-lived with high intensity rainfall. There is likely a balance between storm duration, intensity, and volume that impacts the hydrology within the planter boxes and ultimately the copper attenuation ability; but these factors were not considered or investigated. This study did demonstrate that the application of a zeolite underlayer can have a substantial impact on the copper attenuation, so additional

studies are warranted to understand how the hydrological dynamics can be altered to further increase the copper attenuation.

Reduction of Toxicity via Bioretention Planter Boxes

Bioretention planter boxes have been shown to drastically reduce the toxicity of metals in stormwater runoff from various sources (i.e urban, agricultural, highway, and roofing runoff) by both reducing the concentration of metal in effluents, but also by altering the effluents' water chemistry. These SCMs tend to elevate pH, dissolved organic matter (DOM or NPOC), and the concentration of major cations and anions (i.e. calcium, magnesium, sodium, sulfate, chloride, etc.) (Davis et al. 2003; LaBarre et al. 2017; J. K. McIntyre et al. 2014; McIntyre et al. 2016; McIntyre et al. 2015). By doing so, bioretention planter boxes lower the toxicity of metals by reducing the bioavailability or increasing competition for binding onto gill surfaces or biotic ligand to cause a toxicological effect.

pH

The bioretention planter boxes, containing SHA BSM (mean= 7.72, n=18) and zeolite underlayer (mean=7.88, n=19, p=0.0695) both substantially increased the pH of effluent stormwater compared to average inlet values (Figure 16). The pH of stormwater can greatly alter the potential toxicity of copper by deprotonating dissolved ligands making them available for binding copper, and increasing $[OH^-]$ concentration. Hydroxides have a high binding affinity for copper to form copper hydroxides reducing copper's bioavailability (Di Toro et al. 2001)

This field study yielded similar results as previous bioretention studies including LaBarre et al. (2017). The average Inlet pH of 6.6 compared to 6.4 in this field study was increased to an average of 7.65 from planter boxes containing BSM compared to the 7.72 average pH in the effluents of the SHA BSM planter boxes (LaBarre et al. 2017). In

comparison to these planter boxes containing similar media formulation of standard bioretention media, the planter boxes containing the zeolite underlayer, on average, had a pH of 7.88 in effluent stormwater. Zeolites have been shown to increase the pH of runoff by exchanging H^+ ions in solution and binding these H^+ onto the zeolite surface releasing sodium, calcium, and/or magnesium (Shi et al. 2009). Zeolite when placed as a layer underneath standard bioretention media can be a buffer for the stormwater which can promote additional pH alteration due to zeolite having a higher soil pH compared to the SHA BSM (Table 5). Overall, the ability of zeolite underlayer planter boxes to promote a higher pH in the stormwater effluents compared to SHA BSM planter boxes demonstrates that an amendment of zeolite in bioretention media applications centered around the attenuation of copper, and similar metals, can be beneficial, but the limestone drainage layer likely had the greatest effect of effluent pH.

Dissolved Organic Matter

SCMs, like bioretention planter boxes, can alter the dissolved organic carbon (DOC) in effluents depending on the initial concentration prior to treatment. In highway runoff situations, bioretention planter boxes have been shown to decrease the dissolved organic matter concentration due to the relatively high concentration entering the SCM (McIntyre et al. 2014). In these situation, metals which are bound to the high concentration of dissolved OM are then sequestered in the bioretention cells which limit the ability of the metal-bound DOM to be released in the effluents (McIntyre et al. 2016). In roof runoff situations, similar to this study, where influent DOC concentrations are relatively low and influent metal concentrations are relatively high, bioretention planter boxes have been shown to elevate the DOM in effluents; therefore, binding and reducing the bioavailability of metals (LaBarre et al. 2017). DOM has a relatively high binding affinity for copper, so

in copper roof runoff environments, DOM is extremely important in binding the higher copper concentration in influent stormwater.

Both bioretention planter boxes substantially increased the DOC concentration in effluents compared to inlets values (Figure 16). On average, these bioretention planter boxes increased DOC by a factor of four ranging from 16-18 mg/L C from influent concentrations of about 4.0 mg/L C. In comparison, LaBarre et al. (2017), found similar results, where influent roof runoff DOC concentrations were low, approximately 4.0 mg/L C, and bioretention planter box effluents were increased to about 13 mg/L C. One concern in utilizing any soil amendment as an underlayer in bioretention planter boxes, especially in copper roof runoff situation, was potentially decreasing the DOC in effluents which is important in reducing the toxicity of copper. DOC has been shown to be the most important factor in reducing copper toxicity in aquatic system (Erickson et al. 1996). Due to zeolite's low organic carbon content (Table 5) a concern was that a zeolite underlayer would reduce the DOC concentration in stormwater effluents. While this did occur and the zeolite underlayer planter boxes averaged lower DOC exports compared to the SHA BSM planter boxes, the averages were similar and within standard error. As a result, it does not appear that a zeolite underlayer compromises the DOC concentration in stormwater effluents in any substantial manner that may adversely affect the ability of these planter boxes to reduce the copper concentration and toxicity from copper roof runoff. This study, along with LaBarre et al. (2017) demonstrated that bioretention planter boxes containing BSM or BSM with a zeolite underlayer can both increase the DOC concentration which is highly important in attenuating copper and reducing copper's bioavailability.

Major Cations and Anions

Bioretention SCMs have a substantial effect on the water chemistry, specifically the major ion concentrations, of effluent stormwater (LaBarre et al. 2017). In general, both zeolite and SHA BSM planter boxes greatly increased both the total cation and anion concentrations compared to inlet concentrations (Figure 17). The cation concentrations in effluent stormwater alter the potential toxicity of copper in planter box effluents when ions like calcium, magnesium, potassium, and sodium compete with copper for binding onto the biotic ligand (Santore et al. 2001). The anion concentrations are equally important as cations where ions like, carbonate, bicarbonate, sulfate, and chloride can form inorganic complexes with copper in solution which reduces the bioavailability of copper greatly (Niyogi and Wood 2004). The cation and anion concentrations in bioretention effluents are highly dependent on the media within the planter boxes with substantial difference in individual cation and anion concentrations between zeolite underlayer and SHA BSM planter boxes were observed through the field study.

Both zeolite and SHA BSM planter boxes substantially increased cation and anion concentration from average influent values of approximately 0.15 meq/L (cations) and 0.20 meq/L (anions) with all individual cations and anions increasing in concentration post-treatment. Similarly, in LaBarre et al. (2017) all stormwater samples from bioretention planter box effluents increased all cation and anion concentrations; however, cations like sodium and magnesium increased slightly. In general, the bioretention planter boxes, from this study and LaBarre et al. (2017) had similar impacts on the cation and anion water chemistry in the effluent stormwater, but there were some key differences in individual cation and anion averages between media formulations. One vital difference in the SHA BSM and zeolite planter boxes was the average sodium concentration in stormwater

effluents. On average, SHA BSM increased sodium concentrations rather negligibly from 1.0 mg/L inlet values to approximately 4.1 mg/L which corresponds well with results from the previous field study (LaBarre et al. 2017). In contrast, zeolite planter boxes increased sodium concentrations to approximately 65.9 mg/L on average likely due to the high sodium content of natural clinoptilolite zeolite especially in zeolites from natural sources which tend to have higher concentrations of sodium compared to calcium and potassium (Shi et al. 2009). This large increase in sodium in zeolite compared to SHA BSM planter boxes was the primary source of additional total cation concentration allowing zeolite planter boxes to continually export higher total cation concentrations on average compared to SHA BSM planter boxes. The average concentration of other cations (magnesium, calcium, and potassium) were all slightly higher in SHA BSM planter box effluents and comparable to, LaBarre et al. (2017); however these higher concentrations did not have enough of an effect to increase the total milliequivalence of (+) charge to concentrations similar to zeolite planter box effluents. The elevated export of sodium and the additional attenuation of copper concentrations and loading seen in zeolite underlayer planter boxes was likely related. Sodium ions tends to have the lowest binding affinity and more available for exchange with other cationic species with higher binding affinities like copper, calcium, magnesium, and potassium (Sposito 2008).

