Effect of Incinerator Bottom Ash on Removal Efficiency of Heavy Metals in a Bioretention System: A Column Study

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ABSTRACT

EFFECT OF INCINERATOR BOTTOM ASH ON REMOVAL EFFICIENCY OF HEAVY METALS IN A BIORETENTION SYSTEM: A COLUMN STUDY

by

AKOSUA OFORI-TETTEY

Chairperson: Dr. Susan Morgan

Increased human activities, weathering of building materials and atmospheric deposition contribute heavy metals such as lead, copper, zinc, and cadmium to urban runoff. Bioretention is a green infrastructure as well as a best management practice used to improve the quality of stormwater runoff in addition to reduce its quantity. This stormwater management practice is gaining popularity in commercial development because it can easily be sited in the required natural areas of places such as parking lot medians and streetscapes.

The goal of this research was to evaluate the suitability of bottom ash as a replacement for sand in bioretention media by studying the effect of the bottom ash on the removal and retention of heavy metals. The effect of vegetation on heavy metal removal efficiency of bioretention was also considered. To achieve our objective, a 50:50 ash and wood fines mix was compared to a control of 50:50 sand and wood fines for pollutant removal effectiveness. The 50:50 mixture of incinerator bottom ash and wood fines was chosen because it satisfied drainage requirements of at least 2 feet per day. Eighteen

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columns were constructed of 8-inch diameter PVC pipe and filled with 18 inches of media. Twelve of the 18 columns were planted with switchgrass; the remaining columns were left unplanted. With synthetic rainwater prepared in a laboratory setting, the columns were subjected to dosing. Its composition was based on samples of local rainwater and published literature. The contaminants examined were copper, lead, zinc, iron, nickel, cadmium, and chromium.

Prominent levels of heavy metals were present in the stormwater, but the levels decreased over time for all growth media. The concentration of heavy metals were affected by the type of growth media. The experimental media retained mean lead concentration of 11.2% but the control media leached 29%. Lower mean concentration of zinc, iron, and cadmium were leached from the experimental media (-39%, -5,910%, -2%, respectively) than control media (-57%, -44,758%, -11%, respectively). Overall, vegetation had no effect on metal retention for the first two sampling dates, but had a greater effect thereafter with higher retention for copper, lead, zinc, and iron. This study revealed that media, rather than vegetation, had a greater effect on heavy metals retention. The results suggest incinerator bottom ash has the potential to be a valuable bioretention media for urban planners seeking to protect urban surface water quality due to its excellent infiltration rate, plant suitability, and heavy metal content below water quality standards.

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CHAPTER I

INTRODUCTION AND STATEMENT OF PROBLEM

Introduction

The US Environmental Protection Agency characterizes any rainwater or melted snow that runs off streets, lawns, roofs, and other sites as stormwater (USEPA, 2012). Stormwater runoff from urbanized areas has been identified as the leading cause of degradation to waters in the United States (U.S. EPA, 1996). Increases in urbanization have led to the replacement of the natural land cover, such as forest and grass land, with impervious surfaces. Impervious surfaces are hard surfaces that do not allow water to infiltrate into the soil (California Water & Land Use Partnership, 2013). Examples of such surfaces are roads, rooftops, driveways, pavements, and parking lots. Research has shown that an increase in the number of impervious surfaces significantly alters the hydrological cycle and ultimately decreases water quality (Canadian Geographic, 2011; Barnes et al., 2001). The increase in impervious cover reduces groundwater recharge and infiltration of water into the soil naturally. By so doing, the runoff increases in volume and speed (Konrad et al., 2005), thereby potentially increasing the frequency and magnitude of floods and erosion (Dodds et al., 2003; Walsh et al., 2005). Elevated levels of debris, sediments, and nutrients along with heavy metals are transported with runoff and deposited into receiving water bodies which causes an increase in turbidity and total suspended solids, algal growth, depletion of dissolved oxygen, reduced biodiversity and increased water toxicity (Galloway et al., 2003). All these repercussions result in stream

impairment. Table 1 outlines these major sources of the pollutants in urban stormwater

runoff.

Pollutant	Source	
Total Suspended Solids (TSS)	Soil erosion, vehicle fuels, vegetation debris, bacteria,	
	& microorganisms	
Cadmium (Cd)	Wear of vehicle tire and brake pads, lubrication oil,	
	pesticides, fertilizers, & agricultural chemicals	
Chromium (Cr)	Pesticides, fertilizers, & agricultural chemicals,	
	engine parts, dye & paint, electroplating, timber &	
	paper treatment, metal plating, brake lining wear	
Copper (Cu)	Wear of vehicle tire and brake pads, metal industry	
	and domestic products, insecticides and pesticides	
Iron (Fe)	Automobile rust, highway structures (e.g. guard	
	rails), engine parts	
Lead (Pb)	Petrol additives, paints, industrial activities, auto	
	exhaust, tire and bearing wear, lubricating oil	
Nickel (Ni)	Engine parts, batteries, metal plating, diesel fuel and	
	petrol exhaust, lubricating oil, asphalt paving	
$\text{Zinc}(\text{Zn})$	Wear of vehicle tire and brake pads, corrosion of	
	metal objects, paints, and industrial activities,	
	atmospheric deposition, motor oil, grease	
Total Phosphorus (TP)	Fertilizers, soil erosion, human and animal waste,	
	industrial and household chemical	
Total Nitrogen (TN)	Fertilizers, soil erosion, human and animal waste,	
	industrial and household chemical	
Ammonium (NH4+)	Fertilizers, soil erosion, human and animal waste,	
	industrial and household chemical	
Oxidized Nitrogen (NOX)	Fertilizers, soil erosion, human and animal waste,	
	industrial and household chemical	
Fecal Coliform	Fertilizers, pesticides, manures, & animal feces	

Table 1. Source of Pollutants in Urban Stormwater Runoff

Source: Ball et al., 1998; Wong et al., 2000

Stormwater runoff can be collected and controlled using best management practices (BMPs). Introduction of the Clean Water Act (CWA) led to the National Pollutant Discharge Elimination System (NPDES) permit program, which is responsible for the creation and implementation of stormwater pollution prevention plans that utilize

BMPs. BMPs can be both structural and nonstructural practices implemented to reduce peak flows, manage peak volume, and prevent and/or alleviate detrimental effects of pollutants in stormwater runoff (FHWA, 2000). Examples of BMPs include bioretention cells, green roofs, permeable pavements, as well as sand and organic filters.

The field of stormwater management is fairly new. Extensive research is therefore necessary to provide the needed knowledge in managing stormwater and the various BMPs being utilized to improve our nation's water quality and landscape. Results from this study will serve as a reference for the development of an ideal standard media for bioretention systems.

Statement of Problem

The purpose of this research study was to evaluate the suitability of bottom ash from a wastewater sludge incinerator as a replacement for sand in a bioretention media. Specifically, the removal and retention of heavy metals was investigated. This research designed a bioretention media that would be excellent for pollutant removal and suitable for plant growth.

Metropolitan St. Louis Sewer District (MSD) produces about 47,000 cubic yards of biosolids from the Lemay wastewater treatment plant every year that is incinerated. Bottom ash is the non-hazardous by-product of biosolids incineration. Currently, MSD landfills the ash. This research was funded in whole by MSD in hopes of finding a new use for the incinerator bottom ash as a replacement for sand in bioretention media. Success would generate a sustainable use for bottom ash, a waste product, and extend the

life of landfills while reducing ash disposal fees for MSD and eliminating the cost of sand in bioretention cells.

CHAPTER II

LITERATURE REVIEW

Through laboratory column studies, this thesis examines the effect of incinerator bottom ash on pollutant removal from contaminated stormwater and how having vegetation in the columns affects the treatment efficiency of the bioretention columns. The summary of the related literature is described in this chapter.

Bioretention System Overview

Bioretention emerged as a stormwater BMP in the early 1990s and it was first introduced by the Prince George's County in Maryland (USEPA, 1999). Bioretention is a green infrastructure as well as a stormwater best management practice that can achieve both water quantity and water quality goals through runoff reduction and pollutant removal (CSN, 2013). This stormwater management practice is gaining popularity in commercial development because it can easily be sited in required natural areas of places such as parking lot medians and streetscapes.

The Wisconsin Department of Natural Resources (WDNR) defines bioretention as an infiltration device consisting of an excavated area that is back-filled with an engineered soil, covered with a mulch layer, and planted with a diversity of woody and herbaceous vegetation (WDNR, 2010). Bioretention removes pollutants via physical, biological, and chemical treatment processes (LID Center, 1997). They are usually designed for small drainage areas and can be installed on their own or as part of a treatment chain. This system enhances stormwater infiltration, reduces runoff peak flow

rate and volume, and improves water quality by reducing discharge of stormwater pollutants such as suspended solids, metals, and nutrients (WDNR, 2010). Figure 1 illustrates a cross section of a bioretention system.

Figure 1. Schematic of a Typical Bioretention System (FAWB, 2008)

Low impact development (LID) is an approach to land development that works with nature to manage stormwater in order to reduce the impact of built areas and promote the natural movement of water within the watershed (USEPA, 2013a). Bioretention is among many stormwater practices that are being used in LID programs (USEPA, 2012; DER, 1993). In recent times, LID practices such as bioretention have been used to retrofit existing infrastructure and reduce runoff volumes and peak flows (Damodaram et. al., 2010).

When it rains, runoff is formed, captured, and directed to a bioretention system. There are four mechanisms by which pollutants are then removed by bioretention infrastructure as can be seen in Figure 2. These processes are evapotranspiration, infiltration, adsorption, and biological uptake (Davis, et al., 2003). Stormwater runoff infiltrates through the bioretention soil, some of the stormwater runoff is taken up by plants, which goes through an evapotranspiration process, and then the filtered runoff is allowed to recharge groundwater or is channelled through a pipe and finds its way to streams eventually.

Figure 2. Schematic of Contaminant Behavior in a Stormwater Infiltration System (Grebel et al., 2013)

Design Parameters

Bioretention Media

Bioretention media is usually made up of 60-75% sand (Wetland Studies, 2007). Using bottom ash in place of sand in bioretention media would provide a use for a waste product and extend the life of landfills while reducing ash disposal fees and eliminating environmental and energy cost associated with sand as well as financial costs. Bottom ash is the non-hazardous product of incineration of biosolids from wastewater treatment plants. Metropolitan St. Louis Sewer District's incinerated bottom ash has a relatively small percent fines and is composed of silica and trace metals.

The mixed media employed in bioretention systems has proven to play a critical role in the treatment performance of these systems. The bioretention media must be able to drain the storm event in an acceptable amount of time and also provide essential habitat for plant growth. Soil/sand ratio and organic matter content in bioretention media have been shown to be the properties that impact heavy metal and nutrient removal (Limouzin et al., 2010). The presence of a mulch layer in bioretention systems situated in urban areas where heavy metals constituent a major fraction of pollutants is recommended by lots of studies to aid in metal removal (Davis et al., 2001; 2003; 2007 and FAWB, 2008). Davis et al. (2001) observed that the addition of a mulch layer to the medium could result in significant removal of heavy metal concentrations with specific metal removals of 15 to 145 mg/m² per event. Some studies observed moderate decreases in TKN, ammonium, and phosphorus removal with the addition of organic matter to the bioretention medium

whereas little nitrate was removed (Read et al., 2008; Davis, 2006, Hunt et al., 2008). However, organic matter in the media can act as a source of nitrogen by leaching nutrients and might contribute to the production of nitrate as reported by some studies (Davis et al., 2001; Read et al. 2008). As a result, bioretention mixed media are required to have less than 5% organic matter to prevent leaching of nutrients FAWB (2009). U.S. EPA guidelines also recommend that the mulch layer should be approximately 2-3 inches thick and replaced annually (USEPA, 2000a).

The use of amended soil has been proven to enhance the removal of metals from stormwater runoff. Laboratory column experiments conducted to determine sorption of copper, lead, and zinc showed an increase in metal retention for Dougherty sand when fly ash was added (Zhang et al., 2008). The results also showed that removal of heavy metals in sand mixed with fly ash could continue for over 900 years while sand could only last for 10 years.

Vegetation

Research by EPA suggests that a key component of bioretention infrastructures providing contaminant sorption sites is for the soil media to also support plant growth (USEPA, 2009a). Based on the St. Louis County Phase II Stormwater Management Plan (MSD, 2012), native plant species are required by the Metropolitan St. Louis Sewer District (MSD) for planting in rain gardens, bioretention, bioswales, and stormwater detention and retention infrastructures. The purpose of the plan is to improve water quality by preventing harmful pollutants from being carried by stormwater runoff into

local water bodies (MSD, 2012). According to the Mid-America Regional Council, the use of native plants in green infrastructure helps to save money, time, and water (2013). This recommendation is because native plants thrive well even with no fertilizer, with little maintenance when plants get established, and are drought tolerant. U.S. EPA (2009) also mentions that native plants are tolerant to pollutant loads and accustomed to varying wet and dry conditions.

Subsequent literature shows a rise in the usage of native plants in the Midwest parts of the United States for stormwater management (Grow Native, 2013). This use is largely due to the fact that native plants require less maintenance, create wildlife habitat, are resistant to deer grazing, and enhance our environment aesthetically. Figure 3 below compares the root systems between some native and non-native plants. All the roots of the native plants from the picture have well established and deeper roots as compared to roots of the non-native plants. Having well established roots promotes soil break down and increases porosity, thereby making it easy for water to infiltrate through the soil.

Figure 3. Comparison between Native and Non-Native Root Systems (MSD et al., 2010; MARC, 2013)

The ability of vegetation in bioretention infrastructure to help in the removal of pollutants such as phosphorus and heavy metals has been widely acknowledged. Limouzin et al. (2010) showed the removal of nutrients and metals by using Buffalograss 609 and Big Muhly, both of which are native grasses to Texas. The presence of vegetation proved to help in the removal of NO_x and nutrients but not so much for metals (Limouzin et al., 2010).

Phytoremediation is the process to remove heavy metals via plants using its ability to uptake metals which are essential for plant growth (Fe, Mn, Zn, Cu, Mg, Mo, and Ni) and metals with unknown biological function (Cd, Cr, Pb, Co, Ag, Se, Hg) (Tangahu et al., 2011). These metals end up accumulating into the biomass of plants as they grow.

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Different plants take up concentrations of heavy metals at different intensities. Davis et al. (2007) rated zinc, copper, lead, and cadmium regarding their capability to accumulate in plants, with zinc having the highest capability. Heavy metals were monitored in laboratory bioretention systems at the University of Maryland at College (Davis et al., 2007). Three perennial grass species with high biomass and potential for metal phytoremediation were employed in the bioretention systems. The grasses investigated were Panicum virgatum, Kentucky-31, and Bromus Ciliatus. In this study, 0.5 – 3.3 % of input metals concentration was captured by plants whereas 88-97% was captured in the soil media. Accumulation of the heavy metals in the plants were substantially lower than observed in the mixed media. Davis et al (2007) attributes the low removal efficiency by the plants to low plant biomass.

The study of phytoaccumulation of heavy metals by aquatic plants by Kamal et al. (2004) found higher metal removal. In their study, Kamal et al. present that the three aquatic plants they examined, parrot feather, creeping primrose, and water mint, showed removal efficiencies of 99.8%, 76.6%, 41.62%, and 33.9% for mercury, iron, copper, and zinc, respectively.

The impact of vegetation on pollutant removal efficiency was studied using semisynthetic stormwater passing through a soil filter medium (Read et al., 2008). The study tested 20 Australian plant species. TSS, Al, Cr, Cu, Pb, Zn, N species, and P were measured. The presence of plants was noted to improve the effectiveness of biofilters. However, a disparity in pollutant removal was observed for the different plant species.

This finding proves that selection of plant species could have a significant impact on bioretention effectiveness.

Performance of Bioretention System

The performance of bioretention can be measured by its overall treatment efficiencies. Bioretention is an excellent way to get rid of impurities that impair our streams and may cause harm to aquatic plants and organisms. However, the removal efficiencies of pollutants from bioretention systems varies among studies.

Heavy Metals

Stormwater runoff discharges numerous pollutants, including heavy metals such as copper, lead and zinc, into water bodies and the soil. Not only do these pose a health risk to terrestrial and aquatic organisms, but they also add to the task of curbing environmental pollution. A system such as a bioretention facility is one of several methods that has been suggested as a means to remove pollutants from stormwater runoff.

Laboratory studies on bioretention show excellent removal of heavy metals such copper, lead, and zinc from synthetic stormwater runoff with only small variations in results. Davis et al. evaluated the effect of soil, mulch and plants in removing heavy metals, and this enabled them to determine the treatment capacity of laboratory bioretention systems (2001). They found significant reductions in concentrations of all metals, with specific metal removals of 15 to 145 mg/m² per event. Davis et al. provided evidence to support studies which found that bioretention systems removed low levels of

studies by including two field bioretention systems to the laboratory bioretention facility used by Davis et al. (2001). They also varied runoff characteristics (such as pH, duration, intensity and pollution concentration) and estimated the effect of these characteristics on the removal of heavy metals. Their findings revealed that removal of copper, zinc and lead from the synthetic stormwater runoff was greater than 95% on one site and on the other site the removal of copper, lead and zinc was 43%, 70% and 64% respectively. Also, they found that varying the runoff characteristics had no significant impact on the removal of the metals from the stormwater runoff. However, they noted that there was less removal of the heavy metals when bioretention depths were shallow.

Subsequent studies by Davis et.al evaluated water quality by investigating removal of heavy metals in laboratory bioretention systems (2003; 2007). Davis et al. found that 88 to 97% of metals were captured in the soil media compared to 0.5 to 3.3% accumulated in plants and 2.0 to 11.6% not being captured (2007). The study also revealed that copper, lead, and zinc tend to accumulate in the surface layers of the bioretention media, leading to more than 95% of metals being retained within the top 8 inches of bioretention media.

Using an adsorption experiment to determine the efficacy of mulch in removing heavy metal ions, Jang et al. employed three types of mulches (cypress bark, hardwood bark, and pine bark nugget) to capture heavy metals in urban runoff (2005). They attributed the rapid loss of heavy metal ions to adsorption on adsorbent surface and pores and also to attraction by surface charge. Their research showed that hardwood bark mulch was suited best in removing heavy metals such as copper, lead and zinc. The hardwood

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bark mulch specific surface area was $25-32 \text{ m}^2/\text{g}$ compared to 11-18 and $22-26 \text{ m}^2/\text{g}$ for cypress bark and pine bark mulch, respectively. Their experiment also revealed that the chemical composition of mulch was fundamental to its sorption characteristics.

A column study conducted by Bratieres et al. (2008) quantified the treatment performance of bioretention systems in removing heavy metals and also assessed how different factors affected removal efficiency. They found that 80% of lead and greater than 98% of copper and zinc are removed if the depth of the bioretention system used was greater than 300 mm (12 inches). Hatt et al. analyzed the pollutant removal of three bioretention systems in two different climates (2009). Their study showed that heavy metals (including copper, zinc and lead) were effectively removed in excess of 90% irrespective of the design and depth of the bioretention sytem.

While bioretention systems may effectively remove some heavy metals to a large extent, traces of some heavy metals maybe unable to be removed. Li et al. (2010) used different vegetation types to conduct a pilot bioretention study. They reported that zinc and lead were removed by bioretention; however, copper was unable to be removed from the stormwater runoff. They attributed the inability of bioretention to remove copper to the low levels of copper in their stormwatwer runoff (0.002 mg/L). Their results, however, revealed that the type of vegetation does not have any significant impact on the removal of the heavy metals.

In general, bioretention areas are found to be effective in reducing runoff volume and treating the first flush (first 1.3 cm, or ½ inch) of stormwater runoff (USEPA, 2000a). By evaporation, transpiration, and infiltration of stormwater, bioretention systems reduce runoff volume and help to maintain peak discharge (CSN, 2013). A study was conducted at North Carolina State University to analyse the performance of rain gardens in Charlotte, NC. The study reported 99% volume reduction from 16 storms (Hunt et. al., 2007). Subsequent studies have also shown a significant amount of volume reduced; 80- 100% (NYCDEP, 2012) and 79% (Cahill, 2012).