Also, another difference in cation and anion concentration in effluents was the sulfate concentration which was substantially higher in zeolite planter boxes (59.4 mg/L) compared to SHA BSM planter boxes (10.7 mg/L), both of which increased the sulfate concentration from an average inlet value of 2.9 mg/L. The SHA BSM planter boxes exported similar sulfate concentrations to the bioretention planter boxes in LaBarre et al. (2017) where sulfate concentrations were about 7 mg/L on average. The elevated sulfate

concentrations in zeolite planter boxes effluents provided additional inorganic ligands for the complexation of copper to form copper sulfate in solution reducing the bioavailability of copper in effluents. The higher sulfate concentration may be due to the ability of zeolites to carry and slowly release sulfates from soils (Li 2003). It is possible that between storm events sulfate from the overlying SHA BSM leaches into the zeolite layer which can then be released during storm events resulting in higher sulfate concentration from zeolite planter boxes. Regardless, the elevated sulfate concentration in zeolite planter boxes significantly increases the total milliequivalence of (-) charge in stormwater effluents compared to SHA BSM planter boxes providing additional inorganic ligands for copper complexation.

LC₅₀ and TU

The overall effects of the water chemistry alterations due to the bioretention planter boxes can be modeled using the Biotic Ligand Model (BLM) by analyzing the differences in LC₅₀ to *Daphnia magna* in effluent compared to influent stormwater. Numerous studies have demonstrated the ability of bioretention planter boxes to lower the toxicological effects of metals in highway and urban runoff (McIntyre et al. 2014; McIntyre et al. 2016; McIntyre et al. 2015; Trenouth and Gharabaghi 2015) and specifically from copper roof runoff (LaBarre et al. 2017). These studies have shown that untreated stormwater can have significant toxicological endpoints on aquatic organisms like juvenile Coho salmon, zebrafish, and *Daphnia magna* while similar stormwater post-bioretention treatment has these toxicological effects greatly reduced and in some cases, non-existent. This field study portrayed similar results with both bioretention planter boxes greatly reducing the potential toxicity of copper seen modeled by the theoretical LC₅₀ of copper to *Daphnia magna* using the BLM (Figure 19). For all storm events, the influent copper concentration was

substantially higher than the modeled LC₅₀ for inlets (7 µg/L) so for all storm events influent stormwater would result in acute mortality to *Daphnia magna*. These results were approximately the same as results seen in LaBarre et al. (2017) where the average LC₅₀ for inlet stormwater was 9 µg/L with all influent storm samples having much higher copper concentrations. In general, both zeolite and BSM planter boxes alter the water chemistry to an extent where the modeled LC₅₀ increased by over a factor of 10, comparable to LaBarre et al. (2017). For no storm events did the bioretention planter box effluents contain copper concentrations which exceeded the modeled LC₅₀. Overall, zeolite planter boxes had higher modeled LC₅₀ values compared to SHA BSM likely due to the higher pH, alkalinity, total cation, and total anion concentrations. Bioretention planter boxes equipped with a zeolite underlayer provide a more protective environment compared to BSM without compromising copper attenuation.

In addition, the TU analysis corroborates the results from the LC₅₀ BLM analysis. The TU analysis is more straightforward to understand compared to the LC₅₀ analysis where a higher value is more toxic compared to the LC₅₀ where a higher value corresponds to a better environment. The TU analysis relates the water chemistry alterations and copper attenuation ability of the planter boxes into a cumulative effect. As a result, the TU analysis can provide a full understanding of the overall effects and potential benefits that each bioretention planter boxes can have for attenuating copper and reducing toxicity of copper in stormwater effluents. Any TU greater than 1 would not be a protective environment for aquatic biota, while any TU less than 1 would be protective. For all storm events, the TU associated with the influent stormwater was much greater compared to the TU associated with both the zeolite and SHA BSM planter boxes (Figure 20). For all storm events, influent samples had TU greater than 1 and nearly all planter box effluents samples

had TU less than 1. The zeolite planter boxes consistently had lower TU associated with the effluents compared to the SHA BSM planter boxes for all storm events, similar to the LC₅₀ analysis. The lower TU associated with the zeolite underlayer planter box effluents demonstrate that these planter boxes tend to have higher attenuation of copper and a greater effect on the water quality to protect aquatic biota against the toxicological impacts of copper in copper roof runoff.

Conclusions

This field study set out to answer three questions: How does the soil amendment perform in a field environment? Can this soil amendment consistently achieve effluent copper concentrations $<14 \mu\text{g L}^{-1}$? And can this soil amendment be incorporated into bioretention structures while maintaining LID and LCD designs? The study did accomplish the goals of answering these questions; however, additional questions arise as a result. The field study corroborated results from the column studies that the application of a zeolite underlayer can increase copper attenuation, and while the copper concentrations were not consistently below the proposed $14 \mu\text{g/L}$ regulatory threshold, the concentrations were consistently lower than effluents from previous bioretention studies and the SHA BSM planter boxes from this study (LaBarre et al. 2016). Additionally, the zeolite planter boxes consistently provided a more protective environment by reducing the potential toxicity of copper in stormwater effluents through an increase in cation and anion concentrations, pH, and alkalinity. The accumulation of these two keys results demonstrate that the application of a 1:3 zeolite underlayer in bioretention planter boxes can increase copper attenuation and reduce copper toxicity compared to standard bioretention media, answering the first two questions set out to be answered by this field study. The final question could be answered simply by analyzing the cost of the zeolite compared to the cost of BSM to

determine if the zeolite is cost efficient for the additional copper attenuation and toxicity reduction. The zeolite obtained for this study was available a similar cost compared to the SHA BSM, so the incorporation of the zeolite underlayer did not increase the cost in any substantial manner. As a result, a 1:3 zeolite underlayer can be incorporated into the bioretention planter boxes while maintaining the LIC and LCD designs which would allow homeowners and businesses with copper roofs to utilize these structures to mitigate the potentially hazardous effects of their roofs. Overall, a zeolite underlayer can improve the effectiveness of bioretention planter boxes for copper attenuation, load reduction, and toxicity in copper roof runoff and should be considered for future bioretention projects. Additionally, in general, media formulations within bioretention structures should be customized from each situation depending on the pollutants of concern, as this study and others have demonstrated that the media formulation can greatly impact the performance of these structures (LaBarre et al. 2017; Reddy, Xie, and Dastgheibi 2014a; Trenouth and Gharabaghi 2015; Wang et al. 2016).

Figures and Tables

Table 5. SWMMWW (Stormwater Management Manual of Western Washington) SWMMWW requirements for "custom" bioretention media along with the results from the characterization of the MD SHA BSM and Raw Supply Granular zeolite. pH (n=6) is expressed with range of standard error; CEC is expressed as the standard error range of CEC (n=4) for each amendment/soil type in meq/100 g dry soil, % Organic Matter is expressed as average % Organic Matter by weight (n=3) for each with standard error range, % Fines is expressed as the average percentage smaller (n=4) than #200 Sieve by weight for each, and acid extractable copper is expressed as average (n=5) mg Cu/kg of dry soil for each.