CHAPTER III

METHODOLOGY OF STUDY

This chapter describes the several stages of the column study testing and analysis performed to evaluate the use of incinerator bottom ash as a bioretention medium. The focus was on the amount of heavy metals in the effluent and the ability of plants to survive.

After dosing with synthetic stormwater, representative effluent water samples were obtained from the columns, located in the Southern Illinois University Edwardsville (SIUE) School of Engineering Environmental Laboratory. Influent samples of the synthetic stormwater used to treat the columns were also obtained to be analysed. The samples were analysed for trace metals at the Metropolitan St. Louis Sewer District's (MSD) Department of Environmental Compliance (DEC) laboratory. The DEC laboratory is located at MSD's Bissell Point Wastewater Treatment Plant. Elemental analysis by inductively coupled plasma-atomic emission spectrometry detects up to 24 metals measuring less than 5μm in size (Sarojam, 2010). The experimental procedure followed in this project was adapted from Limouzin et al. (2010). The sections below describe the methods and materials in detail.

Experimental Setup

Column Description

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Bioretention columns with an overlying mixed media and porous rock layer were subjected to testing to mimic real time transport and infiltration mechanisms of

stormwater in the environment or field. To do this, 18 bioretention columns were constructed using 8-inch (20-cm) diameter polyvinyl chloride (PVC) pipes. Each column was filled with 6 inches (15 cm) of pea gravel at the bottom and topped with 18 inches (46 cm) of mixed media (Figure 4). A piece of geotextile fabric was placed between the mixed media and the gravel to prevent the media from clogging the pores in the rocks. All the columns had 3 inches (8 cm) of freeboard at the top to allow for ponding depth (Figure 4). The screens were attached to the columns with polyurethane adhesive and duct tape (Figure 5). The columns were secured with a fiberglass window screen at the bottom to keep the media and gravel in place. The screens were attached to the columns with polyurethane adhesive and duct tape (Figure 5).

Figure 4. Plan of Bioretention Column (Not Drawn to Scale)

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Figure 5. Columns with Fiberglass Window Screen Attached to the Bottom Of the 18 columns, 12 were planted with heavy metal switchgrass and the remaining six columns were left unplanted to assess the impacts of the plants on water quality. The columns were divided into two groups, control and experimental, with nine columns per group (Table 2). They were arranged in a completely randomized design. Group A was identified as the control media and had nine columns containing 50:50 sand and wood fines by volume. The control set characterizes a typical bioretention medium. Group B was identified as the experimental media and had nine columns containing 50:50 incinerator bottom ash and wood fines by volume. The proportion of inorganic to organic component in the bioretention media was based on a hydraulic permeability study on incinerator bottom ash donated by MSD (Eichhorst et al., 2013). In each group, six columns were planted with heavy metal switchgrass and the other three were left unplanted.

Table 2. Column Design

Group	Mixed Medium	Column Number
	50% Sand & 50% Compost	1 - 9
	50% Bottom Ash & 50% Wood Fines	1 - 9

Figure 6. Column Framework and Support

The support system for the columns was equipped with a lighting system to provide a source of light for plant growth due to limited light in the laboratory (Figure 6). The lighting system consisted of 16 fluorescent bulbs placed 28 inches (71 cm) above the tops of the plants. Two days after the April 9, 2013 testing, the columns with plants were moved to a south-facing window that received direct sunlight on the first floor of the SIUE Engineering Building to improve plant growth. The columns were moved to the laboratory a day before they were tested and moved back two days after the testing (to allow complete drainage) until the end of the study in November 2013.

Panicum virgatum, or heavy metal switchgrass, is commonly used in rain gardens in some states of the United States. It is native to the prairies and open ground, open woods, brackish marshes from eastern Canada to central and eastern US and south to Central America (BlueStem Nursery, 2013). Figure 7 shows the distribution where switchgrass is native in the U.S. States shaded in green show where switchgrass has been reported to be naturally present and those shaded in white have reports of no switchgrass sighting.

Figure 7. Distribution of Panicum virgatum in States and Provinces of the United States where they are Considered Native (USDA et al., 2013)

The Perennial Resource and Nature Hills Nursery both describe heavy metal

switchgrass as having pink flowers and a metallic blue foliage color that may turn to

yellow in the fall. It grows straight upright, about $3 - 4$ feet (91 – 122 cm) for mature growth and does not fall over even in heavy rains. Heavy metal switchgrass is a perennial, drought and salt tolerant, and generally requires lower nutrient levels to develop properly (Perennials.com, 2013). Switchgrass has a moderate growth rate and can have a mature spread of about $12 - 18$ inches $(30 - 46$ cm). It is tolerant to many soil types, requires full sun exposure, and has low to average consistent water needs (Perennial Resource, 2013).

Switchgrass was planted in some of the columns and not others to determine its contribution to pollutant removal/export and to determine the plant compatibility of the media. The switchgrass was donated by Bohn's Farm and Greenhouse in Maryville, Illinois. It was not possible to remove all of the soil from the roots of the plants before transferring to the columns, which would be similar to planting within a rain garden. The average height of the switchgrass plants were 27 inches (69 cm) when they were first planted in the columns in late October 2012. The plants started going dormant around the middle of November 2012 and began growing again beginning in March 2013. The foliage and flowers were trimmed down to about 2 inches (5 cm) early in March to allow for new growth. The columns planted with switchgrass were also maintained frequently by removing weeds. Occasionally, the plants were monitored through photographs and their heights were measured using a tape measure.

Synthetic Stormwater Preparation

Synthetic stormwater (SSW) formulated from distilled water was used to dose the bioretention columns over the course of the project. A Barnstead Fistreem II still and الاقم للاستشارات

Siemens DI Reverse Osmosis system were used to make all the distilled water for the synthetic stormwater and for cleaning. A Mettler Toledo AG245 digital scale was used for weighing non-liquid ingredients for the synthetic stormwater. The composition of the synthetic stormwater was based on literature reviewed and samples of local rainwater collected. A summary of the composition of SSW used in previous studies is presented in Table 3.

Table 3. Composition of Synthetic Stormwater from Past Studies

¹Chi-hsu & Davis, 2005; ²Davis et al., 2001; ³Limouzin et al., 2010; ⁴Li et al., 2010; ⁵Lucas & Greenway, 2008; ⁶Hatt et al., 2007; ⁷Bratiereset al., 2008; ⁸Hatt et al., 2009

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Over a one month period, rain water samples were collected at several locations during natural storm events. One collection point was in a large plastic rain barrel located outside the SIUE Engineering Building but not connected to a downspout. Rainwater samples were also collected from other locations around the region using available plastic containers. After rain events, samples of rain water were collected into 500 mL plastic and glass containers, tested for pH, preserved with appropriate acid, and refrigerated until further testing could be conducted. The samples to be analysed for metals were kept in 500 mL plastic containers and preserved with nitric acid whereas the samples for nutrients were kept in 500 mL glass containers and preserved with sulphuric acid. Samples for total suspended solids (TSS) and turbidity were kept in 225 mL plastic containers and refrigerated since they did not require preserving. The samples were analysed for TSS and turbidity in the SIUE Environmental Laboratory while the rest was transported to MSD's DEC Laboratory for nutrients and metals analyses.

Upon successful completion of the rainwater harvesting and testing, the data was compiled and compared to concentrations of SSW found in the literature. Table 4 shows a list of elements that constitute each rain sample collected. The values from the rainwater composition and SSW from the previous studies reviewed were averaged and compared in order to achieve a suitable SSW mix for this project. To arrive at the targeted concentration for each parameter that make up SSW influent, the type of laboratory grade compounds to be utilized were tabulated and the amount computed. A summarized list of the target values can be found in Table 5.

	Concentration (mg/L)				
Parameter	Sample 1	Sample 2	Sample 3	Sample 4	
	(9/1/2012)	(9/5/2012)	(9/25/2012)	(9/26/2012)	AVERAGE
pH (no unit)	6.57	6.18	6.04	6.21	6.25
TSS	$\overline{4}$	$\mathbf{1}$	6	$\overline{2}$	3.25
Total Dissolved					
Solids	\overline{a}		$\overline{}$		$\overline{}$
Organic Nitrogen (as					
N)	$<$ 3	$<$ 3	$<$ 3	$<$ 3	$<$ 3
Nitrite (as N)	\blacksquare	$\overline{}$	\blacksquare	\blacksquare	\blacksquare
Nitrate (as N)	$\overline{}$	$\qquad \qquad \blacksquare$	\blacksquare	\blacksquare	\blacksquare
Nitrate - Nitrite	0.230	0.31	0.36	0.41	0.33
Ortho-Phosphate	< 0.25	\equiv	\mathbb{L}^2	\blacksquare	$\omega_{\rm c}$
Total Phosphorus	${}_{0.25}$	${}_{0.25}$	${}< 0.25$	${}_{0.25}$	< 0.25
Kjeldahl Nitrogen -					
Total (as N)	3.36	2.8	2.8	2.8	2.94
Total Nitrogen	3.59	3.11	3.16	3.21	3.27
Plant Available					
Nitrogen	$<$ 3	$<$ 3	$<$ 3	$<$ 3	\leq 3
Nitrogen Oxide	$\frac{1}{2}$	\blacksquare	\overline{a}	\blacksquare	\blacksquare
Ammonia (as N)	2.80	\leq 2	\leq 2	$<$ 2	2.80
Ammonia (by ISE)	0.211	0.453	0.453	0.461	0.39
Ammonium (as N)	$\overline{}$	\blacksquare	$\overline{}$	$\qquad \qquad \blacksquare$	$\overline{}$
Oxidized Nitrogen	\overline{a}	\overline{a}			\blacksquare
Cadmium	${}< 0.009$	${}_{0.009}$	${}< 0.009$	${}< 0.009$	
Chromium	${}_{0.01}$	${}_{0.01}$	${}_{0.01}$	${}_{0.01}$	$\overline{}$
Copper	0.086	$0.08\,$	0.053	${}_{< 0.009}$	0.073
Iron	< 0.1	0.111	0.125	< 0.1	0.12
Manganese	\Box	\equiv	\blacksquare	\blacksquare	\blacksquare
Nickel	${}_{0.04}$	${}_{0.04}$	${}_{0.04}$	${}_{0.04}$	< 0.04
Lead	${}_{0.02}$	${}_{0.02}$	${}_{0.02}$	${}_{0.02}$	< 0.02
Zinc	0.056	0.06	${}_{0.03}$	${}_{0.03}$	0.058

Table 4. Composition of Local Rainwater

Pollutant	Chemical	Amount	Target
		(mg, except	Concentration
		mL for pH	(mg/L, except
		$&$ CuSO ₄)	pH
pH	Sulfuric acid or sodium hydroxide	Varies	6.1
Total Phosphorus	Monopotassium phosphate (KH_2PO_4)	186.84	0.25
Nitrate (as N)	Sodium nitrate (NaNO ₃)	39.60	0.17
Nitrite (as N)	Sodium nitrite (NaNO ₂)	4.82	0.17
Organic Nitrogen (as N)	Glycine (NH_2CH_2COOH)	2288.16	2.51
Ammonia (as N)	Ammonium Chloride (NH_4Cl)	259.83	0.40
Zinc	Zinc metal (Zn)	10.206	0.06
Lead	Lead chloride $(PbCl2)$	4.563	0.02
Copper	Copper sulfate $(CuSO4)$	16.02	0.075

Table 5. Chemical Makeup of Synthetic Stormwater

To make concentrated synthetic stormwater, all the dry chemicals (KH_2PO_4) , NaNO₃, NaNO₂, NH₂CH₂COOH, NH₄Cl, Zn, and PbCl₂) were combined and mixed together in a beaker in their correct proportions. Then 16.02 mL of CuSO4 solution was added to the salt mixture and stirred to allow for complete dissolution. Distilled water in the amount of 73.98 mL was added to result in a 90 mL stock solution, which was then stirred further to make sure that the mixture was completely dissolved. The stock/concentrated solution was made no longer than 24 hours preceding a sampling event in order to ensure chemical integrity of the SSW.

To prepare the influent stormwater for treating the columns, 10 mL of the concentrated solution was taken and added to a plastic carboy container containing 18.9 litres (5 U.S. gallons) of distilled water to achieve the desired batch of diluted synthetic stormwater mixture. The stormwater was then adjusted to a pH of 6.1 using either sulfuric acid or sodium hydroxide. To do this, once the solution was completely mixed, 50 mL of the SSW was taken out and put in a beaker. Using a pH meter, the pH of the stormwater was checked within 15 minutes of grabbing the sample. The pH was then adjusted up or down by adding either sodium hydroxide (NaOH) or sulfuric (HSO4) acid after each reading until the pH of the batch was reasonably close to the target value of 6.10. Once the pH target was achieved, the column testing began.

Column Testing

Shortly after the SSW was prepared, dosing of the columns with synthetic rainwater began once every two weeks between November 7, 2012 and April 4, 2013 and then monthly until November 16, 2013, for a total of 18 sampling events. This timing change was made to accommodate MSD's DEC Laboratory and to reduce costs. Also, after examining the data, all metal analyses were halted with the exception of lead because all the metals except lead exhibited either a consistent change or no change in concentration.

To treat the columns, 8500 mL of the synthetic stormwater was poured into a clean bucket. A clean 2000 mL beaker was also placed inside a bucket and placed under each column. The stormwater in the bucket was then used to dose the column while

keeping a constant head in the freeboard zone of the column (top 3 inches; Figure 1). This step was repeated for all the columns. The effluent water drained from the bottom of the columns into the beaker in the bucket. Synthetic stormwater from the columns was allowed to drain into a bucket once the 2000 mL beaker got full. This usually took several hours to one day. The volume of effluent in each bucket was then measured and recorded. During each testing event, one or two columns were chosen randomly for duplicate sampling. Information such as date, influent batch number, volume, and column number treated was recorded on the treatment sheet (Table A-16) and chain of custody form (Table A-17). The influent batch used in dosing each column was also recorded.

Influent and Effluent Sampling

For each sampling event, grab samples of the influent and effluent were collected and analysed for water quality parameters such as TSS, pH, turbidity, and heavy metals. Sample collection started in November 2012 and continued through November 2013 (Table A-15).

At least one duplicate sample was taken from each column during each testing event for the duration of the project. The number of influent samples taken was reduced to one composite sample per sampling event starting with the testing in May 2013. A total of 107 influent and 343 effluent samples were collected and analysed for lead; 101 influent and 226 effluent samples were collected and analysed for all other metals.

All samples were collected according to *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998). Both influent and effluent samples for metal

analysis were collected and stored in 500 mL plastic containers. The sampling containers were properly labelled and the samples were adjusted with nitric acid to a pH of less than 2 in order to preserve them. The metal samples had a holding time of 28 days before expiring. The samples were placed in a cooler, packed with ice, and delivered to MSD's DEC Laboratory along with a chain of custody form. All samples were delivered on or within two days of a sampling event.

Analysis of Samples

pH testing was conducted in SIUE's Environmental Engineering Laboratory using an Accumet Research AR50 Dual Channel pH/ION/Conductivity meter and following the procedure in its handbook.

The DEC Laboratory at MSD's Bissell Point Wastewater Treatment Plant conducted all the metals analyses following the EPA Method for *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled (ICP) Plasma-Atomic Emission Spectrometry Method 200.7* (1994). The ICP Optical Emission Spectrometer (Optima2000 DV) was used for testing metals.

Duplicate samples were taken and tested for pH and the relative percent difference was calculated using Equation 1 and are shown in Table 6.

 $D_1 - D_2$ $rac{D_1+D_2}{2}$ (100), Equation 1

	Relative Percent Difference (%)			
Metal	Min	Max	Average	
Lead	-157.1	163.6	-16.2	
Copper	-198.0	170.1	-33.8	
Zinc	-50.0	103.4	13.5	
Nickel	-28.6	θ	3.7	
Iron	-9.2	189	42.1	
Cadmium	$\overline{0}$	0	θ	
Chromium	Ω	96.3	9.6	

Table 6. Relative Percent Difference of pH of Effluent Metal Concentration

The scales, pH meter, and turbidimeter were calibrated each time testing was done. Calibration was performed following the user's manual of the respective equipment being used. This thesis presents and discusses only metals even though nitrogen and phosphorus elements are included in the synthetic stormwater. Analysis of the nutrients along with TSS and turbidity will be presented and discussed in Eichhorst (2014).

Volume Measurements

The filtrate from each column was collected and measured using a graduated cylinder for each run. The volume was measured a few days after testing to ensure that the columns were completely drained. By comparing the effluent volume with that of the influent, the volume of stormwater retained was determined.

Data Analysis

The data results from all the testing were compiled and examined. Using the metal concentrations in the effluent, change in metal concentration (influent minus effluent) and percent reduction of metals were computed as well as SSW volume reduction. Data

results and computed parameters of importance from the stormwater samples can be found in Chapter 4.

Metal concentrations were compared to USEPA water quality criteria (WQC) for aquatic life and human health and USEPA National Drinking Water Regulations (USEPA, 2013b; USEPA, 2009b).

A two-way analysis of variance (ANOVA) was computed at a 95% confidence level using R Statistical Software (v. 3.0.2). With substrate type as the main effect and date as a blocking variable, metal concentrations were compared for differences between media types and presence of vegetation. The interaction of media and vegetation was also investigated.

One quart sample of the experimental media, bottom ash and wood fines, was delivered to MSD's lab for TCLP analysis to account for existing pollutants.

CHAPTER IV

RESULTS AND DISCUSSIONS

The following sections describe the performance of the various columns for metals removal. Similar to many previous laboratory studies, the effluent concentrations of some of the metals were low and many of the laboratory results were below detection limit (Tables 7 and A-1 through A-14). A statistical analysis of the results using regression analysis with analysis of variance (ANOVA) was conducted. All the metals data below their respective detection limits were changed to one half of their detection limit to follow USEPA standards (USEPA, 2000b).

Influent Synthetic Stormwater

The influent concentration of lead, copper, zinc, iron, nickel, cadmium and chromium in the SSW used for this study was analysed per column treated and over time. Statistical analysis was not performed for influent concentrations of nickel, cadmium, and chromium. With their concentration below the detection limit throughout the duration of the research, no major differences were observed in their concentrations. There was no significant difference between influent concentrations of lead, copper, iron, and zinc in the SSW used to treat each column (Table 8). On the other hand, the concentrations showed significant differences between sampling dates (Table 8). The difference in metal concentration in SSW over time might be due to the fact that the composition of distilled water may have changed throughout the study period. Distilled water was obtained from the distillation unit for the environmental engineering laboratory and deionized water from the centralized distillation unit for the chemistry laboratory. Moreover, there may have been variation in the concentrated SSW since preparation of SSW was performed between two research partners for different sampling dates.

Metal	Across Columns	Across Sampling Dates
	P-value	P-value
Pb	0.204	0.000
Cu	0.329	0.000
Zn	0.051	0.000
Fe	0.152	0.016

Table 8. ANOVA Results for Metals Concentrations in Influent SSW*

Data of all influent metal concentrations and sampling dates were investigated to develop a relationship between pH and metal concentrations possibly explain the fluctuations in influent metal concentrations. The relationship was developed using Microsoft Excel 2013. No relationship existed between pH and any influent metal concentration (Figure 8).

Figure 8. Relationship between pH and all Metal Concentrations of Influent Synthetic Stormwater

Effluent

The effect of media type and plants on metal concentrations in the effluent was investigated as well as the mean concentration difference over time. Lead results does not depict testing events on 10/19/2013 and 11/16/2013 due to time constraints. The final paper to be published will show lead results from all sampling dates.