Soil/Amendment	Soil pH	CEC	% Organic Matter	% Fines	Acid Extractable Cu
SWMMWW	5.5 - 7.0	> 5	5-8	2-5	750
BSM	6.99 ±0.07	2.0-2.5	1.23 ±0.29	0.00	15.89±0.53
Zeolite	7.64 ±0.06	1.75-2.45	0.02 ±0.004	0.62 ±0.04	6.26±1.57

Table 6. All stormwater dissolved copper, NPOC, pH, and alkalinity data from every available storm date and site during the testing period. The site date follows the following naming scheme: YearMonthDate (all two digit numeration). Planter Inlets are abbreviated (PI) with inlets (1 and 3) representing the Planter Boxes containing the zeolite underlayer, and (2 and 4) representing the Planter Boxes containing the Bioretention Standard Media (BSM). Planter Outlets are abbreviated (PO) with outlets (1 and 3) representing the Planter Boxes containing the zeolite underlayer, and (2 and 4) representing the Planter Boxes containing the Bioretention Standard Media (BSM). The Plexiglass control structure is abbreviated as (C1). All "NA" denote that the concentration was below the LOQ and therefore not reported.

Storm Date	Site Name	Dissolved Cu (µg/L)	Alkalinity (mg/L CaCO ₃)	NPOC (mg/L)	pH
170605	PI-1	970.2	10	6.777	6.46
170605	PI-2	828.8	12	10.77	6.6
170605	PI-3	1055	8	6.341	6.33
170605	PI-4	799.4	12	7.043	6.31
170605	PO-1	21.01	192	14.46	7.72
170605	PO-2	194.2	112	13.16	7.26
170605	PO-3	36.61	216	21.67	7.83
170605	PO-4	197.3	120	16.04	7.25
170619	PI-1	941.2	8	5.64	6.13
170619	PI-2	691.7	8	5.006	6.22
170619	PI-3	782.9	6	4.429	6.17
170619	PI-4	653.8	6	3.666	6.07
170619	PO-1	31.93	100	9.686	7.54
170619	PO-2	62.3	116	15.91	7.38
170619	PO-3	44.16	232	30.88	7.86
170619	PO-4	51.03	168	23.54	7.48
170624	PI-1	568.5	8	4.474	6.44
170624	PI-2	444.8	6	5.731	6.46
170624	PI-3	259.2	8	5.036	6.54
170624	PI-4	464.3	8	3.72	6.41
170624	PO-1	16.79	160	16.31	7.92
170624	PO-2	18.36	260	24.8	8.24

Storm Date	Site Name	Dissolved Cu ($\mu\text{g/L}$)	Alkalinity (mg/L) CaCO_3	NPOC (mg/L)	pH
170624	PO-3	23.01	320	34.75	8.31
170624	PO-4	17.69	320	28.42	8.25
170706	PI-1	996.7	6	6.703	6.31
170706	PI-2	638.8	4	3.415	6.09
170706	PI-3	589.9	4	2.92	6.12
170706	PI-4	621.9	6	3.379	6.14
170706	PO-1	14.59	164	27.11	7.49
170706	PO-2	64.28	108	14.77	7.66
170706	PO-3	30.01	168	16.69	8.08
170706	PO-4	28.66	120	30.36	7.69
170706	C1	6.927	NA	5.356	5.84
170714	PI-1	749.6	8	4.388	6.34
170714	PI-2	869.6	8	3.84	6.37
170714	PO-1	14.47	160	11.55	7.98
170714	PO-2	23.87	164	17.36	7.71
170714	C1	21.55	NA	6.172	5.94
170722	PI-1	1447	8	5.926	6.41
170722	PI-2	1115	10	5.106	6.51
170722	PI-3	1393	8	4.207	6.48
170722	PI-4	1277	8	4.049	6.49
170722	PO-1	14.84	152	16.69	7.89
170722	PO-2	28.33	160	17.19	7.65
170722	PO-3	31.09	160	14.43	7.95
170722	PO-4	29.11	160	17	7.68
170722	C1	14.15	NA	8.754	6.12
170729	PI-1	1024	8	2.235	6.29
170729	PI-2	823.5	6	2.239	6.21
170729	PI-3	947	6	2.081	6.45
170729	PI-4	849.3	6	3.496	6.56
170729	PO-1	6.185	92	8.377	7.89
170729	PO-2	14.6	100	10.84	7.71
170729	PO-3	7.071	128	11.37	8.12
170729	PO-4	16.79	92	20.99	8.2
170729	C1	4.553	NA	3.581	5.86
170815	PI-1	802.2	8	2.167	6.21
170815	PI-2	1007	8	2.817	6.26
170815	PI-3	1683	8	3.099	6.39
170815	PI-4	1584	8	2.62	6.37
170815	PO-1	4.46	176	14.43	7.77
170815	PO-2	35.23	132	12.64	7.42
170815	PO-3	10.56	140	12.5	7.87

Storm Date	Site Name	Dissolved ($\mu\text{g/L}$)	Cu	Alkalinity (mg/L) CaCO_3	NPOC (mg/L)	pH
170815	PO-4	9.99		140	5.172	7.39
170815	C1	0.779		NA	3.411	5.9
170829	PI-1	1162	8		3.212	6.18
170829	PI-2	1324	6		3.588	6.33
170829	PI-3	878.9	8		3.104	6.32
170829	PI-4	1196	8		2.65	6.3
170829	PO-1	5.97	116		9.871	8.02
170829	PO-3	7.469	136		10.07	8.04
170829	PO-4	24.52	160		17.8	7.97
170829	C1	3.559	NA		5.583	5.87
171008	PI-1	885.5	8		4.613556	6.66
171008	PI-2	926.3	8		4.723556	6.45
171008	PI-3	1390	20		3.902125	6.75
171008	PI-4	885	12		3.827875	6.62
171008	PO-1	6.139	56		14.276	7.54
171008	PO-2	13.08	80		15.83375	7.86
171008	PO-3	8.597	108		19.045	7.97
171008	PO-4	29.82	88		19.91525	8.09

Table 7. All stormwater cation and anion data from every available storm date and site during the testing period. The site date follows the following naming scheme: YearMonthDate (all two digit numeration). Planter Inlets are abbreviated (PI) with inlets (1 and 3) representing the Planter Boxes containing the zeolite underlayer, and (2 and 4) representing the Planter Boxes containing the Bioretention Standard Media (BSM). Planter Outlets are abbreviated (PO) with outlets (1 and 3) representing the Planter Boxes containing the zeolite underlayer, and (2 and 4) representing the Planter Boxes containing the Bioretention Standard Media (BSM). The Plexiglass control structure is abbreviated as (C1). All "NA" denote that the concentration was below the LOQ ($< 1 \text{ mg/L}$) and therefore not reported; for the analysis using the Biotic Ligand Model any cation or anion concentration below LOQ was reported as 1 mg/L for the computation model.