Lead

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Figures 9 and 10 show the effect of media and plants on the change in concentration of lead (influent concentration minus effluent concentration). Both minor removal and leaching of lead occurred throughout the testing period for the control and experimental media. The fluctuations over time were alike for both media (Figure 9) as well as for the presence and absence of plants (Figure 10). Statistical analysis showed no significant effect of media, the presence of vegetation, and their interaction on mean concentration changes, respectively (Table 9). However, the mean change in concentration of lead across the sampling dates proved to be significantly different (Table 9), which was likely due to the statistically significant changes in the influent concentration over time.

Figure 9. Mean Change in Concentration of Lead for 16 Sampling Dates for Control and Experimental Media

Figure 10. Mean Change in Concentration of Lead for 16 Sampling Dates for Vegetated and Non-Vegetated Media

	All Samples		
Source	$11/7/2012 - 5/14/2013$		
	P-Value		
Planted vs. Not-Planted	0.496		
Media	0.109		
Interaction	0.615		
Sampling Date	$2E-16$		

Table 9. Statistical Analysis for Change in Lead Concentration over Sampling Dates*

Table 10 shows the overall average percentage of lead concentration removed or leached from the SSW via media and/or plants for 16 sampling dates. The experimental media, regardless of the presence or absence of plants, removed lead while the control media leached lead, regardless of the presence or absence of plants. For almost all sampling events, the lead either leached or was removed from each column within a

treatment group (e.g., vegetated control). However, over time, the amount of removal or leaching within a treatment group varied (Table 10), but those that leached tended to leach and those that removed tended to remove.

Table 10. Average Removal (Leached) Percentage of Lead for Control and Experimental Media over 16 Sampling Dates

	Removal (Leached) Percentage (%)		
Bioretention Media	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	-46.3	-12.4	
Bottom Ash + Wood Fines (experimental)	0.32	22.1	
Range (Minimum – Maximum)			
Sand + Wood Fines (control)	$-1,233 - 97.6$	$-1,150-92.9$	
Bottom Ash + Wood Fines (experimental)	$-1,150-97.6$	$-317 - 92.9$	

Copper

The effect of media and plants and their interaction on the change in concentration of copper (influent concentration minus effluent concentration) were investigated (Figures 11 and 12). In general, all results show a decline of mean copper leached after the first flush and a fairly sustained copper removal thereafter (Figures 15 and 16). The big difference in the mean concentration change of copper for the first flush attests to possible effects of media type and presence of vegetation on copper concentration. To confirm this reasoning, an ANOVA test was performed to identify any significant difference that media, plants, and their interaction may have on change in concentration

of copper. Table 11 indicates that the only statistically significant differences are for the first sampling event. Afterwards, the concentration difference between the control and experimental media and the vegetated and non-vegetated columns are statistically the same. In all growth media there was a significant change over time from leaching of copper from the first sampling date to copper removal thereafter, indicating that the time also had an effect on change in concentration. The difference in concentration over time was also due in part from the influent copper concentrations.

Figure 11. Mean Change in Concentration of Copper for 12 Sampling Dates for Control and Experimental Media

Figure 12. Mean Change in Concentration of Copper for 12 Sampling Dates for Vegetated and Non-Vegetated Media

	All Samples	First Sample	Last 11 Samples
Source	$11/7/2012 - 5/14/2013$	11/7/2012	$11/19/2012 - 5/14/2013$
	P-Value	P-Value	P-Value
Planted vs. Not-Planted	0.0206	9.32E-05	0.159
Media	0.0150	3.17E-08	0.350
Interaction	0.4438	0.0388	0.862
Sampling Date	$2E-16$	N/A	0.061

Table 11. Statistical Analysis for Mean Change in Copper over Sampling Dates*

Table 12 shows the overall average percentage of copper concentration removed or leached from the SSW via media and/or plants for 12 sampling dates. The removal of copper was relatively stable across the sampling dates. Leaching occurred in both vegetated and non-vegetated experimental media and non-vegetated control media on

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11/7/2012 only. The control media, regardless of the presence or absence of plants,

removed more copper than the experimental media. For almost all sampling events,

copper was removed from each column within a treatment group (e.g., vegetated control).

The experimental media did not seem to influence the degree of removal of copper

however, the presence of vegetation increased the degree of copper removal.

Zinc

In general, all results show leaching of zinc for the first three sampling dates and removal thereafter until the sampling on 5/14/2013 (Figures 13 and 14). The presence of vegetation had a significant effect on the mean change in concentration of zinc and so did time (Table 13). Statistical analysis showed no significant effect of media on mean concentration changes, respectively (Table 13). However, the mean change in concentration of lead across the sampling dates proved to be significantly different (Table

13), which was likely due to the statistically significant changes in the influent concentration over time.

Figure 13. Mean Change in Concentration of Zinc for 12 Sampling Dates for Control and Experimental Media

Figure 14. Mean Change in Concentration of Zinc for 12 Sampling Dates for Vegetated and Non-Vegetated Media

	All Samples
Source	$11/7/2012 - 5/14/2013$
	P-Value
Planted vs. Not-Planted	0.0129
Media	0.2486
Interaction	0.0387
Sampling Date	$2E-16$

Table 13. Statistical Analysis for Change in Zinc Concentration over Sampling Dates*

The overall average percentage of zinc concentration removed or leached from the SSW via media and/or plants for 12 sampling dates are presented in Table 14. Zinc leached out more from the control media than the experimental. The removal or leaching was not relatively stable across the sampling dates. Overall, leaching of zinc was observed; however, the majority of the leaching happened during the first three sampling dates and on the last date. Removal of zinc was observed between 12/18/2012 and 4/9/2013. The existence of vegetation did not seem to help in the removal of zinc in the experimental media but helped in retaining zinc from the control media.

Table 14. Average Removal (Leached) Percentage of Zinc for Control and Experimental Media over 12 Sampling Dates

	Removal (Leached) Percentage (%)		
Bioretention Media	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	-10.4	-103.2	
Bottom Ash + Wood Fines (experimental)	-93.0	149	
Range (Minimum - Maximum)			
Sand + Wood Fines (control)	$-757 - 93.7$	$-1,071 - 82.9$	
Bottom Ash + Wood Fines (experimental)	$-2,671 - 96.6$	$-557 - 91.1$	

Iron

Figures 15 and 16 show the effect of media and plants and their interaction on the change in concentration of lead (influent concentration minus effluent concentration) Leaching of iron occurred throughout the testing period for both control and experimental media. The fluctuations over time were alike for both media (Figure 15) as well as for the presence and absence of plants (Figure 16). Statistical analysis showed significant effect of media, the presence of vegetation, and their interaction on mean concentration changes, respectively (Table 15). There was also a significant difference in concentration change of iron over time, indicating that time has an effect on change in concentration. However, investigation of the data for only the first two sampling dates indicated that

there was no significant effect of vegetation and interaction between media and

Figure 15. Mean Change in Concentration of Iron for 12 Sampling Dates for Control and Experimental Media

Figure 16. Mean Change in Concentration of Iron for 12 Sampling Dates for Vegetated and Non-Vegetated Media

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	All Samples	First 2 Samples
Source	$11/7/2012 - 5/14/2013$	$11/7/2012 - 11/19/2012$
	P-Value	P-Value
Planted vs. Not-Planted	1.34E-08	0.986
Media	\leq 2E-16	1.98E-06
Interaction	8.70E-08	0.776
Sampling Date	0.00135	2.78E-06

Table 15. Statistical Analysis of Change in Iron Concentration over Sampling Dates*

Table 16 shows the overall average percentage of iron concentration removed or leached from the SSW via media and/or plants for 12 sampling dates. The experimental media, regardless of the presence or absence of plants, leached more iron than the control media leached iron, regardless of the presence or absence of plants. The presence of vegetation reduced the amount of leaching of iron in both media types. Henceforth, experimental media and vegetation had a positive effect on concentration change of iron (Table 16).

	Removal (Leached) Percentage (%)		
Bioretention Media	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	$-32,495.1$	$-5,7021.4$	
Bottom Ash + Wood Fines (experimental)	$-5,326.7$	$-6,493.9$	
Range (Minimum – Maximum)			
Sand + Wood Fines (control)	$-141,718 - -476$	$-166, 150 - -2, 598$	
Bottom Ash + Wood Fines (experimental)	$-46,054 - 77.8$	$-30,092 - -49.8$	

Table 16. Average Removal (Leached) Percentage of Iron for Control and Experimental Media over 12 Sampling Dates

Nickel

Figure 17 show the interaction of media and plants on the change in concentration of nickel between the influent and effluent concentrations. Nickel was leached from all the treatment groups during the first two sampling dates. The experimental media leached more nickel than the control media and so did the columns with vegetation. As a result, the type of media and the presence of plants affected the amount of retention (leaching) of nickel (Table 17). Statistical analysis showed significant effect of media and the presence of vegetation on mean concentration changes, respectively (Table 17). The majority of nickel was leached during the first two testing events for both the control and experimental media; zero removal was observed for the rest of the testing period for the control and experimental media. The mean change in concentration of nickel across the sampling dates proved to be significantly different (Table 17).

Figure 17. Mean Change in Concentration of Nickel for 12 Sampling Dates for Control and Experimental Media

Source	All Samples $11/7/2012 - 5/14/2013$ P-Value	First 2 Samples $11/7/2012 - 11/19/2012$ P-Value
Planted vs. Not-Planted	7.72E-05	1.40E-06
Media	0.0283	0.00014
Interaction	0.3517	0.01974
Sampling Date	$2E-16$	1.68E-06

Table 17. Statistical Analysis of Change in Nickel Concentration over Sampling Dates*

Table 18 shows the average percentage of nickel removed or retained from the SSW either via media or plants. Over 12 sampling dates, the average percentage of nickel leached was higher for the experimental media than control media. The degree at which nickel was leached was smaller with the presence of vegetation in the media. The

majority of the leaching occurred between 11/7/2012 and 12/4/2012 with only a few leaching events thereafter but, generally zero removal. The presence of vegetation helped retain nickel from both media types.

Table 18. Average Removal (Leached) Percentage of Nickel for Control and Experimental Media over 12 Sampling Dates

	Removal (Leached) Percentage (%)		
Bioretention Media	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	-49.9	-211.6	
Bottom Ash + Wood Fines (experimental)	-127.5	-382.3	
Range (Minimum – Maximum)			
Sand + Wood Fines (control)	$-395-0$	$-1,557-0$	
Bottom Ash + Wood Fines (experimental)	$-1,805-0$	$-4,110-0$	

Cadmium

Leaching of cadmium was observed for both control and experimental vegetated media on only 11/7/2012 (Figure 18). Non-vegetated media showed no leaching throughout the study. Statistical analysis showed significant effect of media, vegetation, and time on the change in concentration of cadmium the first two sampling dates but no significance for the remainder of the testing period (Table 19).

Figure 18. Mean Change in Concentration of Cadmium for 12 Sampling Dates for Control and Experimental Media

	All Samples	First 2 Samples	Last 10 Samples
Source	$11/7/2012 - 5/14/2013$	$11/7/2012 - 11/19/2012$	$12/4/2012 - 5/14/2013$
	P-Value	P-Value	P-Value
Planted vs. Not-Planted	0.0598	0.04312	0.485
Media	0.0499	0.03853	0.318
Interaction	0.1715	0.23178	0.509
Sampling Date	1.17E-12	0.00231	0.558

Table 19. Statistical Analysis for Change in Cadmium Concentration over Sampling Dates*

The presence of plants did not have any positive effect on the removal of cadmium from SSW (Table 20). Overall, cadmium leached from both vegetated control and experimental media during the first sampling dates and zero removal occurred subsequently for the rest of the sampling dates. Initial leaching of cadmium might be

because of the first flush while the zero removal was due to the fact that majority of the influent and effluent cadmium concentrations were below the detection limits. Vegetated experimental media leached less cadmium than the vegetated control media.

Table 20. Average Removal (Leached) Percentage of Cadmium for Control and Experimental Media over 12 Sampling Dates

	Removal (Leached) Percentage (%)		
Bioretention Media		Vegetated Media Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	-22.1	$\overline{0}$	
Bottom Ash + Wood Fines (experimental)	-3.7	Ω	
Range (Minimum – Maximum)			
Sand + Wood Fines (control)	$-545 - 0$	$0 - 0$	
Bottom Ash + Wood Fines (experimental)	$-352 - 100$	$0 - 0$	

Chromium

Figure 19 show the effect of media and plants on the change in concentration of chromium (influent concentration minus effluent concentration). Chromium was evidently leached from all media types for the first sampling, also known as the first flush. The experimental media leached more chromium than the control media. However, both non-vegetated control and experimental media leached more chromium than the vegetated control and experimental media. As a result, the type of media and the presence of plants affected the leaching of chromium. Moreover, chromium was observed to be leached in greater amounts from the non-vegetated control media than vegetated for

11/19/2012 and 12/4/2013. The presence of plants showed a decrease in the amount of chromium leached. The amount of chromium leached from the non-vegetated control media remained consistent for the rest of the sampling dates, with no removal or leaching occurring in the other media. Strong differences in the change of concentration of chromium due to media type were observed for the first two dates but not for the rest. Hence, statistical analysis established significant effects of media, plants, and time on the change in concentration of chromium (Table 21).

Figure 19. Mean Change in Concentration of Chromium for 12 Sampling Dates for Control and Experimental Media

Source	All Samples $11/7/2012 - 5/14/2013$	First 2 Samples $11/7/2012 -$ 11/19/2013	Last 10 Samples $12/4/2012 - 5/14/2013$
	P-Value	P-value	P-value
Planted vs. Not-Planted	0.000183	4.95E-05	0.0316
Media	0.969997	0.0155	6.51E-07
Interaction	0.724560	0.1196	0.1081
Sampling Date	$2E-16$	7.09E-07	3.98E-05

Table 21. Statistical Analysis for Change in Chromium Concentration over Sampling Dates*

For 12 sampling dates, the average percentage of chromium leached from the media was higher for non-vegetated media than vegetated media in both the control and experimental media (Table 22). The presence of vegetation seem to help retain chromium. Overall, leaching of chromium was relatively unstable across the sampling dates. There was zero removal for some sampling dates, which can be attributed to the small concentration of chromium.

	Removal (Leached) Percentage (%)		
Bioretention Media	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	-98.4	-209.7	
Bottom Ash + Wood Fines (experimental)	-922	-225.3	
Range			
Sand + Wood Fines (control)	$-614-65$	$-1,329 - 0$	
Bottom Ash + Wood Fines (experimental)	$-1,471-65$	$-2,757 - 0$	

Table 22. Average Removal (Leached) Percentage of Chromium for Control and Experimental Media over 12 Sampling Dates

pH

Figure 20 shows the relationship between the average influent and effluent pH for each sampling date. The relationship was developed using Microsoft Excel 2013. Effluent pH was consistently higher than influent pH for both the experimental and control media. ANOVA analysis showed significant difference between influent pH and all four types of effluent pH (P-value $= 0.000$). The experimental media started with an effluent pH higher than the control media, but by the $12th$ sampling period, the pH's had become similar, although still approximately 1 pH unit above the influent pH. Generally, vegetated media showed a slightly higher pH similar to non-vegetated media.

Figure 20. Relationship between pH and Average Influent and Effluent Metal Concentrations

Volume Retention

The volume of effluent was only calculated from 11/7/2012 through 4/9/2013 (11 sampling dates) because a majority of the adhesive and duct tape on the bottom of the columns, especially columns with control media, deteriorated and the resulting leakage made capturing all the effluent impractical. Each data point denotes an average of six replicates for media with plants and three replicates for media without plants.

On the first sampling date, the volume retained by the vegetated control media was much less than the volume retained by the non-vegetated control media and both the vegetated and non-vegetated experimental media (Figure21). On the other sampling dates, the experimental media had higher retention capacity (Figure 21 and Table 23). The average increase in retention capacity due to bottom ash was 4.8% and 3.9% for planted

and unplanted media, respectively (Table 23). Within a media, the vegetation did not appear to affect retention.

Figure 21. Mean Percentage of Water Retained for 11 Sampling Dates. A Constant Ponding Head of 3 inches was Maintained for all Media during Testing

Bioretention Media	Average Retention Capacity (%)		
	Vegetated Media	Non-Vegetated Media	
Overall Average			
Sand + Wood Fines (control)	11 2	124	
Bottom Ash + Wood Fines (experimental)	160	16.3	
Range (Minimum – Maximum)			
Sand + Wood Fines (control)	$6.0 - 30.8$	$4.5 - 51.7$	
Bottom Ash + Wood Fines (experimental)	$9.5 - 65.3$	$11.0 - 55.7$	

Table 23. Average Volume Retained for Control and Experimental Media over 11 Sampling Dates

Plant Performance

The heights of heavy metal switchgrass in each bioretention column were measured on three dates (Figure 23). The plants went dormant not long after planting in the columns (in November 2012) and did not come out of dormancy until February 2013. To allow for new growth once out of dormancy, the plants were trimmed to 2 inches in mid-January.

After one year, switchgrass in the experimental media was taller, averaging 4.75 inches more than the plants in the control media. The greater growth of vegetation in the experimental media can be credited to the higher retention of SSW in the bioretention columns. Switchgrass in both media showed substantial root growth by the end of the study (Figure 22).

Figure 22. Bioretention Column with Plant Roots Probing through Screens at the Bottom

Figure 23. Average Plant Height Observed at Different Dates

Toxicity Characteristic Leaching Procedure

Results of a toxicity characteristic leaching procedure (TCLP) for a sample of bottom ash obtained prior to this study and for the mixture of bottom ash and wood fines used in this study are shown in Table 24. For comparison, the target influent concentrations are also shown in the table.

Compound/Analyte	Influent	Bottom Ash	Bottom Ash + Wood
	SSW (mg/L)	(mg/L)	Fines (mg/L)
Cadmium	0.002	< 0.050	0.006
Chromium	0.001	< 0.050	0.006
Lead	0.0071	< 0.050	0.011

Table 24. Breakdown of TCLP Metals in Bioretention Media

Assuming the metals concentration in the incinerator bottom ash were relatively consistent, it appears that the wood fines contributed small amounts of lead. Therefore, it

appears that leaching of all the metals documented over the duration of the research cannot be credited to metals found in the experimental wood fines.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Column studies were conducted to investigate the effect incinerator bottom ash in a bioretention system had on the pollutant removal efficiency for the heavy metals lead, copper, zinc, iron, nickel, cadmium, and chromium. Influent and effluent samples from control media of a 50:50 sand and wood fines mix were compared to an experimental media of 50:50 bottom ash and wood fines. The effect of vegetation on metal retention was also investigated.

The results varied between media types. In general, media had an effect in retaining metals like copper and iron throughout the duration of the research. In some cases, the effect of media was strong while weak for others. The experimental media seemed significant in retaining almost all metals after the first three sampling dates. This result may be due to bottom ash having a larger surface area.

While vegetation initially significantly reduced the effluent concentration of copper, lead, zinc, and iron, it largely had a significant effect thereafter. The insignificant effect of switchgrass on metal and volume retention might be due to the plants going dormant. Vegetation also had some effect on reducing peak volume, especially in the experimental media.

Over time, there was a substantial decrease of copper, nickel, cadmium, and chromium concentration in the effluent in all columns, indicating that time had a greater effect on removal of some metals in the synthetic stormwater.

The mean effluent metal concentration data was compared to water quality criteria (Table 25). The overall mean lead concentration from the experimental media was well below the values of lead for typical runoff, aquatic life, and drinking water criteria. Overall mean copper concentration from the experimental media was also below copper values reported. However, the overall mean concentration of zinc, whether vegetated or non-vegetated, was above values of zinc reported.