Storm Date	Site Name	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
170605	PI-1	1.51	3.62	NA	3.75	3.13	3.00	NA	3.25
170605	PI-2	2.93	4.56	3.88	3.76	3.48	2.98	NA	3.84
170605	PI-3	1.36	2.42	3.87	3.82	3.06	3.02	NA	3.14
170605	PI-4	1.55	4.17	NA	3.87	3.20	3.13	NA	3.54
170605	PO-1	12.66	8.26	NA	16.76	3.50	6.42	NA	86.27
170605	PO-2	5.45	9.49	5.32	16.79	9.21	NA	NA	5.98
170605	PO-3	24.64	15.64	7.94	31.25	25.81	3.19	NA	201.10
170605	PO-4	6.52	9.93	6.13	16.99	9.26	NA	NA	5.94
170619	PI-1	1.67	2.76	3.97	3.92	2.84	3.03	NA	3.11
170619	PI-2	1.36	2.64	3.90	3.72	2.74	2.93	NA	2.87
170619	PI-3	1.48	2.49	3.90	3.63	2.78	3.01	NA	2.99
170619	PI-4	1.51	2.00	3.86	3.72	2.71	3.15	NA	3.18

Storm Date	Site Name	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
170619	PO-1	71.39	6.17	4.56	15.22	3.05	4.70	NA	67.80
170619	PO-2	5.66	17.33	1.29	33.79	3.67	NA	NA	8.20
170619	PO-3	198.53	16.67	1.19	3.53	7.92	3.80	NA	199.25
170619	PO-4	2.99	14.23	17.72	65.30	2.96	NA	NA	9.78
170624	PI-1	1.32	1.66	3.97	4.18	2.62	2.99	NA	2.85
170624	PI-2	1.26	1.62	3.92	3.88	2.66	2.98	NA	2.83
170624	PI-3	1.26	1.58	4.27	4.19	2.77	2.95	NA	2.91
170624	PI-4	1.37	1.56	3.94	3.83	2.64	2.99	NA	2.61
170624	PO-1	86.37	6.82	NA	13.54	2.77	3.11	NA	21.08
170624	PO-2	2.16	14.25	21.12	65.32	2.88	2.95	NA	12.26
170624	PO-3	165.89	14.28	6.57	23.16	4.55	3.36	NA	65.33
170624	PO-4	1.97	14.16	23.61	8.79	NA	NA	NA	NA
170706	PI-1	0.22	NA	0.46	1.58	2.72	3.59	NA	2.85
170706	PI-2	NA	NA	0.38	1.47	2.97	4.77	NA	2.70
170706	PI-3	0.26	NA	0.35	1.59	2.70	3.53	NA	2.73
170706	PI-4	0.19	NA	0.38	1.75	2.59	3.54	NA	2.99
170706	PO-1	63.61	3.96	NA	9.53	3.04	3.40	2.27	19.43
170706	PO-2	1.99	1.47	3.52	22.42	3.03	NA	2.14	3.79
170706	PO-3	75.44	6.29	0.82	11.76	3.21	3.11	2.26	35.41
170706	PO-4	1.96	12.84	12.24	94.79	2.78	2.90	3.29	13.59
170706	C1	0.66	NA	0.39	2.13	2.55	3.50	NA	2.82
170714	PI-1	0.33	NA	0.35	1.58	2.64	2.96	NA	3.00
170714	PI-2	NA	NA	0.43	1.74	2.73	3.01	NA	3.19
170714	PO-1	92.64	6.72	1.91	17.95	2.90	3.12	NA	104.62
170714	PO-2	3.30	18.22	6.23	36.89	3.62	2.94	2.41	8.08
170714	C1	NA	0.44	0.38	1.84	2.71	3.06	1.91	3.09
170722	PI-1	NA	NA	0.53	1.85	2.75	2.95	NA	3.12
170722	PI-2	NA	NA	0.43	1.87	2.62	3.00	NA	2.99
170722	PI-3	NA	NA	0.44	1.83	2.65	2.95	NA	3.03
170722	PI-4	NA	0.25	0.39	1.97	2.59	3.02	NA	2.93
170722	PO-1	7.64	4.79	1.38	14.28	2.74	3.00	2.05	62.12
170722	PO-2	2.95	15.54	4.97	33.94	3.01	2.89	2.35	4.27
170722	PO-3	73.79	7.13	NA	1.96	2.83	3.01	2.35	24.56
170722	PO-4	2.55	16.79	6.73	36.25	3.11	2.90	2.40	4.57
170722	C1	NA	NA	0.33	1.55	2.69	3.12	NA	2.81
170729	PI-1	NA	NA	0.33	1.55	2.57	2.95	NA	2.75
170729	PI-2	NA	NA	0.28	1.39	2.55	2.94	NA	2.63
170729	PI-3	NA	NA	0.32	1.35	2.54	2.92	NA	2.57
170729	PI-4	NA	NA	0.32	1.60	2.55	2.90	NA	2.53
170729	PO-1	38.73	2.12	NA	6.81	2.63	2.90	2.03	10.05
170729	PO-2	0.76	8.67	3.42	24.49	2.75	NA	2.06	3.34

Storm Date	Site Name	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	PO ₄ ⁻³	SO ₄ ⁻²
170729	PO-3	52.56	5.00	NA	8.51	2.78	3.30	2.19	17.43
170729	PO-4	2.16	15.98	14.90	95.73	3.04	NA	3.32	11.93
170729	C1	NA	NA	0.38	1.75	2.57	2.93	NA	2.67
170815	PI-1	0.62	0.47	NA	0.87	2.68	3.24	NA	2.50
170815	PI-2	0.57	0.44	NA	0.98	2.82	3.38	NA	2.90
170815	PI-3	0.57	0.53	1.25	1.02	2.95	3.36	NA	3.06
170815	PI-4	0.58	0.59	1.27	1.20	2.96	3.51	NA	3.34
170815	PO-1	75.96	5.09	NA	9.80	2.96	3.28	NA	31.84
170815	PO-2	1.42	9.48	8.32	68.41	3.06	3.24	NA	10.43
170815	PO-3	46.61	4.81	NA	7.00	2.86	3.24	NA	12.60
170815	PO-4	0.86	5.38	4.95	33.78	2.86	3.21	NA	3.46
170815	C1	0.57	0.44	1.26	1.12	2.72	3.31	NA	2.62
170829	PI-1	1.36	0.50	1.26	0.99	4.22	3.21	NA	2.99
170829	PI-2	1.74	0.51	1.26	0.96	4.60	3.42	NA	3.41
170829	PI-3	1.19	0.50	NA	0.96	3.89	3.28	NA	2.86
170829	PI-4	1.36	0.52	1.28	1.06	4.15	3.30	NA	NA
170829	PO-1	57.85	3.90	1.60	7.75	3.68	3.22	NA	24.02
170829	PO-3	34.80	3.63	NA	5.93	3.31	3.28	NA	11.94
170829	PO-4	1.23	8.57	10.33	75.33	3.40	3.22	NA	12.98
170829	C1	1.18	0.52	NA	1.15	3.22	3.49	NA	3.00
171008	PI-1	0.59	2.96	0.41	1.63	NA	0.16	NA	NA
171008	PI-2	0.24	1.58	0.26	1.11	NA	NA	NA	NA
171008	PI-3	0.45	4.93	0.70	4.40	0.45	NA	NA	0.86
171008	PI-4	0.16	1.49	0.20	1.04	NA	NA	NA	NA
171008	PO-1	35.64	2.77	0.73	7.87	NA	NA	NA	57.84
171008	PO-2	0.18	3.45	3.02	26.77	NA	NA	NA	9.58
171008	PO-3	58.11	NA	NA	NA	NA	NA	NA	64.69
171008	PO-4	0.97	14.34	9.47	79.42	0.00	NA	NA	50.72

Table 8. All stormwater load reduction and loading reduction percentage data from every available storm date and site during the testing period. The site date follows the following naming scheme: YearMonthDate (all two digit numeration). Planter Outlets are abbreviated (PO) with outlets (1 and 3) representing the Planter Boxes containing the zeolite underlayer, and (2 and 4) representing the Planter Boxes containing the Bioretention Standard Media (BSM).

Storm Date	Site	Load Reduction $\mu\text{g/L Cu}$	Load Reduction %
170605	PO-1	10570.2	97.8
170605	PO-2	7066.9	76.6
170605	PO-3	11340.8	96.5
170605	PO-4	6705.0	75.3
170619	PO-1	27001.7	96.6
170619	PO-2	18690.7	91.0
170619	PO-3	21937.6	94.4
170619	PO-4	17899.9	92.2
170624	PO-1	11775.7	97.0
170624	PO-2	9101.9	95.9
170624	PO-3	5041.2	91.1
170624	PO-4	9532.4	96.2
170706	PO-1	42380.0	98.5
170706	PO-2	24791.7	89.9
170706	PO-3	24160.4	94.9
170706	PO-4	25599.5	95.4
170714	PO-1	16713.9	98.1
170714	PO-2	19228.5	97.3
170722	PO-1	13290.4	99.0
170722	PO-2	10084.3	97.5
170722	PO-3	12638.5	97.8
170722	PO-4	11580.4	97.7
170815	PO-1	22579.2	99.4
170815	PO-2	27505.0	96.5
170815	PO-3	47336.7	99.4
170815	PO-4	44550.8	99.4
170829	PO-1	42911.8	99.5
170829	PO-3	32347.5	99.2
170829	PO-4	43485.3	97.9
171008	PO-1	44882.6	99.3
171008	PO-2	46610.7	98.6
171008	PO-3	70506.8	99.4
171008	PO-4	43648.4	96.6

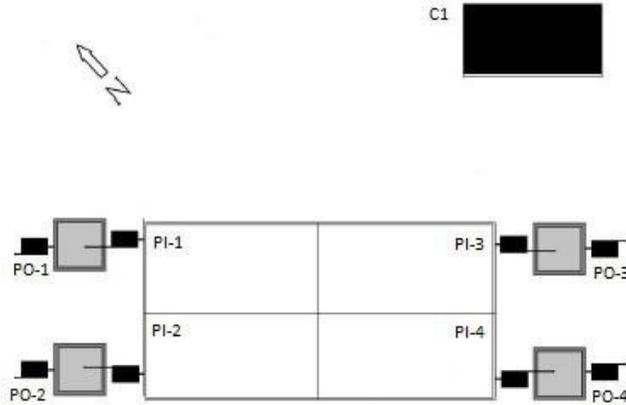


Figure 12. Plan View of Copper Roof Picnic Shelter Study Site. Adapted from (LaBarre et al., 2016). The four section of copper roof drain into each of the four bioretention planter boxes with sampling prior to the planter boxes (PI) and a sampling site at the effluents of the planter boxes (PO). PI-1, PI-3, PO-1, and PO-3 denote the bioretention planter boxes containing the zeolite underlayer, while PI-2, PI-4, PO-2, and PO-4 denote the control bioretention planter boxes containing only bioretention standard media (BSM). Also, C1 denotes the small Plexiglass reference structure which monitors any atmospheric deposition of copper during storm events.

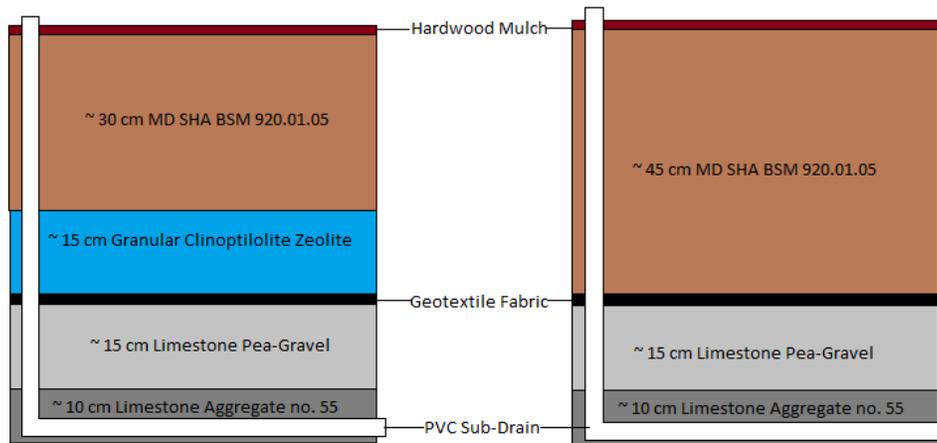


Figure 13. Cross-Section view of zeolite and SHA BSM Planter Boxes. Two of each planter boxes were filled following the fill sequence and media specifications in the figure. Each box contained a perforated PVC sub-drain, a limestone aggregate layer, a pea-gravel layer, geotextile fabric, Maryland State Highway Administration Bioretention Standard Media (MD SHA BSM) and a hardwood mulch layer. The perforated sub-drain had a PVC tube attached which exited through the top of the planter box. This portion was not perforated but was utilized as to wash out the sub-drain if clogging were to have occurred. Additionally, not shown in depiction, is a layer of vegetative cover that was transplanted from previous planter box after excavation.

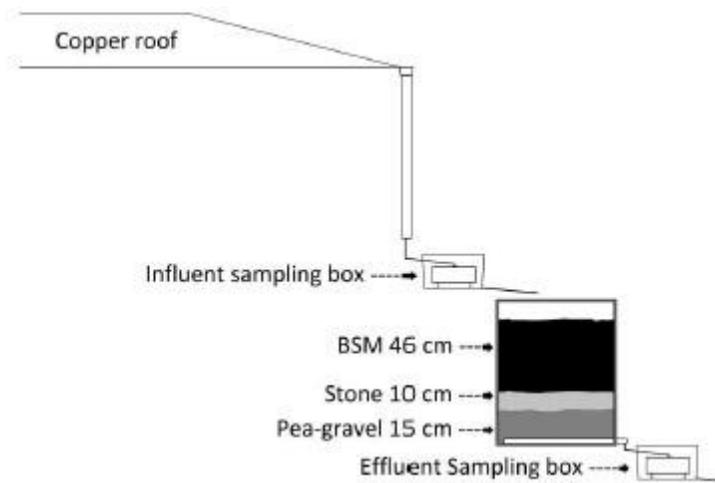


Figure 14. Side View of Copper Roof and Control bioretention Planter Box along with Influent and Effluent Sampling Boxes demonstrating the route that stormwater takes and the sampling process for each planter box (LaBarre et al., 2016). A Control Bioretention planter box is displayed; however, similar sampling design was constructed for all four bioretention planter boxes.

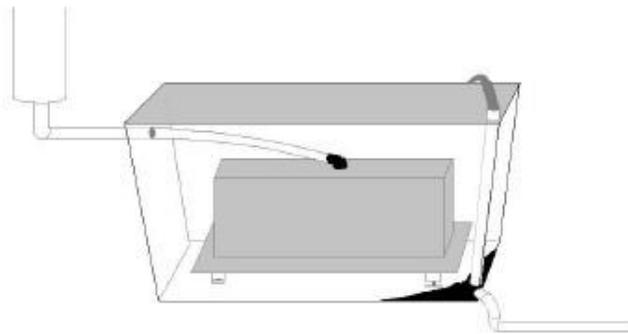


Figure 15. Side View of Sampling Box where stormwater flows into the box via a PVC pipe and into the flow gauge. Each sampling box is canted to allow pooling of water in the corner of the box for sampling via the automatic sampler and the excess then flows out to the planter box (PI) or to the ground (PO) (LaBarre et al., 2016).