			Concentration (mg/L)			
Pollutant	Target Influent	Average Effluent Vegetated	Average Effluent Non-Vegetated	Typical Runoff ¹	Aquatic Life Criteria ^{2*}	Drinking Water Criteria ³
Lead	0.02	0.004	0.004	0.18	0.0065(0.00025)	0.015^{4}
Copper	0.075	0.0265	0.035	0.05	N/A	$1.0**$
Zinc	0.06	0.028	0.025	0.02	0.012(0.012)	$5**$
Iron	N/A	1.239	1.449	N/A	(0.1)	$0.3**$
Nickel	N/A	0.012	0.0248	N/A	0.047(0.0052)	N/A
Cadmium	N/A	0.0016	0.0016	N/A	0.0002 (0.000025)	0.005^{4}
Chromium	N/A	0.00093	0.0011	N/A	0.0016(0.0011)	0.1^*

Table 25. Comparison of Results to Water Quality Data

¹Bastian, 1997; ²USEPA, 2013b; ³USEPA, 2009

*Numbers in parenthesis show acute levels and those without show chronic levels

**Secondary Maximum Contaminant Level

¥Primary Maximum Contaminant Level

Overall, it appearsthat bottom ash drom incinerating biosolids could be used in

place of sand in bioretention media. However, future work using stormwater runoff

(rather than synthetic stormwater) is needed. In addition a field study is recommended to

investigate if the bioretention media would behave similarly in a typical full-scale

application. Other research related to this study may also include testing other organic materials to see if they have the same effect as wood fines and using other plant species. In addition, many studies describe percentages of various components but fail to provide quantitative information on particle size distribution, organic matter content, type of organic matter, permeability, cation exchange capacity, water holding capacity, or other properties (Limouzin et al., 2011). Consequently, to understand and be able to account for the differences in stormwater pollutant removal and changes in permeability, future research should incorporate a detailed characterization of the mixed media properties to be used.

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APPENDIX A

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

Table A-1: Lead Concentration in Influent Synthetic Stormwater for 18 Sampling Dates for Control and Experimental Bioretention Media

	Copper Concentration in Synthetic Stormwater, mg/L												
Bioretention Media Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12	
	11/7/2012	11/1/2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013	
1	0.041	0.042	0.041	0.047	0.087	0.053	0.051	0.039	0.041	0.038	0.042	0.045	
$\boldsymbol{2}$	0.040	0.043	0.040	0.049	0.087	0.130	0.049	0.040	0.070	0.034	0.048	0.045	
$\mathbf{3}$	0.040	0.041	0.082	0.059	0.089	0.091	0.090	0.039	0.056	0.054	0.050	0.045	
$\overline{\mathbf{4}}$	0.057	0.041	0.053	0.045	0.058	0.058	0.050	0.043	0.048	0.086	0.061	0.045	
5	0.049	0.045	0.045	0.043	0.076	0.079	0.180	0.039	0.040	0.060	0.039	0.045	
6	0.058	0.044	0.049	0.041	0.197	0.050	0.038	0.042	0.049	0.059	0.050	0.045	
7	0.047	0.038	0.043	0.043	0.043	0.047	0.047	0.049	0.042	0.054	0.047	0.045	
8	0.056	0.035	0.005	0.043	0.042	0.062	0.046	0.060	0.046	0.046	0.052	0.045	
9	0.052	0.038	0.040	0.041	0.046	0.058	0.044	0.074	0.059	0.042	0.045	0.045	

Table A-2: Copper Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

							Zinc Concentration in Synthetic Stormwater, mg/L					
Bioretention Media Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
	11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013
1	0.042	0.033	0.030	0.022	0.059	0.040	0.068	0.052	0.035	0.061	0.039	0.0035
$\mathbf{2}$	0.042	0.026	0.031	0.035	0.059	0.062	0.062	0.051	0.046	0.058	0.060	0.0035
3	0.042	0.027	0.057	0.073	0.052	0.054	0.072	0.049	0.040	0.077	0.053	0.0035
4	0.042	0.031	0.284	0.044	0.045	0.044	0.120	0.029	0.052	0.104	0.066	0.0035
5	0.044	0.041	0.047	0.046	0.053	0.055	0.077	0.052	0.040	0.115	0.044	0.0035
6	0.045	0.056	0.034	0.049	0.079	0.042	0.053	0.059	0.050	0.078	0.068	0.0035
$\overline{7}$	0.058	0.039	0.032	0.045	0.037	0.041	0.061	0.064	0.044	0.079	0.056	0.0035
8	0.046	0.043	0.0035	0.048	0.041	0.041	0.066	0.063	0.049	0.090	0.065	0.0035
9	0.037	0.044	0.029	0.045	0.045	0.058	0.056	0.069	0.057	0.082	0.046	0.0035

Table A-3: Zinc Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Table A-4: Iron Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

		Nickel Concentration in Synthetic Stormwater, mg/L													
Bioretention Media Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12			
	11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013			
1	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
$\mathbf{2}$	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
$\mathbf{3}$	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
4	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
5	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
6	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
7	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
8	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			
9	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053			

Table A-5: Nickel Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Table A-6: Cadmium Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

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Table A-7: Chromium Concentration in Influent Synthetic Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Biorentention										Lead Concentration in Synthetic Stormwater, mg/L							
Media	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12	Trial 13	Trial 14	Trial 15	Trial 16
		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013	6/13/2013	7/13/2013	8/17/2013	9/21/2013
	$\mathbf{1}$	0.007	0.004	0.005	0.0012	0.003	0.007	0.016	0.009	0.004	0.0012	0.0012	0.0012	0.004	0.0012	0.0012	0.0012
	$\overline{2}$	0.005	0.004	0.003	0.0012	0.010	0.008	0.021	0.010	0.004	0.0012	0.0012	0.004	0.006	0.0012	0.003	0.0012
	$\mathbf{3}$	0.006	0.004	0.005	0.0012	0.003	0.012	0.016	0.014	0.0012	0.0012	0.0012	0.006	0.005	0.006	0.0012	0.0012
	$\overline{\mathbf{4}}$	0.005	0.0012	0.004	0.0012	0.0012	0.0012	0.009	0.004	0.003	0.005	0.0012	0.006	0.009	0.013	0.0012	0.0012
Control	5	0.006	0.004	0.0035	0.0012	0.006	0.013	0.012	0.016	0.0012	0.0012	0.0012	0.007	0.0012	0.0012	0.003	0.0012
	6	0.004	0.004	0.0012	0.005	0.006	0.015	0.015	0.012	0.0012	0.0012	0.0012	0.006	0.003	0.0012	0.006	0.0012
	$\overline{7}$	0.006	0.0012	0.0012	0.0012	0.004	0.018	0.024	0.012	0.0012	0.0012	0.0012	0.004	0.005	0.0012	0.0012	0.0012
	8	0.005	0.004	0.004	0.0012	0.0012	0.015	0.020	0.018	0.0012	0.0012	0.0012	0.005	0.008	0.0012	0.0012	0.0012
	9	0.007	0.0012	0.005	0.0012	0.004	0.013	0.021	0.009	0.0012	0.0012	0.0012	0.006	0.006	0.0012	0.003	0.0012
	1	0.009	0.013	0.005	0.0012	0.0012	0.007	0.009	0.0012	0.0012	0.0012	0.0012	0.005	0.005	0.0012	0.003	0.0012
	$\overline{2}$	0.003	0.004	0.0012	0.003	0.009	0.015	0.006	0.0012	0.003	0.0012	0.006	0.006	0.008	0.0012	0.0012	0.0012
	$\mathbf{3}$	0.003	0.005	0.0012	0.0025	0.0030	0.014	0.015	0.004	0.0012	0.0012	0.0012	0.007	0.009	0.0012	0.0012	0.003
	$\overline{\mathbf{4}}$	0.006	0.0012	0.006	0.0012	0.006	0.005	0.009	0.004	0.0012	0.0012	0.0012	0.006	0.005	0.0012	0.004	0.0012
Experimental	5	0.004	0.0012	0.004	0.0012	0.0012	0.003	0.009	0.0012	0.0012	0.0012	0.0012	0.004	0.010	0.0012	0.005	0.0012
	6	0.005	0.006	0.0012	0.005	0.006	0.0012	0.006	0.0012	0.0012	0.0012	0.0012	0.016	0.008	0.0012	0.0012	0.0012
	7	0.006	0.003	0.0012	0.0012	0.016	0.005	0.004	0.005	0.0012	0.0012	0.0012	0.009	0.009	0.0012	0.0012	0.0012
	8	0.005	0.003	0.0012	0.0012	0.0012	0.005	0.011	0.004	0.005	0.0012	0.003	0.011	0.005	0.0012	0.004	0.0012
	\boldsymbol{q}	0.005	0.005	0.0012	0.0012	0.0012	0.0012	0.010	0.0012	0.0012	0.0012	0.0012	0.013	0.004	0.0012	0.003	0.0012

Table A-8: Lead Concentration in Effluent Stormwater for 16 Sampling Dates for Control and Experimental Bioretention Media.