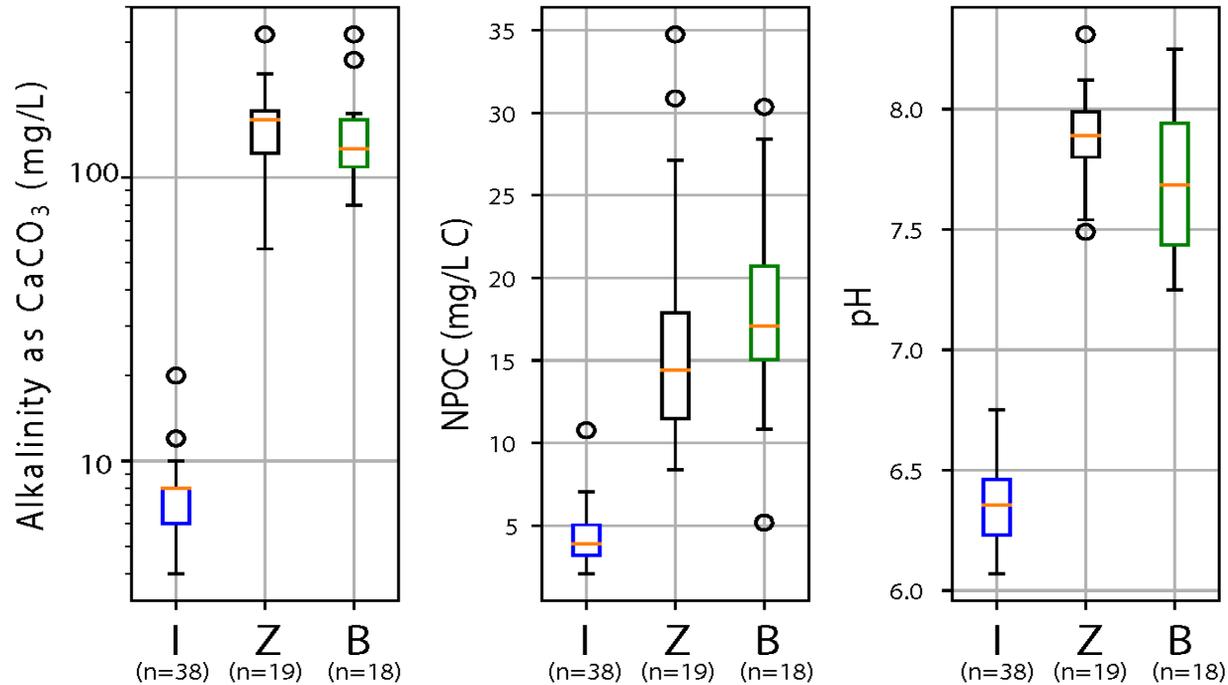


Figure 16. Box-and-Whisker Plots for Alkalinity, pH, and NPOC for all Inlet (I), zeolite underlayer Bioretention Planter Boxes (Z), and SHA BSM Bioretention Planter Boxes (B). Inlets are colored blue, zeolite planter box outlets are colored black, and SHA BSM planter box outlets with the orange line within each box-and-whisker plot denoting the median for each and the number of data points denoted by the (n-value) below each label. All open circles denote data points from each set that do not fall within the 3 x Interquartile Range (IQR). Individual data for all plots can be found in Table 4.3. Both zeolite and BSM planter boxes substantially increased the alkalinity of the effluents compared to inlet values (log-scale) with zeolite outlets averaging a higher alkalinity compared to BSM outlets. Also, zeolite and BSM planter boxes increased the average NPOC within effluents compared to inlet values; however, BSM outlets averaged higher NPOC concentration which corresponds to the low % C of zeolite. Finally, both planter boxes increased the pH of effluents compared to inlet values with zeolite planter boxes averaging a higher pH of effluents compared to BSM planter boxes. In general, these plots demonstrate that both planter boxes greatly affect the water chemistry of the effluents and provide a more protective environment (higher alkalinity, higher NPOC, and higher pH) compared to inlets with zeolite potentially outperforming BSM planter boxes.

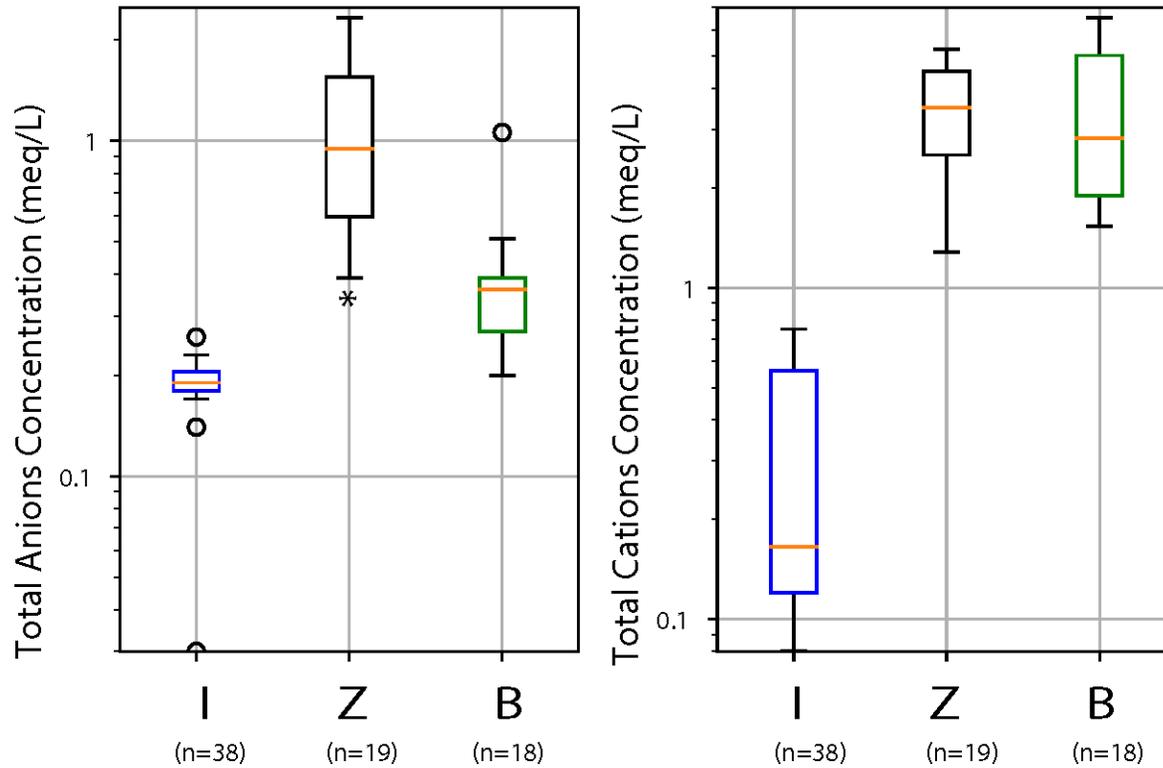


Figure 17. Box-and-Whisker Plots for Total Cation and Anion Concentration for all Inlet (I), zeolite underlayer Bioretention Planter Boxes (Z), and SHA BSM Bioretention Planter Boxes (B). Inlets are colored blue, zeolite planter box outlets are colored black, and SHA BSM planter box outlets with the orange line within each box-and-whisker plot denoting the median for each and the number of data points denoted by the (n-value) below each label. All open circles denote data points from each set that do not fall within the 3 x Interquartile Range (IQR). All (*) symbols denote statistically significant difference between the zeolite and BSM planter boxes. Individual data for all plots can be found in Table 4.3. Zeolite and BSM planter boxes both greatly increased the total anion and cation concentrations compared to inlet values (log-scale) with zeolite planter boxes averaging both higher anion and cation values. Total anion concentrations were statistically significant (p -value=0.002) in zeolite planter boxes effluent compared to BSM planter box effluents when analyzed using a one-way ANOVA with alpha of 0.05. In general, these plots demonstrate that both planter boxes greatly affect the water chemistry of the effluents and provide a more protective environment (higher total anion and cation concentrations) compared to inlets with zeolite outperforming BSM planter boxes.

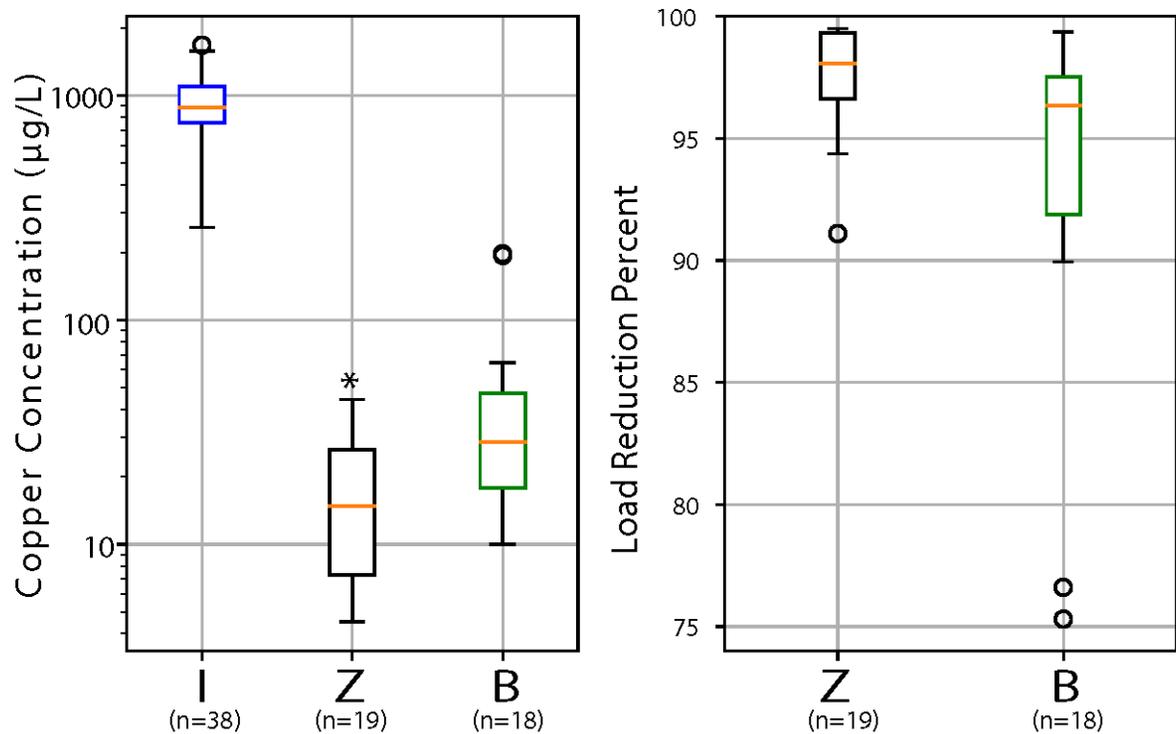


Figure 18. Box-and-Whisker Plots for Copper Concentration and Copper Load Reduction Percentage for all Inlet (I), zeolite underlayer Bioretention Planter Boxes (Z), and SHA BSM Bioretention Planter Boxes (B). Inlets are colored blue, zeolite planter box outlets are colored black, and SHA BSM planter box outlets with the orange line within each box-and-whisker plot denoting the median for each and the number of data points denoted by the (n-value) below each label. All open circles denote data points from each set that do not fall within the 3 x Interquartile Range (IQR). All (*) symbols denote statistically significant difference between the zeolite and BSM planter boxes. Individual data for all plots can be found in Table 4.2. Zeolite and BSM planter boxes both greatly reduced the copper concentration in effluents compared to inlet values. Zeolite planter boxes averaged lower copper concentrations in effluents which were statistically significant to the BSM planter boxes (p -value=0.028) when analyzed using a one-way ANOVA with $\alpha=0.05$. Copper load reduction percentage was substantially higher for zeolite planter boxes compared to BSM planter boxes demonstrating the ability of the zeolite planter boxes to attenuate additional copper in stormwater. In general, these plots demonstrate that both planter boxes greatly affect the copper concentration of the effluents and compared to inlets with zeolite outperforming BSM planter boxes.

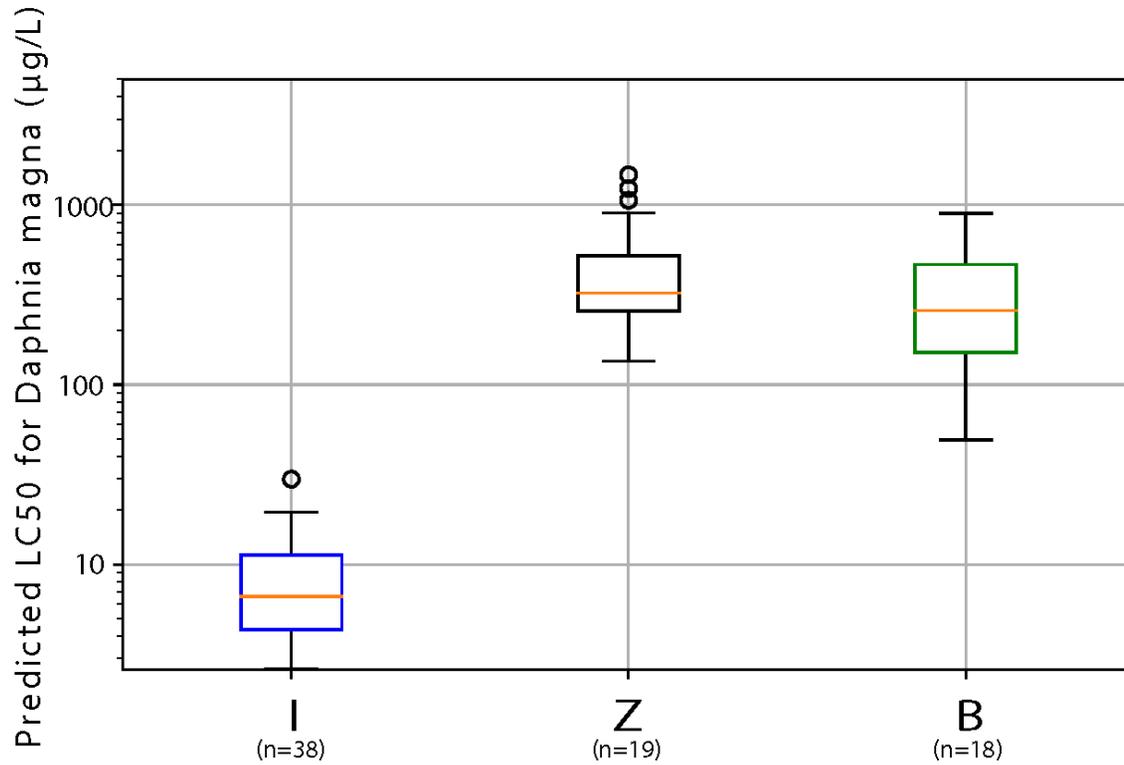


Figure 19. Box-and-Whisker Plots for LC₅₀ Copper Concentration for Daphnia magna for all Inlet (I), zeolite underlayer Bioretention Planter Boxes (Z), and SHA BSM Bioretention Planter Boxes (B). Inlets are colored blue, zeolite planter box outlets are colored black, and SHA BSM planter box outlets with the orange line within each box-and-whisker plot denoting the median for each and the number of data points denoted by the (n-value) below each label. All open circles denote data points from each set that do not fall within the 3 x Interquartile Range (IQR). The graph convey that both zeolite and BSM planter boxes drastically alter the potential toxicity of copper to Daphnia magna increasing the LC₅₀ by almost a factor of 100 (log-scale) compared to inlet values. Additionally, zeolite planter boxes averaged a higher LC₅₀ value compared to BSM planter boxes demonstrating that zeolite planter boxes alter the water chemistry of effluents in a manner which better protects aquatic biota from the potential toxicological effects of copper. Overall, these plots show that both planter boxes greatly reduce the potential toxicity of copper in the effluents from each planter box with the zeolite planter boxes likely outperforming the BSM planter boxes.