Biorentention Media						Copper Concentration in Synthetic Stormwater, mg/L							
	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013
	1	0.037	0.010	0.005	0.006	0.021	0.022	0.014	0.009	0.0011	0.004	0.007	0.013
	$\overline{2}$	0.019	0.010	0.003	0.003	0.101	0.011	0.004	0.004	0.003	0.003	0.013	0.010
	$\mathbf{3}$	0.014	0.017	0.004	0.003	0.041	0.028	0.003	0.003	0.0011	0.003	0.008	0.021
	$\overline{\mathbf{4}}$	0.017	0.005	0.0011	0.0011	0.064	0.016	0.006	0.007	0.004	0.008	0.013	0.013
Control	5	0.012	0.011	0.0045	0.0011	0.019	0.010	0.008	0.005	0.0011	0.0011	0.021	0.011
	6	0.023	0.009	0.006	0.0011	0.104	0.011	0.0011	0.008	0.006	0.005	0.014	0.012
	$\overline{7}$	0.109	0.017	0.005	0.003	0.007	0.004	0.007	0.004	0.003	0.0011	0.0011	0.007
	8	0.079	0.018	0.021	0.0011	0.005	0.029	0.0011	0.003	0.0065	0.0011	0.009	0.008
	9	0.095	0.013	0.0011	0.0011	0.007	0.016	0.0011	0.003	0.009	0.0011	0.009	0.008
	$\mathbf{1}$	0.255	0.0011	0.0011	0.0011	0.012	0.017	0.007	0.013	0.0011	0.005	0.010	0.010
	$\overline{2}$	0.144	0.0011	0.0011	0.0011	0.005	0.012	0.008	0.0011	0.0011	0.0011	0.028	0.004
	$\mathbf{3}$	0.248	0.0011	0.0011	0.0011	0.019	0.017	0.004	0.0011	0.0011	0.007	0.009	0.029
	$\overline{4}$	0.283	0.019	0.0011	0.0011	0.1145	0.035	0.0011	0.004	0.0011	0.0011	0.011	0.0011
Experimental	5	0.155	0.0011	0.0011	0.0011	0.036	0.041	0.007	0.005	0.0011	0.0011	0.004	0.016
	6	0.195	0.0011	0.0011	0.0011	0.005	0.007	0.0011	0.007	0.0011	0.0011	0.009	0.008
	$\overline{7}$	0.310	0.0011	0.0011	0.0011	0.006	0.016	0.0011	0.0011	0.0011	0.0011	0.0011	0.005
	8	0.399	0.016	0.0011	0.0011	0.0011	0.024	0.0011	0.0011	0.0011	0.003	0.005	0.003
	9	0.459	0.0011	0.0011	0.0011	0.021	0.0096	0.0011	0.0011	0.0011	0.0011	0.004	0.006

Table A-9: Copper Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

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Biorentention								Zinc Concentration in Synthetic Stormwater, mg/L					
	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
Media Control Experimental		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013
	$\mathbf{1}$	0.169	0.035	0.050	0.024	0.042	0.020	0.026	0.018	0.016	0.021	0.017	0.026
	$\overline{2}$	0.033	0.048	0.025	0.016	0.0305	0.018	0.026	0.021	0.019	0.016	0.022	0.016
	$\mathbf{3}$	0.058	0.048	0.029	0.014	0.025	0.020	0.013	0.009	0.010	0.007	0.012	0.025
	$\overline{4}$	0.034	0.026	0.018	0.016	0.029	0.012	0.025	0.013	0.010	0.024	0.026	0.030
	5	0.041	0.028	0.034	0.016	0.034	0.020	0.022	0.017	0.013	0.012	0.019	0.025
	6	0.040	0.023	0.030	0.020	0.061	0.016	0.016	0.014	0.017	0.011	0.068	0.022
	$\overline{7}$	0.190	0.067	0.054	0.024	0.031	0.028	0.055	0.020	0.023	0.016	0.034	0.028
	8	0.145	0.054	0.041	0.061	0.033	0.036	0.029	0.024	0.023	0.023	0.065	0.033
	9	0.183	0.053	0.058	0.036	0.030	0.018	0.022	0.018	0.021	0.014	0.065	0.036
	$\mathbf{1}$	0.098	0.222	0.043	0.025	0.017	0.013	0.012	0.011	0.012	0.011	0.046	0.085
	$\overline{2}$	0.036	0.019	0.014	0.010	0.016	0.009	0.010	0.011	0.011	0.009	0.068	0.097
	$\mathbf{3}$	0.054	0.013	0.012	0.005	0.020	0.019	0.023	0.016	0.016	0.0035	0.027	0.050
	$\overline{4}$	0.057	0.013	0.014	0.013	0.0225	0.013	0.013	0.0035	0.010	0.0035	0.039	0.054
	5	0.036	0.012	0.012	0.012	0.017	0.017	0.016	0.009	0.038	0.008	0.015	0.053
	6	0.040	0.017	0.014	0.011	0.016	0.016	0.012	0.007	0.011	0.014	0.022	0.010
	$\overline{7}$	0.099	0.027	0.027	0.012	0.024	0.014	0.026	0.011	0.011	0.007	0.013	0.0035
	8	0.101	0.042	0.023	0.025	0.024	0.021	0.016	0.012	0.010	0.016	0.020	0.011
	9	0.111	0.038	0.015	0.023	0.032	0.026	0.030	0.010	0.010	0.015	0.017	0.0035

Table A-10: Zinc Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

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Biorentention								Iron Concentration in Synthetic Stormwater, mg/L					
Media	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
		11/7/2012	11/1/2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	3/28/2013	4/9/2013	5/14/2013
	$\mathbf{1}$	1.21	8.292	7.04	5.28	2.20	6.01	4.78	4.79	4.09	3.64	3.33	4.26
	$\overline{2}$	1.12	7.490	5.92	4.05	2.945	7.97	10.90	10.10	4.78	4.87	1.98	1.30
	$\mathbf{3}$	3.39	6.76	15.6	9.82	7.14	11.70	9.97	9.78	6.59	2.94	6.79	0.511
	$\overline{4}$	3.69	5.34	4.21	5.53	1.76	0.72	2.99	2.33	1.39	1.31	1.04	1.74
Control	5	4.22	12.4	13.1	6.780	6.95	9.400	9.05	7.04	7.76	7.160	6.68	1.71
	6	1.63	9.47	12.5	10.00	9.92	10.4	9.36	11.20	8.56	8.32	7.08	9.78
	$\overline{7}$	2.37	11.9	16.4	2.56	18.1	19.3	19.6	15.9	16.10	13.000	12.10	11.9
	8	1.94	5.11	9.9	11.2	10.9	12.8	15.3	15.3	10.99	17.2	14.90	14.20
	9	2.84	7.05	26.6	5.86	7.97	8.43	12.5	11.6	10.40	9.210	6.05	1.81
	$\mathbf{1}$	0.692	3.825	0.777	0.32	0.075	1.09	1.55	0.777	0.841	0.909	0.473	0.085
	$\overline{2}$	0.414	2.120	0.152	0.163	0.519	0.369	0.299	0.168	0.11	0.106	0.538	0.052
	$\mathbf{3}$	0.945	1.97	0.344	0.109	0.3845	2.42	2.84	1.63	1.39	0.806	1.07	0.0317
	$\overline{4}$	0.941	3.73	0.418	0.859	1.775	1.3	1.26	1.44	2.820	6.830	3.99	4.86
Experimental	5	0.498	1.44	0.283	0.280	0.39	0.864	0.397	0.171	0.139	0.388	0.184	1.81
	6	0.614	1.71	0.162	0.115	0.685	0.434	0.655	0.47	1.210	1.920	0.651	12.00
	$\overline{7}$	1.300	1.650	0.602	0.704	0.843	0.723	1.54	1.95	2.19	3.41	4.02	2.31
	8	1.24	1.65	0.441	0.395	2.120	1.07	0.9475	1.49	1.15	1.61	1.49	7.85
	9	1.27	3.64	0.345	0.282	0.092	0.203	0.47	0.644	1.080	1.00	0.839	0.098

Table A-11: Iron Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Biorentention								Nickel Concentration in Synthetic Stormwater, mg/L					
	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
Media Control Experimental		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013
	$\mathbf{1}$	0.026	0.012	0.015	0.0053	0.0053	0.011	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{2}$	0.021	0.015	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\mathbf{3}$	0.018	0.012	0.016	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{4}$	0.020	0.0053	0.011	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	5	0.023	0.015	0.086	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	6	0.022	0.011	0.015	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{7}$	0.087	0.033	0.019	0.0053	0.0053	0.014	0.012	0.0053	0.0053	0.0053	0.013	0.0053
	8	0.074	0.021	0.017	0.016	0.0053	0.011	0.011	0.0053	0.0053	0.0053	0.0053	0.0053
	9	0.087	0.028	0.029	0.012	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\mathbf{1}$	0.080	0.1265	0.018	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{2}$	0.050	0.017	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.013
	$\mathbf{3}$	0.092	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{4}$	0.100	0.014	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{5}$	0.043	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	6	0.070	0.015	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	$\overline{7}$	0.201	0.036	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	8	0.221	0.032	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053
	9	0.218	0.046	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053	0.0053

Table A-12: Nickel Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

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Biorentention Media Control Experimental								Cadmium Concentration in Synthetic Stormwater, mg/L					
	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	328/2013	4/9/2013	5/14/2013
	1	0.010	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\overline{2}$	0.004	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\mathbf{3}$	0.005	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\overline{4}$	0.004	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	5	0.006	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	6	0.005	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\overline{7}$	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	8	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	9	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\mathbf{1}$	0.007	0.0016	0.0016	0.0000	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\mathbf{2}$	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\mathbf{3}$	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	4	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	5	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	6	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	$\overline{7}$	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	8	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	9	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016

Table A-13: Cadmium Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Biorentention Media Control Experimental								Chromium Concentration in Synthetic Stormwater, mg/L					
	Column	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
		11/7/2012	11/1//2012	12/4/2012	12/18/2012	1/15/2013	1/29/2013	2/12/2013	2/26/2013	3/12/2013	3/28/2013	4/9/2013	5/14/2013
	1	0.005	0.002	0.0007	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	$\boldsymbol{2}$	0.003	0.003	0.0007	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.003
	3	0.003	0.002	0.003	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	$\overline{\mathbf{4}}$	0.003	0.002	0.004	0.0007	0.004	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	5	0.004	0.003	0.002	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.003
	6	0.004	0.002	0.002	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	7	0.009	0.004	0.003	0.0007	0.002	0.002	0.002	0.0007	0.002	0.0007	0.0007	0.0007
	8	0.008	0.003	0.002	0.0007	0.0007	0.002	0.002	0.002	0.002	0.002	0.002	0.0007
	9	0.010	0.003	0.004	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.002
	$\mathbf{1}$	0.009	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	$\overline{2}$	0.006	0.004	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	$\mathbf{3}$	0.010	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	$\overline{\mathbf{4}}$	0.011	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	5	0.004	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	6	0.007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.002
	7	0.014	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	8	0.020	0.002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	9	0.020	0.002	0.0007	0.0007	0.0007	0.0007	0.002	0.0007	0.0007	0.0007	0.0007	0.0007

Table A-14: Chromium Concentration in Effluent Stormwater for 12 Sampling Dates for Control and Experimental Bioretention Media.

Table A-16: Treatment and Collection Sheet

Number of Samples Transferred