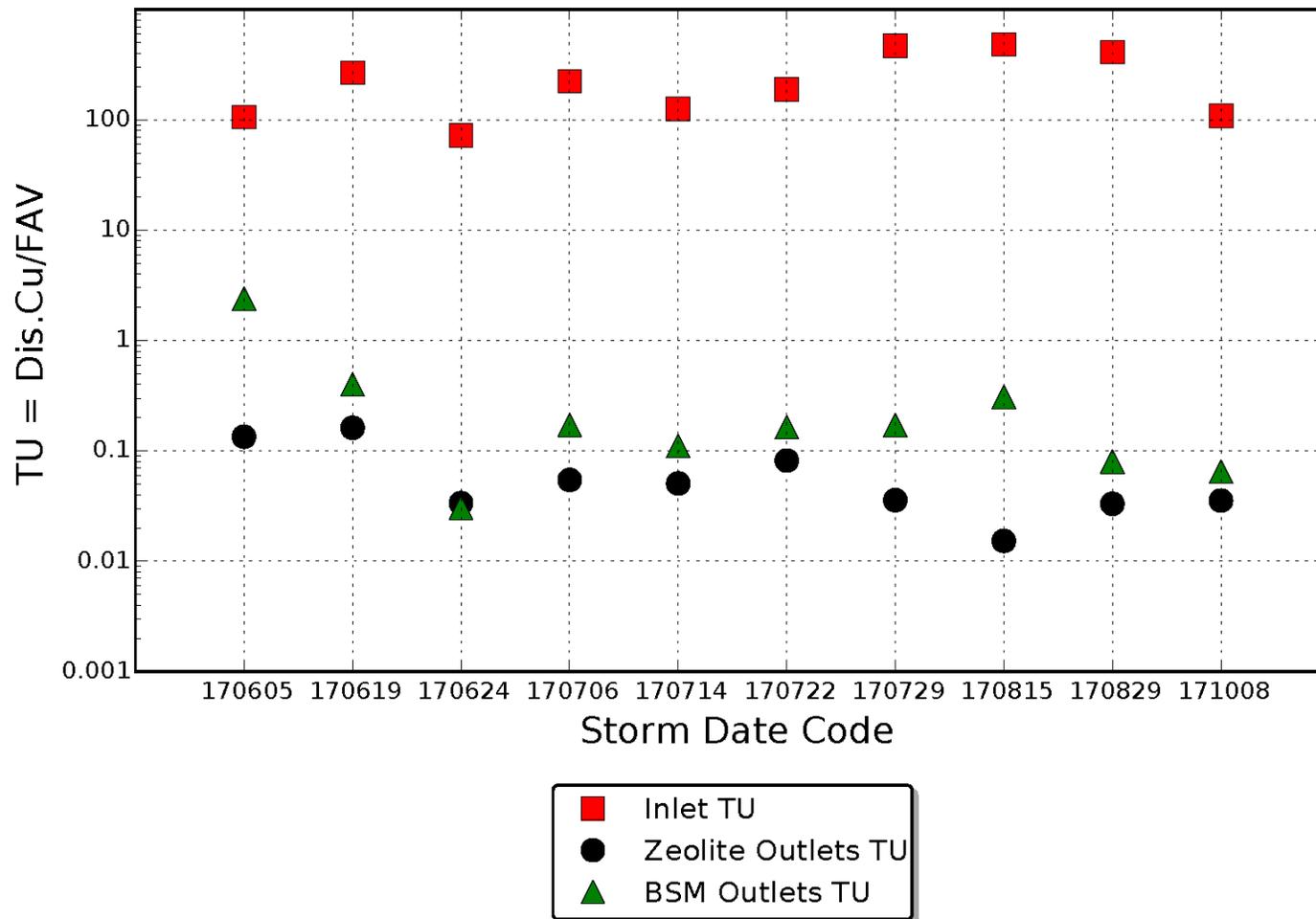


Figure 20. Time series plot depicting the Toxic Units of Cu all Inlet, zeolite underlayer Bioretention Planter Boxes, and SHA BSM Bioretention Planter Boxes. Inlets are red squares, zeolite planter box outlets are black circles, and SHA BSM planter box outlets are green triangles. Toxic Units (TU) are calculated by dividing the dissolved copper concentration by Final Acute Value (FAV) calculated using the Biotic Ligand Model (BLM), so that TU greater than 1 would not be protective of aquatic biota and any TU less than 1 would be protective. This graph shows that for all storm events both set of bioretention planter boxes greatly reduced the TU from influent compared to planter box effluents. In general, the reduction was greater than 1000x (log-scale) with for the zeolite underlayer planter boxes outperforming and reducing the TU to a greater extent compared to the SHA BSM planter boxes for all storm events.

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EDUCATION

Towson University - Towson, MD

August 2015 - December 2017

M.S. Environmental Sciences - Water Resource Management and Assessment

Thesis: Performance of Commercially Available Soil Amendments for Enhanced Copper Attenuation in Bioretention Media

Overall GPA: 3.943

Washington College - Chestertown, MD

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B.A. in Environmental Studies

Hodson Trust Scholar

Overall GPA: 3.601

Thesis: Determining Trace Metal Concentrations in Estuarine Sediments of the Chester River Using Aluminum as a Reference Element

RESEARCH EXPERIENCE

Towson University

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Research Assistant

Towson, MD

- Conducted laboratory column experiments to determine performance of various soil amendment additions to bioretention media for copper attenuation.
- Conducted field study to determine performance of bioretention planter boxes to minimize copper exports from copper roof runoff.
- Utilized Biotic Ligand Model (BLM) to determine potential copper toxicity of pre and post-treatment runoff from copper roof.
- Analyzed water sample for various water quality parameters including: trace metals (ICP-MS), dissolved ions (IC), total organic carbon (TOC/TN), alkalinity, and pH.

Washington College

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Research Lab Aide

Chestertown, MD

- Performed trace metal analysis of soil samples using ICP-MS.
- Utilized gravimetric methods to prepare trace metal standards for ICP-MS.
- Performed microwave-aided digestions on estuarine sediments for ICP-MS analysis.

Maryland Department of Natural Resources

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Research Intern

Annapolis, MD

- Aided in field work application of leveling and submerged aquatic vegetation sampling.
- Proposed and performed a small research project on biomass sampling on the lower Patuxent River.
- Analyzed data collected and presented to faculty the results of biomass sampling research project.

PUBLICATIONS AND PRESENTATIONS

Platform - *Performance of Commercially Available Soil Amendments for Enhance Copper Attenuation in Bioretention Media* - SETAC 38th North American Meeting - Minneapolis, MN - Nov. 2017

Poster - *Performance of Commercially Available Soil Amendments for Enhance Copper Attenuation in Bioretention Media* - SETAC 37th North American Meeting - Orlando, FL - Nov. 2016

